

Reactivity of Hybrid Silylene and *a*NHC Toward Transition Metal Complexes

विद्या वाचस्पति की उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

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of the degree of Doctor of Philosophy

द्वारा / By

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INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH PUNE

2025

Dedicated to my Abba, Ammi

&

In Loving Memory of My Daadu



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भारतीय विज्ञान शिक्षा एवं अनुसंधान संस्थान पुणे

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I declare that this written submission represents my ideas in my own words and where others' ideas have been included; I have adequately cited and referenced the original sources. I declare that I have acknowledged collaborative work and discussions wherever such work has been included. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated, or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause of disciplinary action by the institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

The work reported in this Thesis is the original work done by me under the guidance of Dr. Shabana Khan.

Ms. Ruksana Akhtar

Date: September 09, 2025



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Certificate

Certified that the work incorporated in the thesis entitled “***Reactivity of Hybrid Silylene and aNHC Towards Transition Metal Complexes***”, submitted by Ms. Ruksana Akhtar, was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.

Date: September 09, 2025

A handwritten signature in blue ink, appearing to read 'shabana khan'.

Prof. Shabana Khan

Acknowledgment

“So verily, with hardship comes ease. Indeed, with hardship comes ease.”

~ Qur'an, Surah Ash-Sharh (94:5–6)

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“No one is useless in this world who lightens the burdens of another.” -Charles Dickens

Ruksana Akhtar

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Synopsis

The main focus of this thesis, entitled "*Reactivity of Hybrid Silylene and aNHC Towards Transition Metal Complexes*," is to deepen our understanding of the structure and bonding

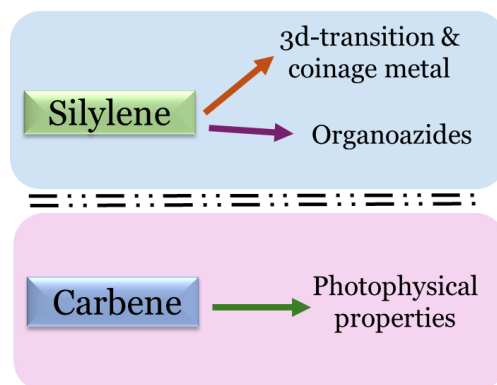
characteristics of phosphine-based hybrid silylene towards 3d-transition and coinage metal halide complexes. The magnetic properties of phosphine-based hybrid silylene 3d-transition metal halide complexes have been investigated. Parallely, the versatility of *a*NHC ligands has been explored, with emphasis on their photophysical behaviour and *a*NHC→BH₃ adduct reactivity towards group-6 carbonyl complexes. The thesis is structured into chapters that reflect these diverse applications and categorise the results according to their relevance in distinct domains.

Chapter 1: Introduction

“Main-group organometallic chemistry is not limited to classical Lewis-acidic or -basic catalysis.”

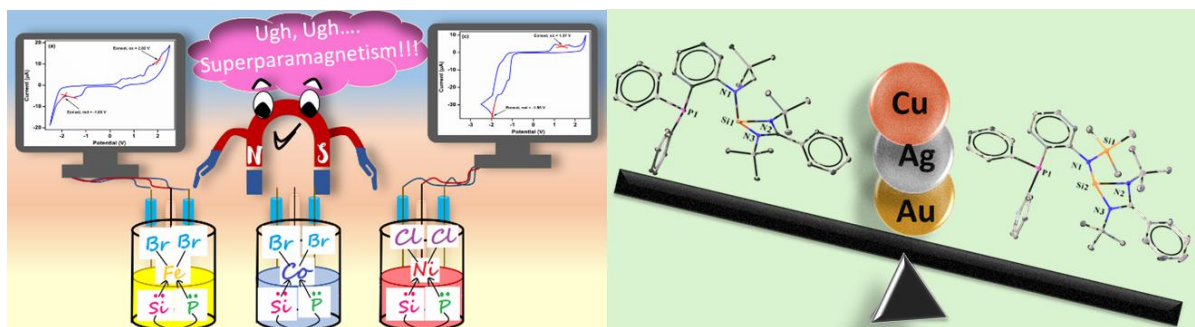
-Guy Bertrand, Introduction to Main Group Chemistry

As noted by the pioneering Prof. Robert West, silicon is the second most abundant element on earth, widely exploited as a semiconductor material, unlike its low-valent counterpart, which typically exists in the +2 oxidation state. The group 14 elements, known as N-heterocyclic tetrylenes (NHTs), generally possess six electrons in their valence shell. Once considered rare and transient laboratory curiosities, NHTs have now emerged as some of the most extensively explored ancillary ligands in modern main-group chemistry. NHCs, first isolated by Arduengo and co-workers in 1991, have shown remarkable potential compared to their heavier congeners. The foundation for their role as ancillary ligands was laid earlier by Nobel laureate Ernst Otto Fischer in 1973. In contrast, the chemistry of their heavier analogue, silylenes, has largely remained confined to small-molecule activation and only recently begun to expand into transition-metal-mediated homogeneous catalysis. With this spirit, we aim to expand our understanding of NHTs in 3d-transition and coinage metal chemistry, where they have enabled access to redox-active and magnetically responsive complexes with diverse bonding modes. Furthermore, NHTs (*a*NHCs) are also explored in the area of photoemitters.



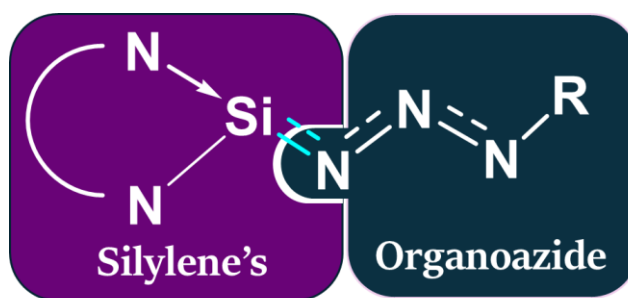
Chapter 2: Synthesis and Coordination of Phosphine-Silylene-Based Hybrid Ligand Towards 3d-Transition and Coinage Metals

In this chapter, we explored the reactivity of newly designed phosphine-silylene hybrid ligands with both 3d transition- (Fe, Co, Ni) and coinage-metal halide salts (Cu, Ag, Au). Reactions with 3d transition-metal halides furnished four-coordinate, six-membered metallacyclic complexes, in which both the Si(II) and P(III) donor sites actively participate in coordination. These base-metal complexes exhibit intriguing redox activity and magnetic behaviour, highlighting the multifunctional role of the hybrid ligands. Specifically, the Fe and Co derivatives display paramagnetism at room temperature and superparamagnetism at low temperature, whereas the Ni complexes exhibit superparamagnetism across both temperature ranges, underscoring the subtle dependence of magnetic properties on the central metal. In contrast, reactions with group 11 precursors (Cu, Ag, Au) led to a series of coinage-metal complexes featuring diverse structural motifs. Copper(I) halides yielded dimeric species stabilised by bridging anions, while silver(I) and gold(I) afforded monomeric complexes in which coordination occurs selectively through the silylene donor centre, leaving the phosphine moiety non-coordinated. The molecular structures of all newly synthesised compounds were rigorously established through single-crystal X-ray diffraction, multinuclear NMR spectroscopy, and mass spectrometry. Together, these studies provide valuable insights into the coordination versatility and donor flexibility of phosphine-silylene hybrid ligands toward both base metals and coinage metals, offering a foundation for further exploration of their electronic, redox, and magnetic properties.



Chapter 3: Multifaceted Reactivity of Organoazides with Silylenes and Disilenes

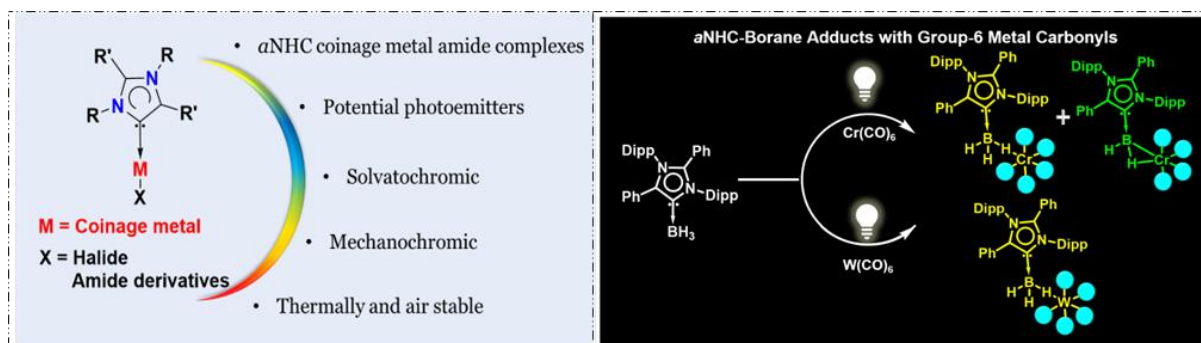
Low-valent silicon chemistry has advanced significantly since the isolation of stable Si=C and Si=Si species, which overturned the “double bond rule” and demonstrated the feasibility of multiple bonding in silicon. Among these, hybrid silylenes, bis-silylenes, and disilenes have emerged as versatile platforms, where ligand design plays a decisive role in stabilising reactive intermediates and enabling unique reactivity. A key frontier is the stabilisation of Si–N multiple bonds, which are highly sought after for their fundamental bonding insights and potential applications in catalysis and materials. Organoazides provide an ideal entry point to this chemistry, as their reactions with Si(II) species often generate silaimines or related Si–N functionalities. In this study, we therefore examine the reactivity of different Si(II) frameworks with organoazides to understand how ligand architecture governs stability and product selectivity.



Chapter 4: Expanding the Photophysical and Reactivity Landscape of Abnormal NHC Complexes.

In recent years, carbene-based ligands such as N-heterocyclic carbenes (NHCs) and cyclic (alkyl)(amino) carbenes (CAACs) have attracted considerable attention for their coordination with coinage metal amide complexes, owing to their straightforward synthesis and distinctive photophysical properties. These systems have demonstrated pronounced ligand-dependent

effects on the optical and electronic behaviour of the resulting complexes. In contrast, the chemistry of abnormal NHCs (*a*NHCs) with coinage metals remains far less explored. In this chapter, we present the synthesis of a new family of luminescent *a*NHC-coinage metal (Cu, Ag, Au) amide complexes. Notably, the nature of the amide substituent strongly influences the origin of emission. This work reports, for the first time, imidazolylidene-based *a*NHC luminescent complexes that exhibit solvatochromism, mechanochromism, and thermally activated delayed fluorescence (TADF), providing new insights into structure–property relationships in this class of materials. Importantly, this work is not only limited to the access of *a*NHC–metal–amide complexes; an *a*NHC→BH₃ adduct was also isolated, and its reactivity with group-6 metal carbonyls was explored, further highlighting the synthetic versatility of *a*NHCs beyond their photophysical applications.



List of Abbreviations

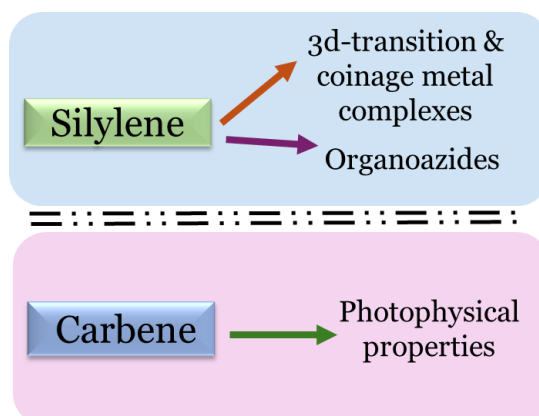
NHTs	N-heterocyclic terylene's
NHCs	N-heterocyclic carbenes
NHSis	N-heterocyclic silylenes
HOMO	Highly occupied molecular orbital
LUMO	Lowest occupied molecular orbital
<i>a</i> NHC	abnormal N-Heterocyclic carbene
OLED	Organic light-emitting diode
NiBr ₂ .DME	Nickel dibromide ethylene glycol dimethyl ether complex
FeBr ₂	Iron dibromide
CoBr ₂	Cobalt dibromide
TMSN ₃	Trimethylsilylazide
AdN ₃	1-azidoadamantane
CAAC	cyclic (alkyl) (amino) carbene

MAC	Monoamidocarbenes
DAC	Diamidocarbenes
RISC	Reverse intersystem crossing
TADF	Thermally activated delayed fluorescence
PLQY	Photoluminescence quantum yield
CPL	Circularly polarised luminescence
RTP	Room-temperature phosphorescence
Cbz	Carbazole
UV	Ultraviolet
LE state	Locally excited state
MeCy	Methylcyclohexane
PS films	Polystyrene film
MLCT	Metal-ligand charge transfer
EQE	External quantum efficiency
CMA	Carbene-metal-amide
LEDs	Light-emitting diode
THF	Tetrahydrofuran
DCM	Dichloromethane
CT	Charge transfer
FWHM	Full-width half maximum
TCSPC	Time-correlated single photon counting
λ_{em}	Emission maximum
PMMA	Polymethyl methacrylate
PXRD	Powder X-ray diffraction
c-LED	Converted LED
Hz	Hertz
ppm	parts per million
SQUID	Superconducting quantum interference device magnetometry
ZFC	Zero-field-cooled
FC	Field-cooled
TGA	Thermogravimetric analysis
mmol	Millimole

List of Publications

8. **Ruksana Akhtar**, Rishukumar Panday, Shabana Khan Versatile Reactivity of Amido Phosphine Aluminium Complexes toward Chalcogens and Boron Hydride. (*Manuscript under permission*)
7. **Ruksana Akhtar**, Rishukumar Panday, Shabana Khan* Reactivity of *a*NHC-Borane Adducts with Group-6 Metal Carbonyls. (*Manuscript under submission*)
6. **Ruksana Akhtar**, Abhijit Chatterjee, Prakash Panwaria, Himanshu Sharma, Sakshi Yadav, Ashwath Kudlu, Rishukumar Panday, Geethu Venugopal, Rahul Verma, Kumar Vanka, Pankaj Mandal,* and Shabana Khan* Air-Stable “Abnormal” Carbene-Metal Amide TADF Emitters: An Approach towards Near-Unity Quantum Yield. (*Manuscript under permission*)
5. **Ruksana Akhtar**, Rishukumar Panday, Shabana Khan* Multifaceted Reactivity of Organoazides with Silylenes and Disilenes (*Manuscript under permission*)
4. **Ruksana Akhtar**, Rishukumar Panday, Shabana Khan* Synthesis and Coordination of Phosphine-Silylene-Based Hybrid Ligand Towards Coinage Metals (*Manuscript under permission*)
3. **Ruksana Akhtar**, Kumar Gaurav, Shabana Khan* Applications of low-valent compounds with heavy group-14 elements [Chem. Soc. Rev., 2024,53, 6150-6243](#)
2. **Ruksana Akhtar**,[#] Sandeep H. Kaulage,[#] Mayur P. Sangole, Srinu Tothadi, Parameswaran Parvathy, Pattiyil Parameswaran* Kirandeep Kirandeep Singh*, and Shabana Khan* First-Row Transition Metal Complexes of a Phosphine–Silylene-Based Hybrid Ligand [Inorg. Chem. 2022, 61, 13330–13341](#)
1. Javed Hossain[#] **Ruksana Akhtar**,[#] Shabana Khan* Luminescent coinage metal complexes of carbenes [Polyhedron 2021, 201, 115151–115186](#);

Chapter 1: Introduction



Partly adapted from: ***R. Akhtar***, K. Gaurav, S. Khan* Applications of low-valent compounds with heavy group-14 elements [*Chem. Soc. Rev.*, **2024**,*53*, 6150-6243](#) J. Hossain[#] ***R. Akhtar***,[#] S. Khan* Luminescent coinage metal complexes of carbenes [*Polyhedron* **2021**, *201*, 115151–115186;](#)

“I was born not knowing and have had only a little time to change that.”- Richard Feynman

1.1 Introduction.

1A.1 Overview of N-heterocyclic tetrylenes (NHTs).

The groundbreaking discoveries in main group chemistry have witnessed a remarkable evolution, propelling this domain into a pivotal field.¹⁻² Among them, a class is tetrylenes, which are neutral divalent species ($R_2E:$) ($E = C, Si, Ge, Sn,$ and Pb) of the group 14 elements, bearing a vacant p -orbital and a lone pair of electrons.³ To gain a better understanding of the tetrylenes, we began with N-heterocyclic carbenes (NHCs), where significant milestones have shaped the evolution of this ligand.⁴ NHCs were considered as a highly unstable and transient intermediate in the initial stages of research, due to their coordinative unsaturation and incomplete electron octets.⁵⁻⁸ Efforts to isolate free, uncoordinated carbenes date back to 1835, but success remained out of reach until the late 1980s and early 1990s. In 1988, Bertrand and co-workers described the first isolable carbene, while in 1994, Arduengo and coworkers achieved the isolation of the first bottleable carbene, {1,3-di(adamantyl)imidazol-2-ylidene}.⁹⁻¹⁰ However, the first thermally stable N-heterocyclic silylene (NHSi) was documented by West and Denk in 1994.¹¹ In this regard, NHCs have demonstrated their versatility as spectator ligands across diverse domains, including organometallic chemistry, homogeneous catalysis, medicinal chemistry, and materials science (Chart 1A.1).¹²

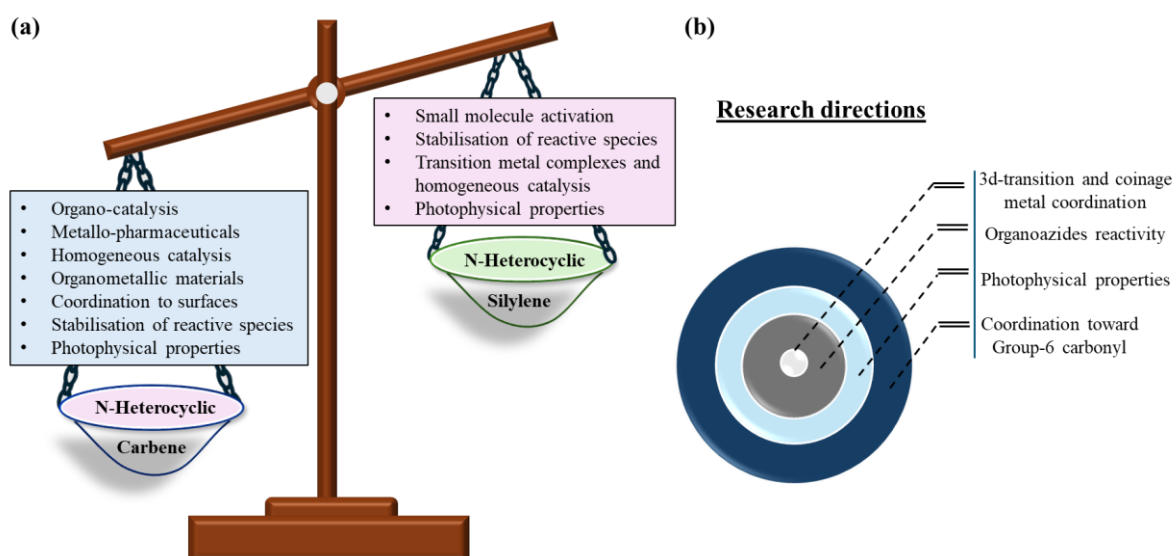


Chart 1A.1: (a) Schematic diagram of broad applications of NHCs and NHSis; (b) Research areas covered in this thesis.

It would be an understatement to say that the chemistry of NHCs is now thoroughly established, and their role has clearly extended far beyond serving as simple “phosphine analogues.”¹³⁻¹⁶ In contrast, the field of low-valent compounds of the heavier group 14 elements (Si, Ge, Sn, and Pb) is still in its early stages. Owing to their distinct physical and chemical characteristics, however, these species are anticipated to open new avenues for innovative applications.¹⁷ Within this family, silylenes have been studied most extensively, particularly for their ability to activate small molecules and to coordinate with transition metals.¹⁸⁻²¹ The resulting transition-metal complexes have shown considerable promise in a range of catalytic organic transformations.²²⁻²⁶ Despite this progress, the interaction of silylenes with coinage metals (Cu, Ag, and Au) remained largely underexplored until more recent investigations.²⁷

1A.2 Bonding and electronic properties of silylenes.

“Silylenes” are neutral divalent species ($R_2Si:$) of the group 14 elements, bearing a vacant p -orbital and a lone pair of electrons. They can be broadly divided into acyclic silylenes and cyclic silylenes.^{11, 23, 26} The first stable silicon(II) compound was isolated by Jutzi and co-workers, where the silicon atom is joined to two pentamethylcyclopentadienyl ligands in a η^5 -configuration.²⁸ In the case of the parent $H_2C:$, its ground state appears as a triplet state, while that for $H_2Si:$ is a singlet state.⁵ The energy distinctions between the singlet and triplet states, denoted as singlet-triplet energy differences for H_2Si ($\Delta E_{ST} = E(\text{triplet}) - E(\text{singlet})$), have been determined through theoretical calculations. The values are recorded as 16.7 kcal/mol for $E = Si$, 21.8 kcal/mol for $E = Ge$, 24.8 kcal/mol for $E = Sn$, and 34.8 kcal/mol for $E = Pb$. Notably, in the case of $H_2C:$ the corresponding singlet-triplet energy difference is calculated to be 14.0 kcal/mol (Chart 1A.2.1).^{8, 21} These calculations provide insights into the energetic disparities between the singlet and triplet states for these molecules, offering a quantitative understanding of their stability and reactivity. In silylenes, the lone pair of electrons resides in the low-energy HOMO, while the vacant p -orbital lies at a relatively higher energy level. This electronic configuration allows them to function both as Lewis bases and Lewis acids, accounting for their pronounced reactivity. To stabilise such highly reactive species, a combination of thermodynamic and kinetic protection is typically employed, most often achieved through heteroatom-containing ligands bearing bulky substituents. While significant progress has been made in understanding and isolating singlet silylenes, the synthesis and control of “triplet silylenes” remains a considerable challenge.²⁹⁻³¹

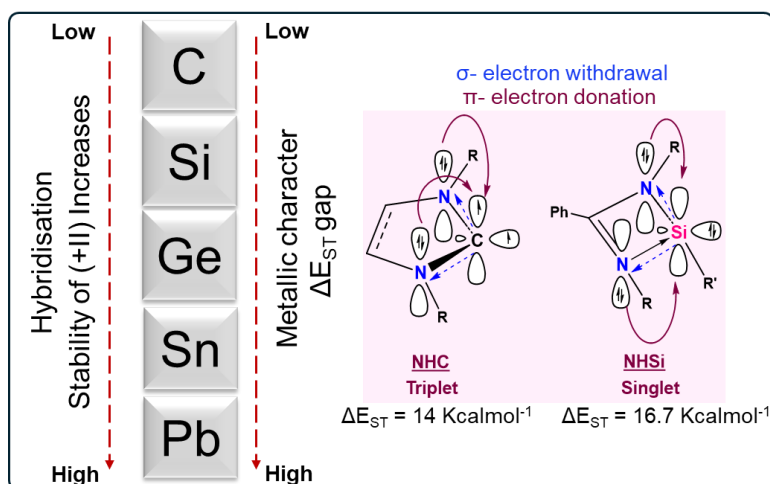


Chart 1A.2.1. Group 14 elements general trend.

In this context, the contributions of the research groups of Schulz,³² Inoue,³³ Aldridge,³⁴ Jones,³⁵ and Rivard³⁶ have been noteworthy, as they succeeded in isolating silylenes with comparatively small HOMO-LUMO gaps. Such electronic features correspond to reduced singlet-triplet excitation energies, which in turn facilitate reactions such as dihydrogen activation.³⁷⁻³⁹ Following this pivotal discovery, a cascade of silylenes was isolated, marking a significant stride within the realm of main-group chemistry (Chart 1A.2.2).³⁸⁻⁴⁵ Their development and impact have also been comprehensively captured in several detailed reviews.^{22-24, 26, 38, 46-50}

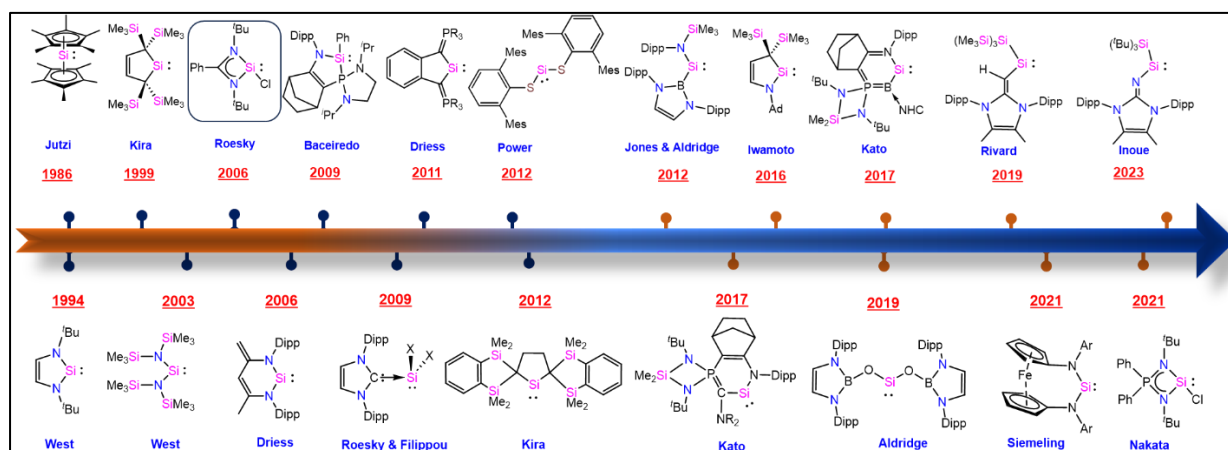


Chart 1A.2.2. Selective recent milestones in the timeline of silylenes.

1A.3 Motivation of the thesis.

N-heterocyclic tetrylene's (NHTs) are neutral divalent species of group 14 elements, which show ambiphilic behaviour due to a vacant *p*-orbital and a lone pair of electrons. They are currently one of the most rigorously investigated groups of ancillary ligands in modern main-

group chemistry. The discovery of bottleable N-heterocyclic carbenes (NHCs) by Arduengo in 1991, followed by the first N-heterocyclic silylene (NHSi) by West and Denk in 1994, and the first metal-free *a*NHC (abnormal N-Heterocyclic carbene) by Bertrand in 2009, sparked widespread interest. Since then, researchers across academia and industry have actively explored NHCs and their potential applications in catalysis, synthesis, stoichiometric transformations, photoemitters and OLED (Organic light-emitting diode) fabrication, marking the start of a new era in low-valent main-group chemistry. While NHCs have demonstrated superior potential than their heavier congeners and *a*NHC in these areas, recent advancements in transition-metal complexes bearing isolable NHSi and *a*NHC ligands have led to new synthetic strategies with diverse properties, significantly impacting organic methodologies, particularly small-molecule activation and a very small number of organic transformation reactions. However, NHSi has only one report in the domain of photoemitters, while *a*NHC remained completely unexplored. Therefore, through this thesis, we have expanded our understanding of NHTs (NHSi and *a*NHC) by exploring their versatility in transition metal chemistry, main-group reactivity, and photophysical properties.

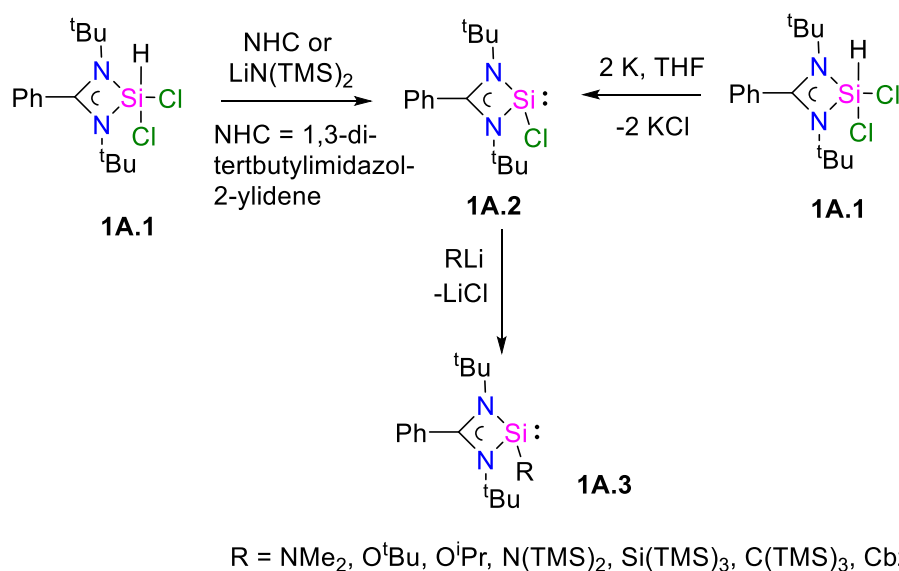
The first section of the thesis demonstrated how phosphine-based hybrid silylene opt coordination with 3d-transition metal halides. These complexes show coordination-driven redox-active and magnetic behaviour. Magnetization in an external magnetic field displays paramagnetic behaviour at room temperature and superparamagnetic at low temperatures. The phosphine-based hybrid silylenes were also utilised in isolating several coinage metal complexes and exploring their unique reactivity and bonding patterns. Furthermore, various silylenes, including phosphine-based hybrid silylene, disilene, carbazole-substituted silylene, and bis-silylene ligand backbones, were examined for their reactivity with azide derivatives, leading to the formation of silaimines. Thus, this part of the thesis investigates the reactivity of silylenes with transition metal halides, emphasising their coordination-driven redox activity, magnetic behaviour, and diverse reactivities with azides.

Driven by the untapped potential of *a*NHCs in photophysical applications, we explored their unique properties as photoemitters. Unlike conventional NHCs, *a*NHCs donate *via* the C5 position, making it less thermodynamically stable but a strong σ -donor. Thus, the *a*NHC-coinage metal (Cu, Ag, and Au)-amide framework was synthesised, thoroughly characterised and further investigated for its photophysical properties. Our work aims to pledge new insights for designing the next generation of stable abnormal carbene-metal-amide photoemitters. However, the last part of the thesis dealt with *a*NHC reactivity with boron hydride and its

coordination towards metal carbonyls. Overall recognising the vital role of main group ligands in modern synthetic chemistry, this thesis highlights the unique potential of NHTs, particularly NHSis and *a*NHC, in real-time applications, aiming to advance the understanding of fundamental main group chemistry.

1A.4 Synthesis and functionalization of four-membered benzamidinato silylene.

A major milestone in silylene chemistry was achieved in 2006, when Roesky and co-workers successfully isolated the four-membered NHSi (**1A.2**).⁵¹ Since then, this compound has become an important platform, serving as a ligand and functional unit in small-molecule activation as well as in both catalytic and stoichiometric transformations involving transition metals. Initially, the synthesis of **1A.2** from the trichlorosilane precursor (**1A.1**) using metallic potassium furnished only a modest isolated yield of about 10 % (Scheme 1A.1). In 2009, the same group improved the methodology by employing $\text{LiN}(\text{SiMe}_3)_2$ as the reducing agent, which promoted base-induced elimination of HCl from the corresponding chlorohydridosilane (**1A.1**).⁵² This modification dramatically increased the yield to 90 %. The availability of **1A.2** in high yield enabled its broader utilisation and subsequent functionalization in diverse molecular frameworks. More recently, the precursor **1A.1** has also been applied in salt-elimination strategies to generate a variety of functionalized monosilylenes (**1A.3**) and bis-silylenes (Scheme 1A.4.1).



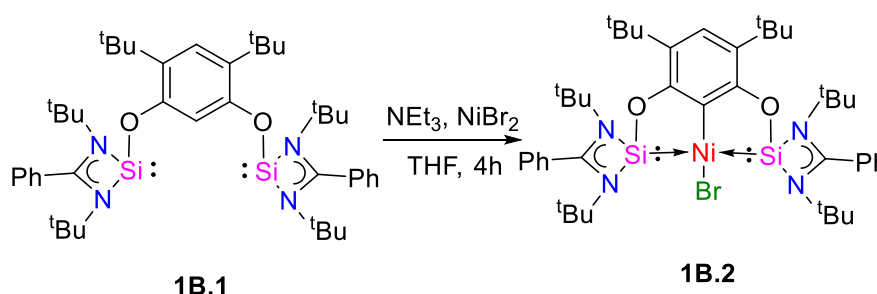
Scheme 1A.4.1. Functionalized benzamidinato silylenes (**1A.2** and **1A.3**): Synthesis of a four-membered NHSi species.

1B. Isolation of hybrid silylene-based 3d transition and coinage metal complexes.

1B.1 Isolation of silylene-based 3d transition metal halide complexes.

Significant progress in silylene chemistry has been achieved over the past several decades; however, the field remains underdeveloped, largely due to the inherent instability of 3d-transition metal halide complexes and the limited synthetic strategies available for their preparation.¹⁷ While silylene-transition metal carbonyl coordination chemistry has been more extensively explored, reports on silylene-transition metal halide complexes are comparatively scarce.⁵³ In contrast, the coordination chemistry of N-heterocyclic carbenes (NHCs) with transition metals benefits from a wide range of established synthetic methodologies, whereas silylene-transition metal complexes are primarily accessed *via* direct coordination of free silylenes.⁴ The coordination chemistry of silylenes with transition metal halides has attracted considerable attention due to the ambiphilic nature of the Si(II) center. As strong σ -donors, silylenes stabilise electron-deficient metal halide fragments, while their vacant p -orbital enables π -acceptor interactions, thereby fine-tuning the electronic properties of the metal center. This dual donor-acceptor ability makes silylenes highly versatile ligands, often surpassing traditional phosphines or carbenes, and allows for the isolation of unusual metal oxidation states, halide-bridged architectures, and unique reactivity patterns in small molecule activation.⁵³⁻⁵⁴ In this section, we will discuss the NHSi ligated 3d-transition metal halides.

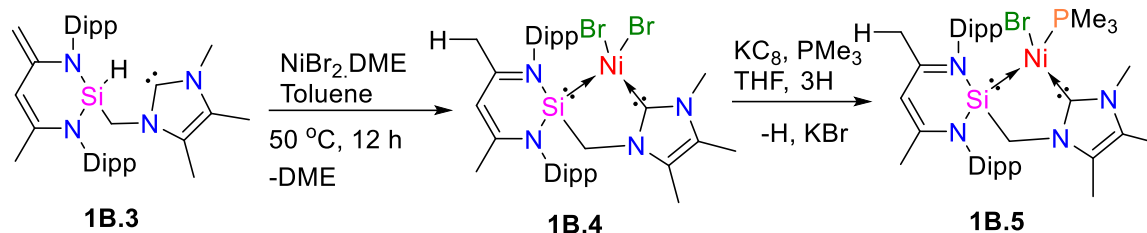
In 2013, Driess and Hartwig reported the design and synthesis of the [SiCSi] pincer bis-silylene ligand **1B.1** (Scheme 1B.1.1).⁵⁵ The corresponding nickel complex **1B.2**, representing the first pincer bis-silylene-nickel species, was obtained *via* C-H activation of the ligand with [NiBr₂(DME)]. Complex **1B.2** proved to be an effective catalyst for the Sonogashira coupling reaction.



Scheme 1B.1.1. Synthesis of **1B.2**

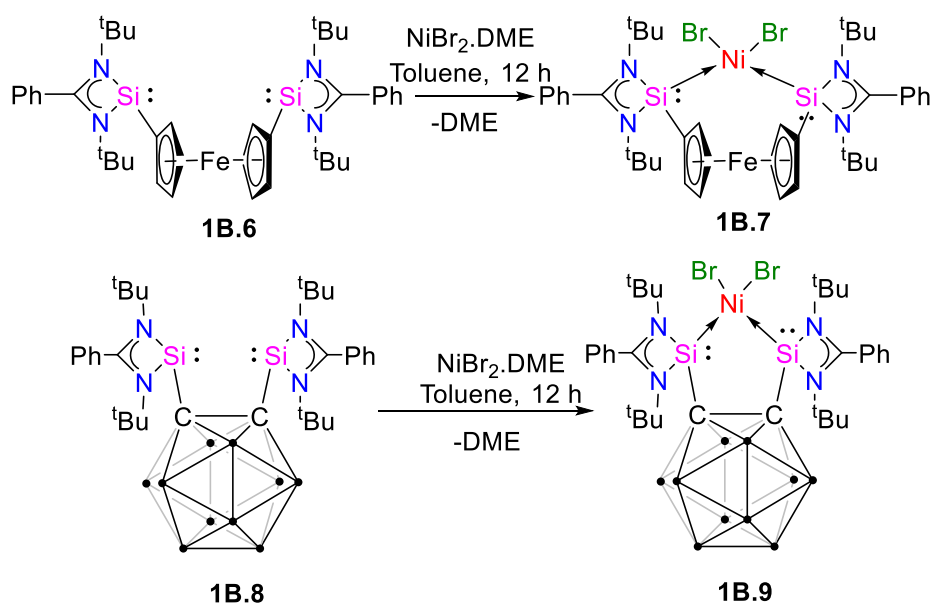
In 2014, the same group employed a mixed bidentate silylene-carbene ligand **1B.3** to access a series of nickel complexes **1B.4** and **1B.5** in different oxidation states (Scheme 1B.1.2).⁵⁶ Treatment of ligand **1B.3** with [NiBr₂(DME)] yielded the NHSi-NHC nickel(II) complex **1B.4**.

Subsequent reduction of **1B.4** with KC_8 in the presence of PMe_3 generated the nickel(I) species **1B.5**. Notably, complex **1B.5** displayed catalytic activity in Kumada cross-coupling reactions.



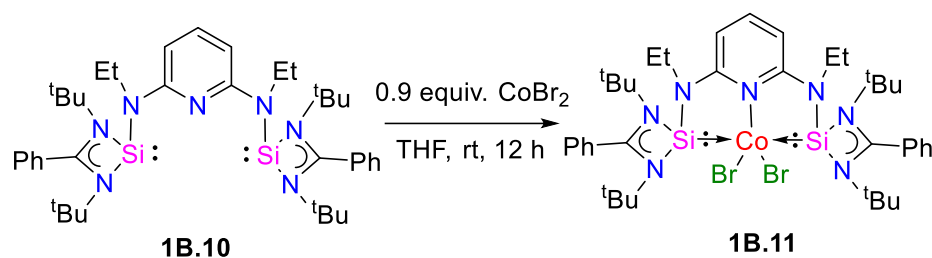
Scheme 1B.1.2. Synthesis of **1B.4** and **1B.5**.

In 2016, Driess and coworkers synthesised and structurally characterised the first 1,2-bis(NHSi)-substituted ortho-carborane and ferrocene nickel bromide complexes (Scheme 1B.1.3).⁵⁷ Furthermore, the strong donor ability of silylens allows **1B.7** and **1B.9** to function as an exceptionally efficient precatalyst) in arene amination reactions.

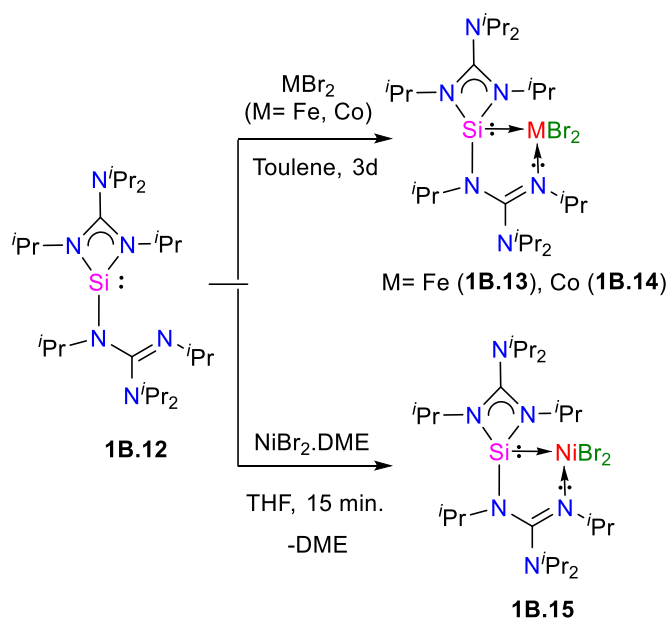


Scheme 1B.1.3. Synthesis of **1B.7** and **1B.9**.

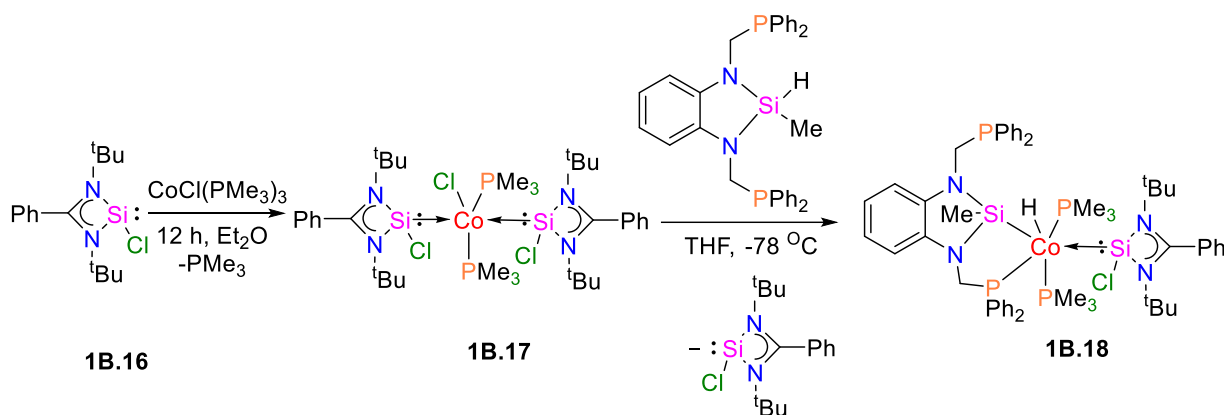
In 2017, Cui and Driess reported the Co(II) complex **1B.11**, stabilised by the bis(silylene)–pyridine [SiNSi] pincer ligand **1B.10**, which demonstrated efficient catalytic activity in C–H bond borylation (Scheme 1B.1.4).⁵⁸

Scheme 1B.1.4. Synthesis of **1B.11**.

Tacke and co-workers produced the divalent metal silylene complex **1B.12** (Scheme 1B.1.5) in 2017 by directly reacting the first freshly synthesised bis (guanidiny) silylene **1B.12** with the metal salts FeBr_2 , CoBr_2 , and $\text{NiBr}_2\cdot\text{DME}$ (**1B.13-1B.15**).⁵⁹ The bond distance of Si-M is 2.3876 (7) Å (Si-Fe), 2.3245(13) Å (Si-Co), and 2.1186(11) Å (Si-Ni), respectively.

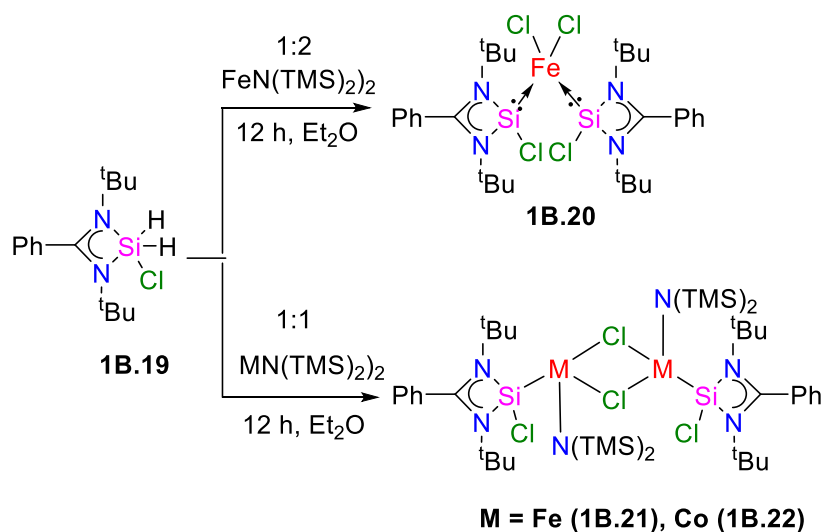
Scheme 1B.1.5. Synthesis of **1B.13-1B.14**.

Li and co-workers synthesised the five-coordinate bis(silylene) cobalt(I) complex **1B.17** by treating the chloro-silylene **1B.16** with $[\text{CoCl}(\text{PMe}_3)_3]$ (Scheme 1B.1.6).⁶⁰ Subsequent reaction of complex **1B.17** with the [PSiP] pincer ligand afforded a new silylene cobalt hydride **1B.18**. Experimental studies further demonstrated that the silylene cobalt hydride **1B.18** exhibits excellent catalytic activity in the Kumada cross-coupling reaction.



Scheme 1B.1.6. Synthesis of **1B.17-1B.18**.

In 2020, Krogman and coworkers investigated a new methodology to isolate the silylene metal complex (Scheme 1B.1.7).⁶¹ A silylene dinuclear iron complex bridged by chloride (**1B.20**) was produced when $[\text{Fe}(\text{N}(\text{SiMe}_3)_2)_2]$ reacted with two equivalents of silylene precursor $[(\text{PhC}(\text{N}^t\text{Bu})_2\text{SiH}_2\text{Cl})]$ (**1B.19**), while a bis-silylene iron dichloride complex **1B.21** was isolated when $[\text{M}(\text{N}(\text{SiMe}_3)_2)_2]$ ($\text{M} = \text{Fe, Co}$) reacted with two equivalents of **1B.21** and **1B.22**.

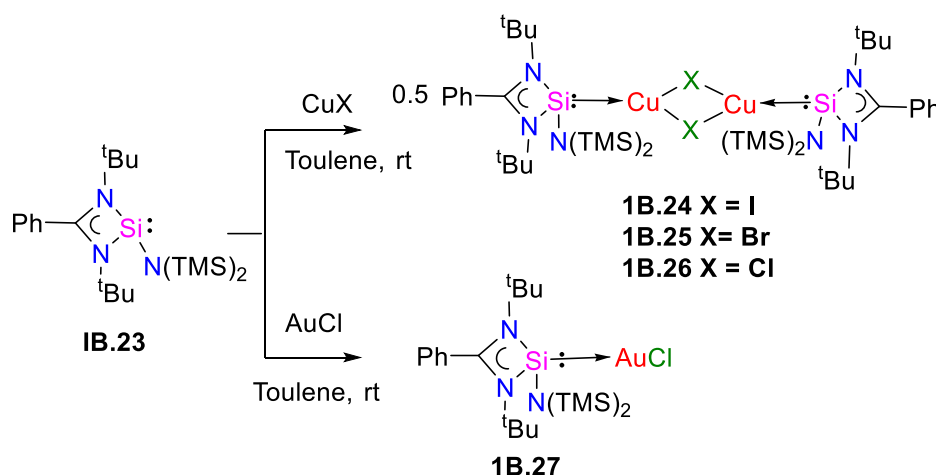


Scheme 1B.1.7. Synthesis of **1B.20-1B.22**.

1B.2 Isolation of amidinate silylene-based coinage metal halide complexes

Prior to the experimental isolation of structurally characterised silylene complexes with coinage metals ($\text{M} = \text{Cu, Ag, Au}$), Frenking and co-workers (1998) proposed a theoretical model for Cu, Ag, Au-tetrylene interactions.⁶² For comparison, they analyzed five-membered N-heterocyclic tetrylene-coinage metal complexes and suggested that NHSi-M bonds are predominantly ionic with minimal covalent contribution, following the stability trend $\text{Si-Au} > \text{Si-Cu} > \text{Si-Ag}$. While

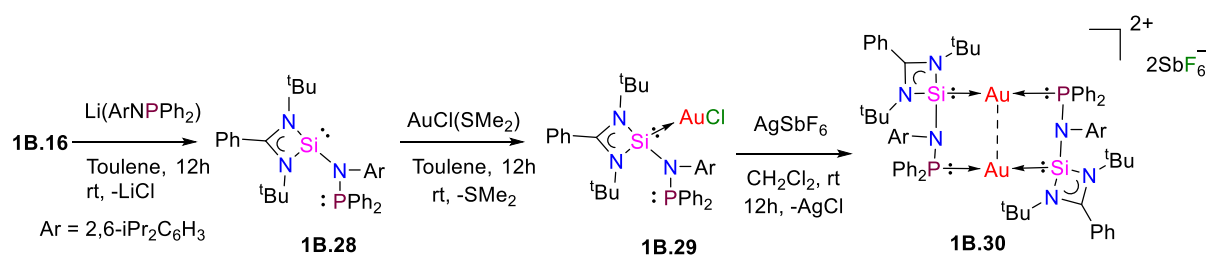
describing the bonding features of NHCs, Frenking provided detailed insights into the structural and electronic factors governing NHSi/NHGe–M complexes. Based on the closed-shell electronic configuration (s^0d^{10}) of the coinage metals, their study showed that the tetraylene lone pair donates into the metal s -orbital, accompanied by a slight decrease in population at the dz^2 -orbital, consistent with weak back-donation from M to the ligand. The predicted bond lengths indicated a shortening of the M–Cl bond for Cu and Ag, but an elongation for Au, relative to the corresponding free M–Cl bond. This anomaly was attributed to the pronounced relativistic effects in gold. These quantum chemical insights were pivotal in rationalizing the bonding and electronic distribution in five-membered NHSi-coinage metal complexes, which later gained significance following the successful isolation of such systems. The NHSi transition metal complexes, whereas the group-11 remained unexplored.^{53–54} Therefore, it is imperative to thoroughly investigate the coinage metal (Cu(I)/Ag(I)/Au(I)) chemistry of silylenes, as their uniquely tunable electron-donating and -accepting properties hold great promise for widespread applications in the future. Our group, in recent developments, has utilized a sterically demanding trimethylsilylamide-substituted benzamidinato silylene (**1B.23**) and isolated several Cu(I), and Au(I) complexes (**1B.24–27**) (Scheme 1B.2.1).^{63–65}



Scheme 1B.2.1. Reactivity of sterically demanding NHSi (**1B.23**) towards various coinage metal salts.

Further, we functionalized **1B.16** with a (2,6- i Pr₂C₆H₃NPPh₂) moiety, affording the hybrid bidentate silylene **1B.28**.⁶⁶ Its reaction with one equivalent of AuCl(SMe₂) furnished the monocoordinate Au(I) complex **1B.29**, in which only the silylene binds to the metal center, while the PPh₂ fragment remains uncoordinated (Scheme 1B.2.2). This observation highlights the superior σ -donor strength of the silylene relative to the phosphine. Subsequent halide

abstraction from **1B.29** using AgSbF_6 generated the dimeric, dinuclear Au(I) complex **1B.30** (Scheme 1B.2.2). Notably, **1B.30** represents the first example of a silylene-stabilised Au(I) complex that exhibits an aurophilic interaction between two gold atoms, supported by both Si(II) and P(III) centres (Figure 1B.2.1). While phosphines and NHCs are well known to form such $\text{Au}\cdots\text{Au}$ interacting systems often associated with intriguing photophysical properties, no precedent of this type had previously been reported for silylenes.⁶⁷⁻⁶⁸



Scheme 1B.2.2. Reactivity of sterically hybrid NHSi (**1B.28**) towards $\text{AuCl}\cdot\text{SMe}_2$ (**1B.29**-**1B.30**).

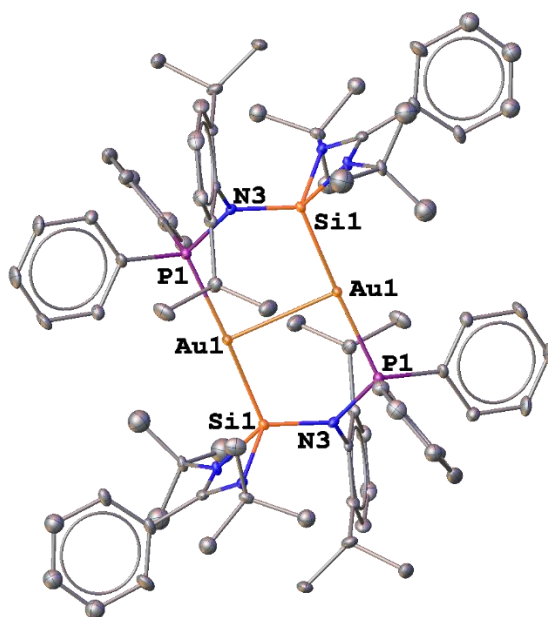
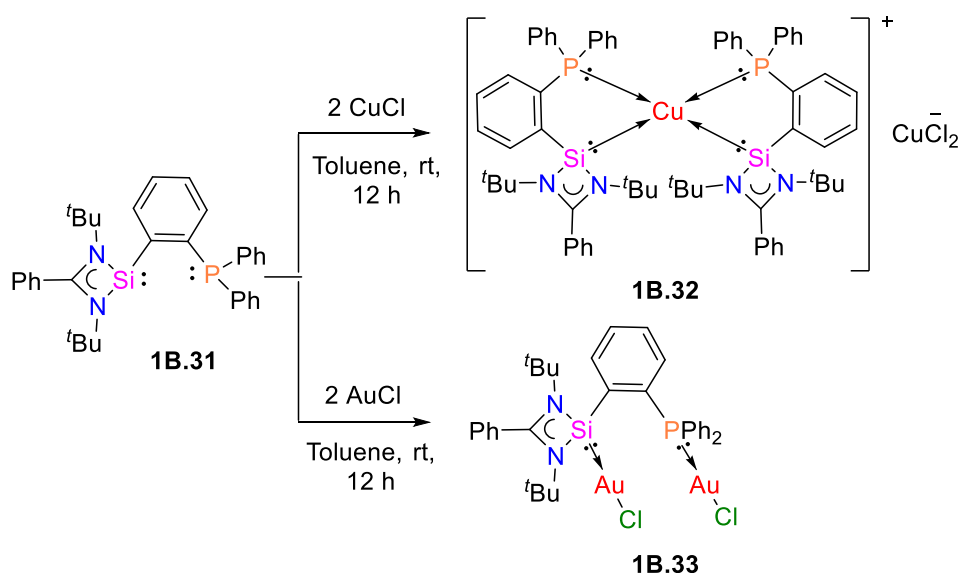


Figure 1B.2.1. Molecular structure of compound **1B.30** displaying aurophilic interaction. Hydrogen, counter anion and solvent are omitted for clarity.

Roesky and co-workers have recently synthesised a benzamidinato silylene-derived bidentate ligand featuring an additional phosphine donor (PPh_2) appended to a phenyl backbone (**1B.31**).⁶⁹ The incorporation of both the PPh_2 and Si(II) units on the same phenyl framework imparts rigidity to the ligand scaffold. When this ligand (**1B.31**) was treated with CuCl , it afforded complex **1B.32** (Scheme 1B.2.3), which contains a distorted tetrahedral copper(I)

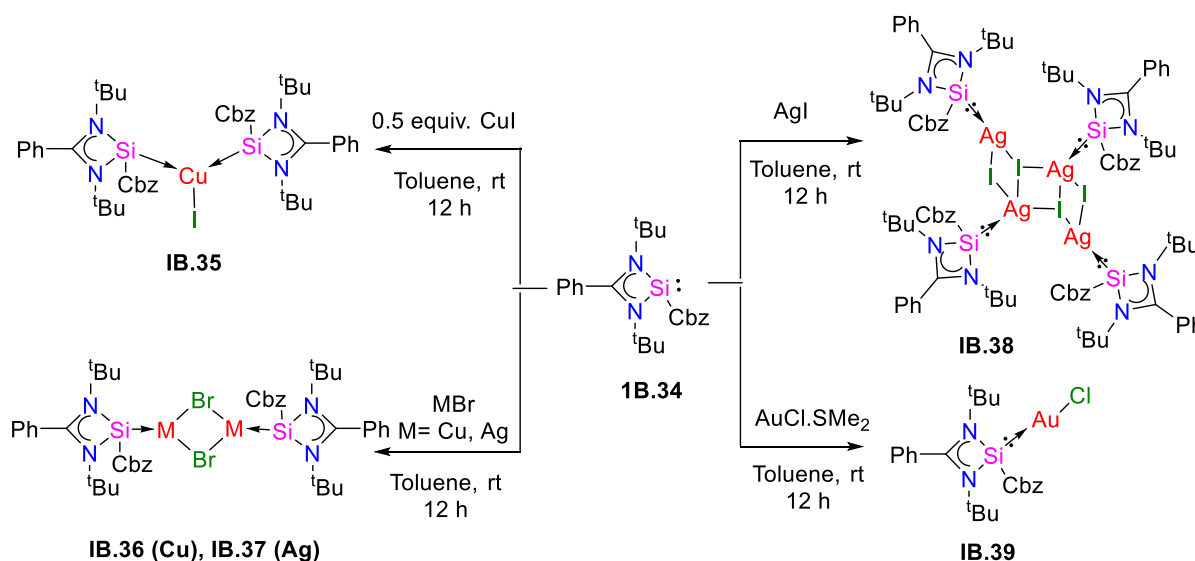
center along with a CuCl_2^- counter anion. Interestingly, the reactivity pattern observed here differs from earlier reports of Si(II) interacting with CuCl .⁶⁴ The central copper species was characterised as diamagnetic Cu(I) , since EPR measurements revealed no signal that would be expected for a paramagnetic Cu(II) state in a hypothetical $\text{Cu(0)}/\text{Cu(II)}$ combination. Treatment of **1B.31** with two equivalents of $\text{AuCl}\cdot\text{SMe}_2$ afforded complex **1B.33**, in which both the silylene and phosphine units coordinated with the different Au atom.



Scheme 1B.2.3. Synthesis of complexes **1B.32-1B.33**.

Khan and coworkers synthesised a new carbazole-substituted amidate silylene (**1B.34**) and explored it towards coinage metals (Scheme 1B.2.4).⁷⁰ The formation of **1B.35** was serendipitous by treating **1B.34** with CuSPh , whereas CuSPh was prepared in situ from CuI and LiSPh . Structurally, **1B.35** is distinctive as it features two molecules of **1B.34** bound to a single copper(I) centre. The ^{29}Si NMR spectrum of **1B.35** displays a singlet at δ 5.01 ppm. Treatment of **1B.34** with CuBr and AgBr provides the dimeric complexes **1B.36** and **1B.37**. The ^{29}Si NMR of **1B.36** and **1B.37** shows a peak at δ -0.72 ppm and δ 4.36 ppm. The reactivity pattern observed here matches well with the earlier reports of Si(II) interacting with CuBr/AgBr salts.⁶³⁻⁶⁴ However, AgI reaction with **1B.34** provides a unique tetrameric stair-step complex **1B.38**. The coordination of the silicon atom to the Ag(I) center is confirmed by ^{29}Si NMR, which resonates at δ 2.69 ppm. Complex **1B.38** crystallizes in the triclinic $P\bar{1}$ space group, incorporating three molecules of dichloromethane (Figure 1B.2.2). Owing to the steric demand of the iodide ligands, two Ag_2I_2 units fuse to alleviate structural strain, with each Ag(I) center coordinated by a silylene ligand. In complex **1B.38**, the Ag centers adopt a rectangular arrangement with $\text{Ag}\cdots\text{Ag}$ separations of 3.305 and 3.385 Å, values slightly shorter than the

distance for argentophilic interactions (3.44 Å, corresponding to the sum of the van der Waals radii of two silver atoms) (Scheme 1B.2.4). In the end, **1B.34** was treated with AuCl.SMe₂ and afforded the linearly coordinated complex **1B.39**.



Scheme 1B.2.4. Synthesis of complexes **1B.35**-**1B.39**.

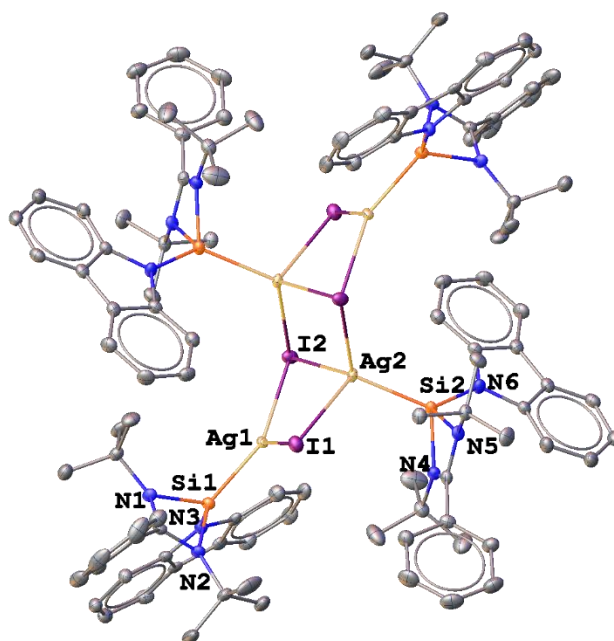
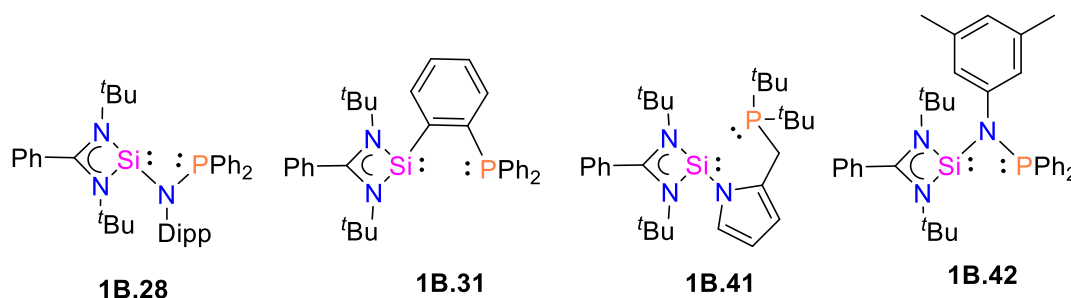


Figure 1B.2.2. Molecular structure of compound **1B.38** displaying tetrameric stair-step complexation. Hydrogen and solvent are omitted for clarity.

1B.3 Motivation and objectives.

The synthesis and isolation of NHSi-coordinated 3d-transition and coinage metal halides have so far been restricted mainly to monodentate and bidentate silylenes. Among these, bidentate

silylenes have received more attention owing to their ability to stabilise metal halides and promote diverse organic transformations. However, phosphine-based hybrid silylenes remain largely unexplored, despite their promising potential. The reported frameworks of such hybrid ligands, as outlined in Scheme 1B.3, highlight the unique feature of incorporating both silicon and phosphorus donor centers, which impart enhanced electronic effects and make these systems more efficient than their monodentate analogues.



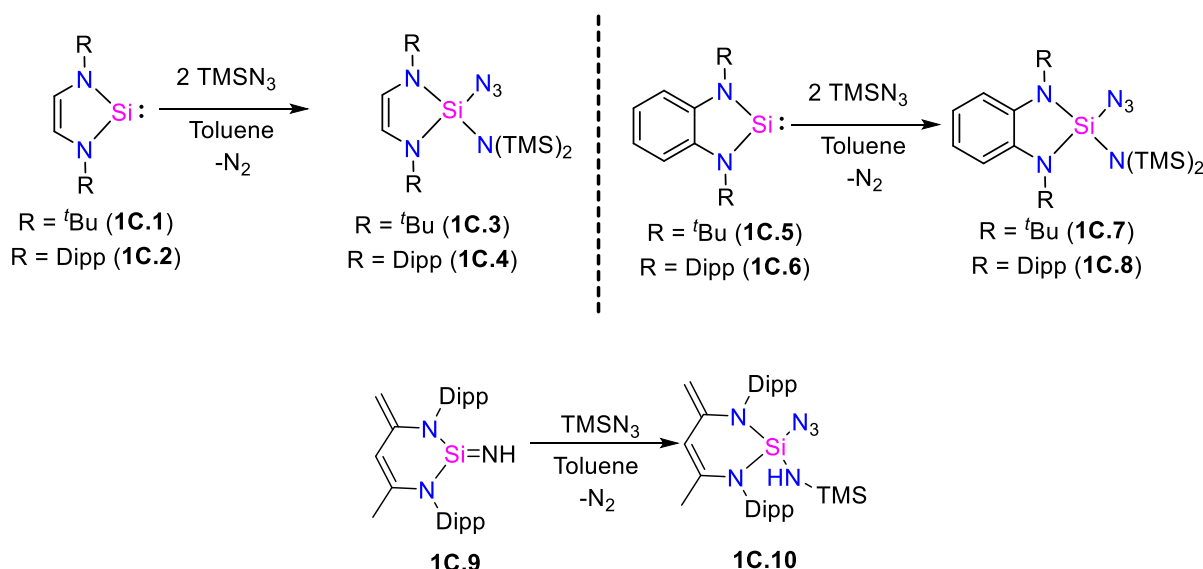
Scheme 1B.3: Isolated phosphine-based hybrid silylene motifs.

Building on this concept, Khan and co-workers successfully isolated a Si(II)–Au(I) complex that exhibited pronounced Au(I)⋯Au(I) aurophilic interactions. Subsequent investigations by Roesky and co-workers extended the coordination chemistry of these ligands to transition metals such as CuCl and ZnCl₂, as well as to main-group precursors including Se and GeCl₂. Cabeza and co-workers further explored their coordination abilities with late transition metals (Ni, Pd, and Pt), while Xi and co-workers studied their interaction in detail with Ni(COD)₂. These pioneering studies underline the versatility of phosphine-based hybrid silylenes, yet their application in stabilising 3d-transition metal halides and coinage metals remains relatively underdeveloped. Motivated by this gap, we sought to investigate the potential of phosphine-based hybrid silylenes as robust supporting ligands for 3d transition metals and coinage metal halides, which were hitherto less explored.

1C. Reactivity of Si(II) species towards organoazides (TMSN₃ and AdN₃).

Over the past few decades, there has been a significant upsurge in the study of Si(II) in organometallic chemistry.^{2, 17-18, 37, 53} Traditionally, the “double bond rule” implied that heavier congeners of carbon were incapable of forming stable multiple bonds due to the lack of formation of effective π -bonds.⁷¹ This long-held notion was challenged in 1981 with the landmark isolation of a compound containing a Si=C bond, which also paved the way for the synthesis of disilene (Si=Si) species that had previously been regarded only as transient intermediates.⁷²⁻⁷³ Since then, a variety of synthetic approaches have enabled the stabilization

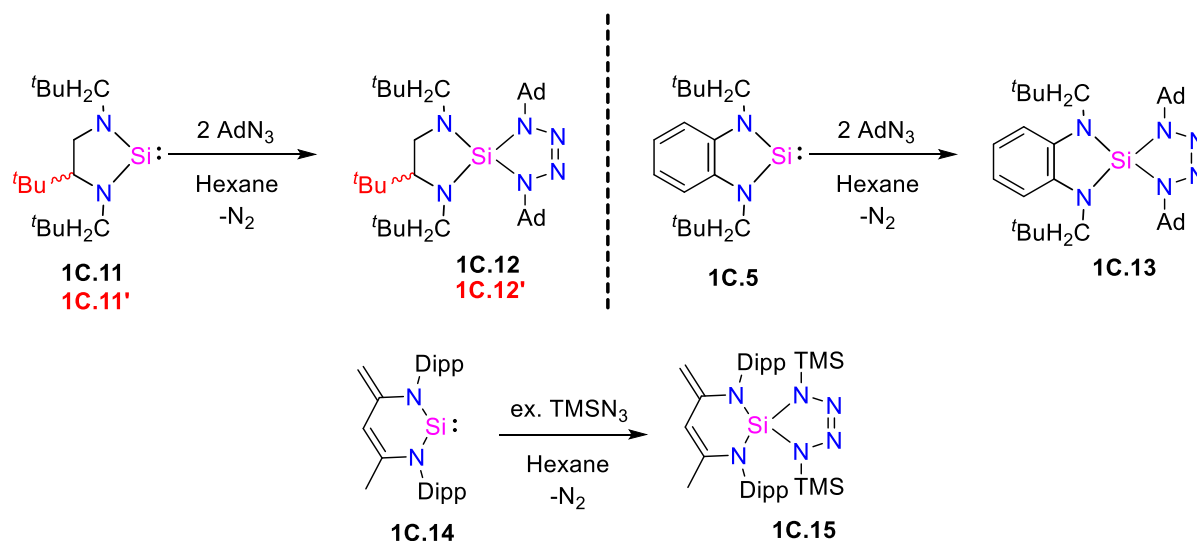
of such multiple-bonded silicon compounds, revealing bonding modes and reactivity patterns that are fundamentally distinct from those of carbon analogues.⁷¹ The ability of silicon to engage in multiple bonding has not only reshaped the understanding of its valency and electronic structure but also expanded its role in small-molecule activation and main-group catalysis.¹⁷ In particular, low-valent Si(II) frameworks have emerged as highly reactive and versatile species.¹⁹ Their pronounced affinity toward nitrogen-based reagents, such as organoazides, offers direct access to Si-N bond formation and unusual silicon-nitrogen functionalities.⁷⁴ These reactions often proceed through the generation of a Si=N double bond, providing a unique platform for constructing silicon-nitrogen frameworks and deepening our understanding of low-valent silicon chemistry. In this discussion, silylene reactivity was explored toward organoazide. The reactivity of silylenes with azides was first explored in 1994 by Denk *et al*, which opened the domain.⁷⁵ The reaction of **1C.1** and **1C.2** with two equivalents of TMSN₃ did not afford the corresponding silimine species but generated **1C.3** and **1C.4** bearing an azide group on the Si atom.⁷⁶⁻⁷⁷ Analogous to **1C.1** and **1C.2**, the reaction of **1C.7** and **1C.8** with TMSN₃ afforded the products **1C.7** and **1C.8** in 74 % yield.⁷⁸ In 2014, the Driess group investigated the formation of the iminosilane intermediate **1C.9** through the reaction of an aminosilane with amino lithium. **1C.9** subsequent trapping with TMSN₃ furnished the insertion product **1C.10** in 60% yield.⁷⁹



Scheme 1C.1: Synthesis of **1C.3-1C.4**, **1C.7-1C.8**, and **1C.10**.

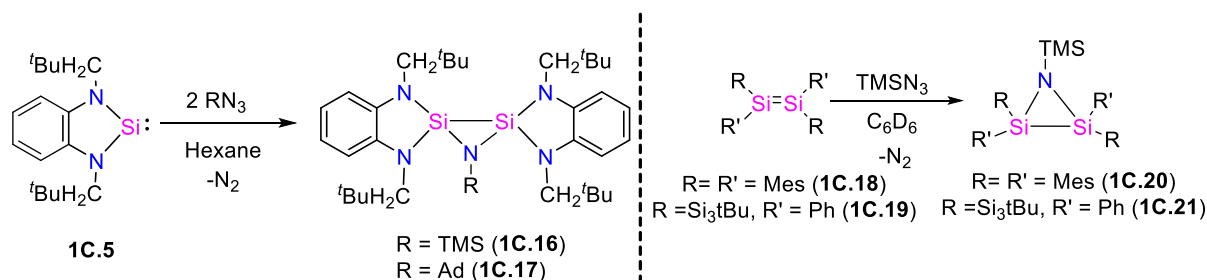
A silatetrazoline, **1C.12**, was also produced by the reaction of **1C.11** with 1-adamantyl azide AdN₃.⁸⁰⁻⁸¹ This was probably caused by the first synthesis of a silimine, which was followed by [2+3] cycloaddition between the Si=N moiety and the second azide. Similar to **1C.11**, **1C.5**,

and **1C.14** reacted with AdN_3 and TMSN_3 to produce **1C.13** and **1C.15** with a 74 % and 67 % yield.⁷⁸ In all the cases, the silicon centre is four-coordinated, and the formation of siltetrazoline was favourable due to the steric hindrance of either the organoazide or silylene moiety.



Scheme 1C.2: Synthesis of **1C.12**, **1C.13** and **1C.15**.

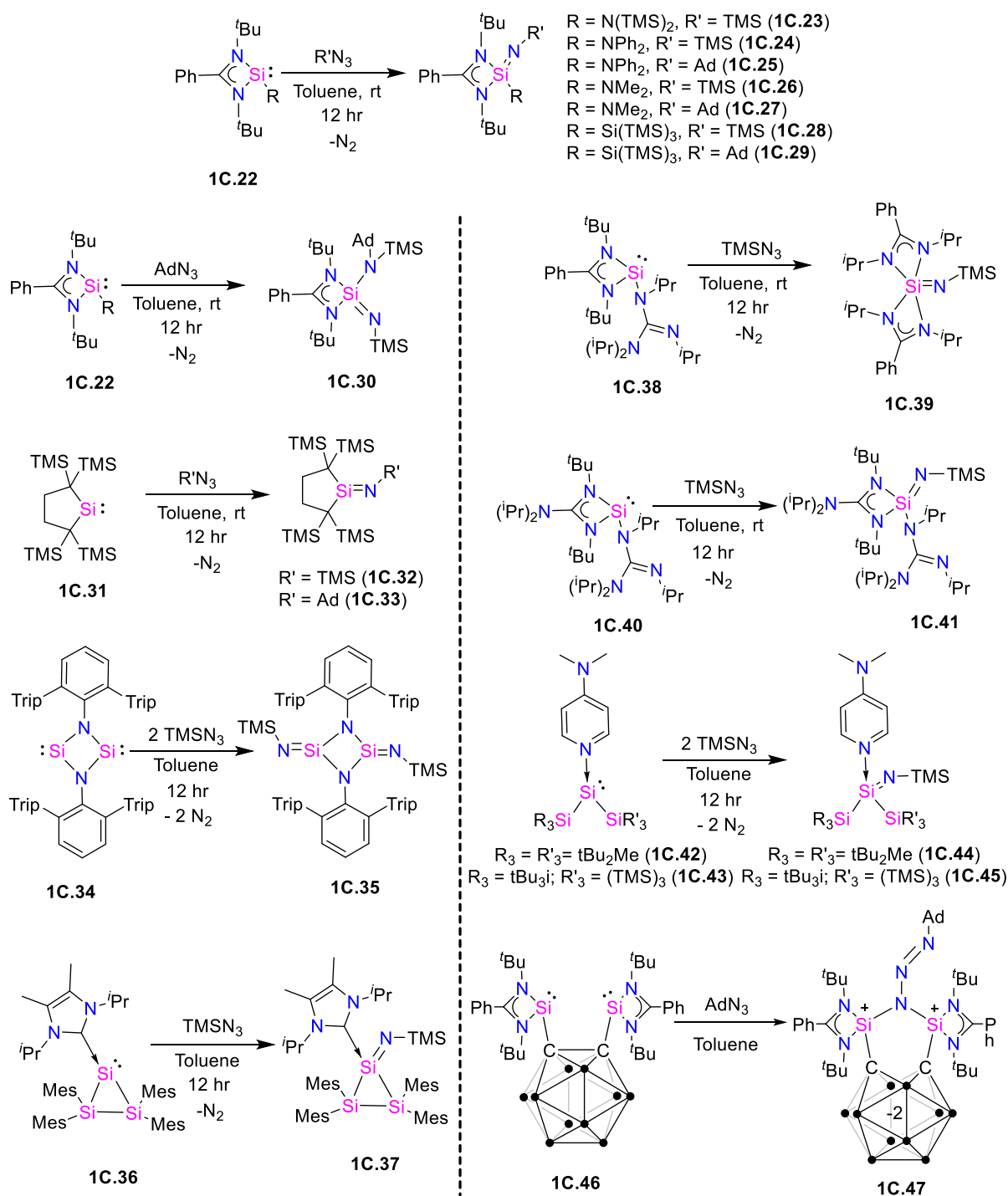
In 2001, Lappert and co-workers reported the reactivity of the benzo-fused N-heterocyclic silylene **1C.5** with azides (Scheme 1C.3).⁷⁸ The reaction of **1C.5** with 0.5 equivalent of AdN_3 or with a stoichiometric amount of TMSN_3 furnished the corresponding azadisilacyclopropane derivatives, **1C.16** and **1C.17**, respectively. The reaction of disilene (**1C.18**) with TMSN_3 exclusively yielded the disilaaziridine (**1C.20**) in 46% yield, with no other intermediates observed.⁸² In 2002, Wiberg and co-workers reported that the disilene **1C.19** reacted with TMSN_3 to give the disilaaziridine complex **1C.21** in 98% yield.⁸³



Scheme 1C.3: Synthesis of **1C.16-1C.17** and **1C.20-1C.21**.

Since 2012, several groups have investigated the reactivity of amidinate-stabilized silylenes with a range of organoazides (Scheme 1C.4).⁸⁴⁻⁸⁶ The silylenes **1C.22**, bearing different substituents at the silicon center, reacted smoothly with various azides to afford the corresponding silaimine products **1C.23-1C.29** in high yields (Scheme 65a). In the case of

1C.22, treatment with AdN_3 produced the silaimine **1C.30** featuring a terminal TMS group (Scheme 1C.4). The formation of **1C.30** is attributed to the migration of one TMS group from the $\text{N}(\text{TMS})_2$ substituent to the nitrogen atom of the initially formed $\text{Si}=\text{N}-\text{Ad}$ intermediate. Tacke,⁸⁷ Iwamoto,⁸⁸ Kira,⁸⁸ Roesky,^{86, 89-90} Filippou,⁹¹ Frenking,⁹² Lips,⁹³ Inoue,⁹⁴ and Driess⁹⁵ also observe a similar reactivity pattern (**1C.31-1C.47**). Further, when **1C.47** is treated with KC_8 , it leads to the formation of nitrene species.⁹⁵



Scheme 1C.4: Reactivity of TMS_3 and AdN_3 towards Si(II) species to afford silaimine.

1C.1 Motivation and objectives.

The reactivity of silylenes with organoazides has been well established, leading to a variety of silicon-nitrogen species such as silaimines, silatetrazolines, and diverse Si-N cyclic frameworks. These studies have significantly advanced our understanding of Si-N bond formation and the role of low-valent silicon in small-molecule activation. However, while monodentate N-heterocyclic silylenes are well explored, the corresponding disilenes and bissilylenes remain comparatively underdeveloped in their reactivity with azides, and phosphine-based hybrid silylenes are not utilized in this domain. Given their distinct electronic structures, these systems are expected to exhibit reactivity patterns that differ fundamentally from conventional silylenes. In this regard, bidentate silylene ligands represent a promising strategy to expand silicon-azide chemistry. Their chelating nature not only enhances the stability of reactive intermediates but also offers the possibility of cooperative effects at the silicon center. This could allow access to unprecedented reactivity, enabling selective formation of silaimines, novel silatetrazolines, and structurally diverse Si-N heterocycles. Exploring such reactivity will not only deepen the mechanistic understanding of azide activation by silicon but also open opportunities for designing new nitrogen-rich frameworks with potential applications in catalysis and materials chemistry. Addressing these gaps is crucial for advancing our understanding of silicon's role in main-group chemistry and for leveraging its unique properties in sustainable catalysis and functional material design. Therefore, in chapter 3, we will explore the reactivity of phosphine-based hybrid silylene, carbazole-substituted amidinate silylene, bissilylene, and Jutzi disilene toward organoazides (TMSN_3 and AdN_3) to fill this gap.

1D. Carbenes in the domain of emitters.

1D.1. Introduction of carbene and its importance as an emitter.

Carbenes, as a class of highly active and short-lived species, have been widely observed in synthetic organic chemistry. Since the isolation of the first room-temperature stable N-heterocyclic carbene, a number of variations of carbenes have been isolated.^{5, 9} Among them, some of the commonly used carbenes are N-heterocyclic carbenes (NHCs), cyclic (alkyl) (amino) carbene (CAAC), Monoamidocarbenes (MAC), N,N'-Diamidocarbenes (DAC), and less explored abnormal carbene (*a*NHC) (Figure 1D.1.1).^{14, 96-99} The NHC contains two σ -withdrawing and π -donating nitrogen atoms, while in CAAC, one nitrogen atom is replaced by

a σ -donating carbon atom. Therefore, CAAC contains only one sigma withdrawing and a π -donating nitrogen atom, which leads to a lesser HOMO-LUMO gap in CAAC with respect to NHC. Another derivative of carbene, DAC, was developed by Bielawski and co-workers.⁹⁶ DAC and MAC include carbonyl groups, which increase the carbene's π -accepting properties and concomitantly lower the energy of the LUMO. However, *a*NHC are the carbenes where C4/5 positions are available to the metal center for coordination. The C5 position makes *a*NHC less thermodynamically stable and more electron-donating than NHCs. Crabtree and co-workers were the ones who isolated the first iridium cationic *a*NHC complex, serendipitously.¹⁰⁰ They treated iridium hydride with an imidazolium salt and concluded that it is not always a C2 substitution from the imidazolium salt that is obtained in carbenes. Owing to their high intrinsic nucleophilicity, N-heterocyclic carbenes are frequently utilised as ligands in transition metal complexes as well as catalysts.¹⁰¹ Similarly, CAAC carbenes are well known for the stabilisation of reactive species and radicals. *a*NHCs are only restricted to structure bonding and organic transformations.¹⁴ Recently, many reports appeared with highly luminescent, d^{10} metal complexes (Cu(I), Ag(I), Au(I)) supported by carbenes.^{99, 102-104} More importantly, luminescence colour can be altered using different carbenes of varying electrophilicity. Owing to their excellent photophysical properties, they are excellent candidates for application in photocatalysis, biosensing, dye-sensitised solar cells, and as dopants in organic light-emitting diodes (OLEDs) due to their fast radiative lifetimes.⁴ The small energy separation between their lowest singlet and triplet excited states (ΔE_{ST}) and spin-orbit coupling *via* the metal ion are the responsible factors for their fast radiative lifetimes, and that can be tuned by changing the ligand system.

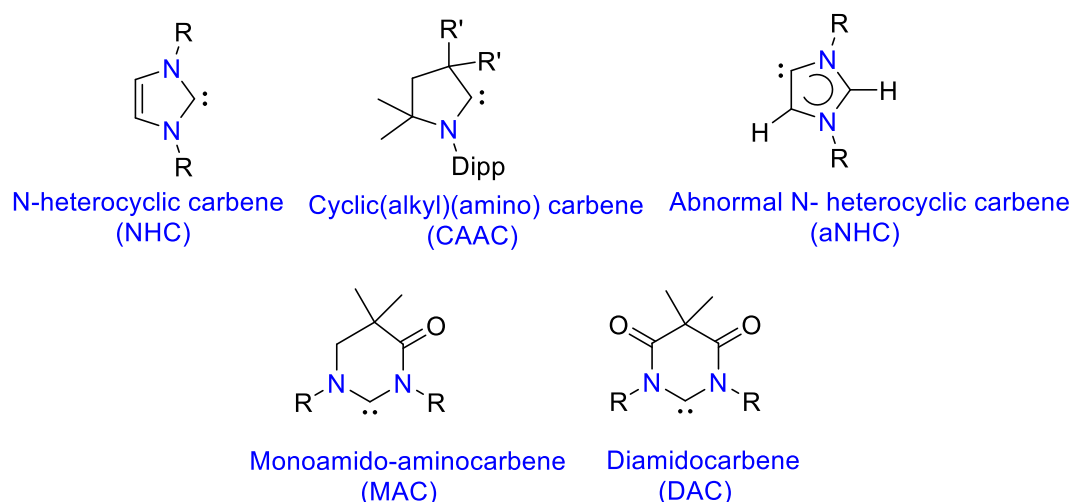


Figure 1D.1.1: Commonly used carbene derivatives (where R = alkyl or phenyl group).

1D.2. Carbene copper complexes as emitters.

Our discussion will be limited to carbene-copper chloride complexes, carbazole, and tert-butyl-substituted carbazole derivatives. Amouri and co-workers synthesised a linearly coordinated Cu(I) complex, **1D.1** and **1D.2**, with naphthalimide chromophore.¹⁰⁵ Both the complexes were synthesised *via* the transmetallation route (Chart 1D.1.1). In **1D.1**, naphthalimide is directly attached to the NHC ligand, while **1D.2** has a spacer (phenyl alkyne bridge) separating naphthalimide group. **1D.1** and **1D.2** both show blue emission, but the efficiency of the emission is higher in **1D.2** [ϕ = 7% (**1D.1**); 20% (**1D.2**)], and that is mainly due to the presence of the extended π -conjugation in **1D.2**. In 2017, Thompson *et al.* explored CAAC as a ligand to make linear coordinate copper(I) complexes **1D.3**, which show photoluminescence with solid state PLQYs up to 96% with nanosecond lifetime.¹⁰⁶ Romanov and co-workers isolated **1D.4** with another variation of CAAC.¹⁰⁷ They exhibit phosphorescence ($\lambda_{\text{max.}}$ = 511 nm) in the yellowish-green region with PLQYs (%) of 60 with lifetimes of 26 μ s. Both chloro-complexes (**1D.3** and **1D.5**) have high luminescent PLQYs (ϕ) in their crystalline and powder form, and emission profiles indicate CT nature for the emissive state (λ_{max} = 424 nm; ϕ = 86% for **1D.5** and λ_{max} = 436 nm; ϕ = 96% for **1D.3**), a similar observation was made by Romanov *et al.* Upon cooling, **1D.5** shows a red shift in emission (λ_{max} = 52 nm), whereas **1D.3** displays temperature-independent luminescence. In 2019, Ung and coworkers first introduced a chiral CAAC-supported C1-symmetrical copper(I) complex (**1D.6** and **1D.7**) that displays yellow circularly polarised luminescence (CPL), which occurs in the presence of significant spin-orbit coupling without helical or axial chirality.¹⁰⁸ **1D.6** and **1D.7** exhibit absorption maxima at 280 nm and 350 nm, accompanied by a broad emission spectrum centred at 555 nm with a PLQY of 1.8%. The **1D.6** isomer displays light blue emission, while the **1D.7** isomer displays dark blue emission. Ramanov in 2020 synthesised the linear copper chloride complexes **1D.8** and **1D.9** that depict emission at 456 and 555 nm with 14 and 40 % quantum yield.¹⁰⁹ Complexes **1D.10** and **1D.11** are exhibiting a unique dual emission property from nanosecond fluorescence and millisecond phosphorescence.¹¹⁰ It describes the crucial role of intermolecular forces inducing short fluorescence and long room-temperature phosphorescence (RTP) in the crystal originating from the carbazole unit. The molecular structures of **1D.10** and **1D.11** disclose an almost linear geometry at the Cu(I) center, where Cbz and NHC are not coplanar. These two complexes exhibit absorption peaks at 256 nm and 292 nm due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The steady-state photoluminescent (PL) spectrum of **1D.10** shows two emission bands; a) 400-550 nm (blue zone) which is insensitive towards oxygen with a nano-second

lifetime ($\tau_F = 16, 24$ ns) regarded as fluorescence, b) 550-750 nm are highly air-sensitive, with a long decay lifetime ($\tau_P = 55$ ms), acknowledged as phosphorescence. The low-energy band was described to arise from the weak spin-orbit interaction between the carbazole and copper, as spin-orbit coupling influences the decay lifetime of the low-energy band by influencing the intersystem crossing. The PLQY for **1D.10** and **1D.11** were found at 32.6% and 12.7%, respectively. Due to the difference between τ_F and τ_P , a red afterglow was observed after the removal of Cbz excitation (365 nm) under anaerobic conditions. Upon deuteration of the carbazole moiety emission properties of **1D.10** and **1D.11** were enhanced significantly. Based on experimental data, emission of **1D.10** and **1D.11** was proposed to be derived from the carbazole group as a singlet locally excited state (1LE state).

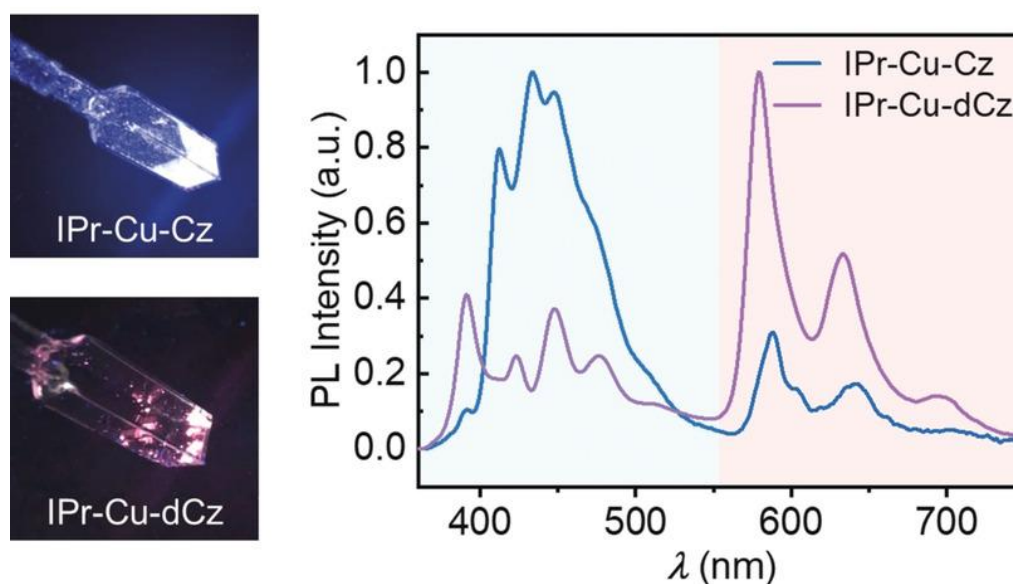


Figure 1D.1 Steady-state PL spectra and photos of **1D.10** under argon.¹¹⁰

The group of Thompson prepared a benzimidazolyl analogue **1D.12**, which emits in the blue region and has high luminescence efficiencies ($\phi_{PL} > 80\%$) and displays deep blue narrow emission in MeCy and PS films.¹¹¹ Che and coworkers synthesised compound **1D.13-1D.15**, exhibiting emission maxima at 567 nm, 581 nm and 426 nm in mCP (2 wt%) with PLQY of 88, 14 and 52 %, respectively.¹¹² Traskovskis and co-workers reported **1D.16-1D.19** compounds, which depict emission maxima at 467-510 nm with PLQY from 68-86%, the emission mechanism attributed to a TADF process.¹¹³ The same group further synthesized compound **1D.20**, displaying 84 % PLQY with emission at 482 nm in a PMMA film.¹¹⁴ In 2017, Di et al. introduced a copper-based CAAC-metal-amide (CMA) complex **1D.21**, which enables solution-processed LEDs with good internal quantum efficiency at high brightness.¹¹⁵

In 2018, Taffet et al. calculated that the bending of the CMA bond angle of **1D.21** enhances the singlet-triplet interaction strength and reduces the singlet-triplet energy gap (ΔE_{ST}).¹¹⁶ Later, Thompson and co-workers synthesised a series of CAAC-copper-amide (CMA-type) complexes (**1D.21-1D.24**) which display PLQY greater than 99% with lifetime in microseconds.¹¹⁷ This enhancement was done by eliminating non-radiative decay as a result of coplanar conformation, reduced structural reorganisation, and sufficient orbital overlap for efficient charge transfer. Absorption spectra of **1D.21-1D.24** reveal high energy bands ($\lambda < 350$ nm) due to $\pi-\pi^*$ transitions of the ligands. All the complexes are highly luminescent in fluid solution or in polystyrene matrices, but powdered form is weakly emissive. By increasing the steric bulk on the CAAC ligand, the PLQY was increased from 10% to 100% as well as decreasing the rate of non-radiative decay, which is very much unexpected for a copper complex. The blue OLED, which was prepared using **1D.21**, displays $E_{QE_{max}} = 9.0\%$ and 16 cd/A at 2 mA/cm². In solid phase, **1D.24** exhibits emission bands centred at 651 nm (red region), with PLQY of $\Phi = 32\%$ in the solid state, and it was because of a very efficient TADF process involving ^{1/3}LLCT states. Linear complex **1D.25** exhibits outstanding deep-red TADF emission ($\lambda_{max} = 621$ nm, $\phi = 0.32$, $\tau_{av} = 366$ ns) with a radiative rate constant ($k_r \approx 9 \times 10^5$ s⁻¹), which surpasses the values reported for commonly used Ir^{III}- and Pt^{II}-based emitters.¹¹⁸ Romanov synthesised compounds **1D.26-1D.27** featuring monocyclic (C6) and bicyclic (BIC6) cyclic (alkyl)(amino)carbene ligands, which demonstrate the influence of LUMO stabilisation, conformational flexibility, excited-state energy, and geometry on photoluminescent properties, achieving 100 % quantum yields with short excited-state lifetimes.¹⁰⁹ Thompson and co-workers isolated compound **1D.28** and investigated the effect of a π -extended ligand on its photophysical properties.¹¹⁹ In both toluene and PS films, **1D.28** exhibited a near-unity quantum yield with emission maxima around 500 nm, governed by a TADF mechanism. The complex **1D.29** was used in OLED fabrication, and the fabricated device emits bright green light ($\lambda_{max} = 534$ and 555 nm) with high EQE (15.4-19.4 %).¹²⁰ However, complexes **1D.30-1D.31** exhibit emission maxima at 556 and 534 nm, with short lifetimes of 0.72 and 0.39 μ s and PLQYs of 70 % and 58 %, respectively.¹²¹ In the follow-up work, Shi *et al.* used DAC-supported copper complexes along with carbazolyl group **1D.32** (Chart 1D.1.1), which shows the PLQY up to 12 %.¹²² Upon freezing, all of them show a hypsochromic shift in the emission spectra. Doping of **1D.32** into 1wt % in polystyrene (PS) shifts the emission maxima from 658 nm to 704 nm. Only two reports exist on abnormal carbene-metal-amide emitters. Compounds **1D.33-1D.34** exhibit TADF via intermolecular charge transfer, while compounds **1D.35-1D.37** display dual emission with maxima ranging from 456 to 570 nm, with low PLQYs.¹²³⁻¹²⁴

Abnormal carbene-metal-amide emitters, therefore, represent a promising yet largely unexplored domain, offering significant opportunities for advancing the understanding of their photophysical behaviour and expanding their potential applications in OLED fabrication.

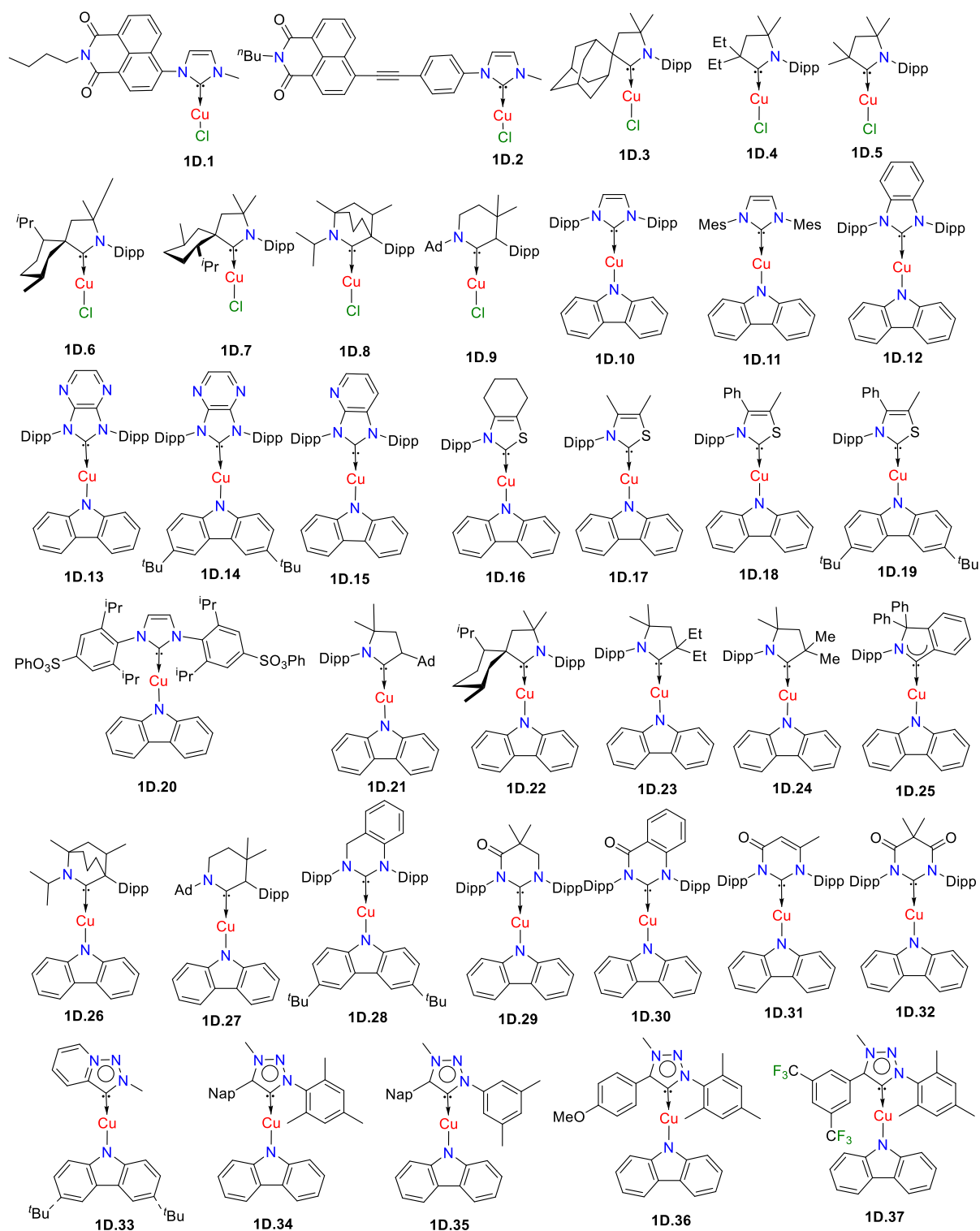


Chart 1D.1: Reported examples of carbene-copper complexes (NHC, CAAC, MAC, DAC, aNHC) functionalized with chloride, carbazole, and *tert*-butyl carbazole ligands

1D.3. Carbene silver complexes as emitters.

The synthetic route of luminescent CAAC-silver complexes is very similar to their copper analogues. Only silver halide is used instead of copper halide, and further, the CAAC-silver halide complex was treated with appropriate substrates in the presence of base (NaO^tBu) to get the luminescent CAAC-silver complexes. **1D.38-1D.40** supported silver halide complexes and their photophysical properties were uncovered by Romanov *et al.*, which show featureless blue emissions with low PLQYs ($\sim 5\%$) around 430-470 nm in the solid state.^{109, 125} The absorption spectra of **1D.39** and **1D.41** show a very weak absorption band around 250-370 nm, which is presumably originating from the interligand ($\text{Cz/bpy} \rightarrow \text{NHC}$) and metal-ligand charge transfer (MLCT).¹²⁵ These MLCT transitions are mainly based on the HOMO $\rightarrow$ LUMO electronic transition of the complexes. **1D.39** and **1D.41** emit at 360 nm and 407 nm with PLQYs of 14.2%, 16.9%, and 18.6%, respectively. The neutral two-coordinate linear silver(I) complex **1D.42** was synthesised with a sterically bulky benzimidazolyl carbene, 1,3-bis(2,6-diisopropylphenyl)-1-H-benzo[d]imidazol-2-ylidene (BZI), and carbazolidine (Cz) ligands.¹¹¹ In this complex, **1D.42** carbene is a redox-active acceptor ligand, and an amide is a donor ligand connected to the silver metal. The redox gap of **1D.42** is large ($\Delta E_{\text{redox}} > 3\text{V}$), which is in well agreement with the high energy absorption band ($> 400\text{ nm}$ in CH_2Cl_2) corresponding to the carbazolidine-to-carbene ICT transition. The PLQY of **1D.42** is $> 80\%$ and displays deep blue emission in MeCy and PS films. Electrochemical studies disclosed that the coordinated BZI carbene's electrophilicity is lower than the CAAC and MAC (Monoamidocarbene) ligands in analogous complexes. **1D.42** also shows negative solvatochromic in the polar solvent which is mainly due to the large change in the molecular dipole moments between the ground and excited ICT states. The same group also prepared **1D.43**, where 1-benzyl-3-(2-pyridylmethyl)benzimidazolylidene NHC was utilised as a ligand along with bipyridine and carbazole ligands.¹²⁶ Solid-state absorption and emission spectra were collected for **1D.43**. A weak absorption band in the range 355-370 nm was observed, which was assigned to the metal-to-ligand charge transfer (MLCT) process. The emissions in solid-state for **1D.43** were observed at 515 nm and described to be originating due to the metal perturbed IL transitions. Further, Bochmann and co-workers utilized mononuclear silver complexes (**1D.44** and **1D.45**) (Chart 2) for the fabrication of efficient solution and vacuum-processed OLEDs.¹²⁰ **1D.44** and **1D.45** unveil broad green to yellow emission at room temperature with PLQY of 74% and 55% in toluene under an inert atmosphere. Their emissions are highly quenched by O_2 , implying the triplet state decay mechanism. The low PLQYs (up to 17%) were observed for both complexes,

which can be significantly improved by grinding (to 33%) or by drop-casting as thin films (to 45%). The luminescence was assigned as TADF-type PL with lower activation energy and rapid triplet harvesting. OLED with 20 wt% dopant in 1,3-bis (9-carbazolyl) benzene show electroluminescence at 502 nm with 4.3% EQE (in evaporated method) and with 3.8% EQE (in solution processed method) of complex **224** and at 509 nm with 13.7% EQE (in evaporated method) and with 11.0% EQE (in solution processed method) of complex **225**. These results demonstrate that **1D.44** is a better candidate for OLED fabrication. In 2019, Hamze et al. reported the complex **1D.46**, which exhibits high PLQY of 80-100% with emission lifetimes of 0.33-2.8 μs (short) in 1% PS film.¹²⁷ The emission of **1D.46** is assigned due to TADF, which is predominantly dependent upon the ΔE_{ST} at room temperature. The ΔE_{ST} values are directly correlated with the radiative decay rate of the compounds. They found (theoretically as well as experimentally) that silver complexes have a smaller ΔE_{ST} value (18 meV) compared to copper and gold complexes ($\Delta E \sim 70\text{-}73$ meV), leading to the fastest radiative rate constant ($K_r > 10^6 \text{ s}^{-1}$) for silver complexes. They demonstrated that **1D.44-1D.45** complexes have a short lifetime and the radiative rates are more than 10^6 s^{-1} , which is much faster than the Ir-based emitters used in OLEDs. Due to this reason, silver complexes are not suitable for OLED fabrication. Romanov synthesise complex **1D.47** and **1D.48**, which show emission maxima at 558 and 530 nm with 53 and 41 % quantum yield.¹²¹ Further, they isolated **1D.49**, which shows blue emission (496 nm) in a zeonox matrix with $\sim 5\%$ PLQY.¹²⁰ MAC-based analogous silver(I) complex **1D.50** was also probed for the emission properties and OLED fabrication ($\lambda_{\text{max}} = 512$ nm (PS film) $\phi = 44\%$), but it did not show the same promising results.¹⁰⁹

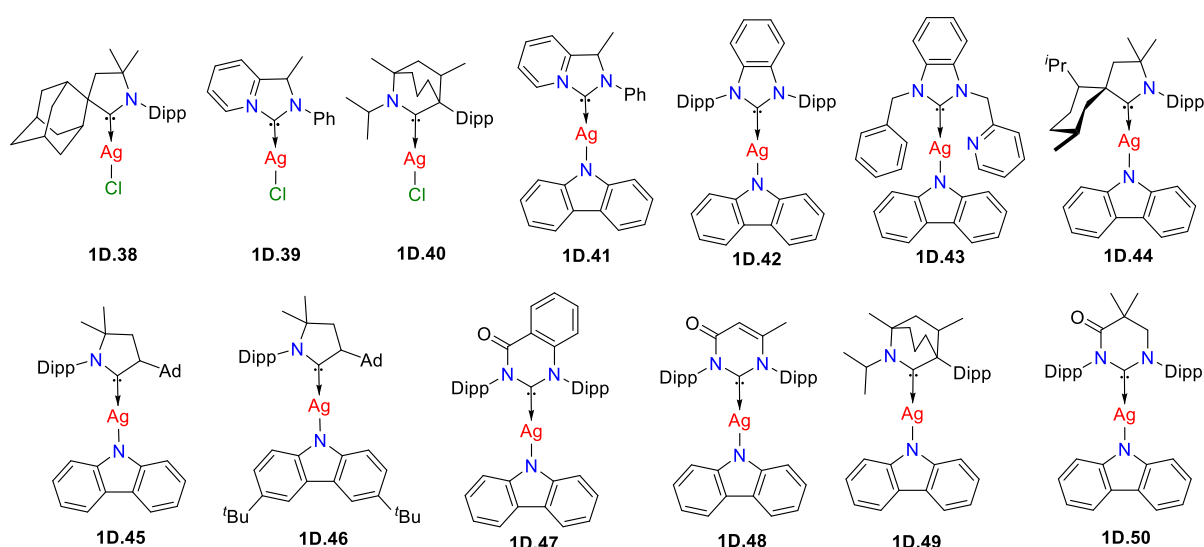


Chart 1D.2: Reported examples of carbene-silver complexes (NHC, CAAC, MAC, DAC, aNHC) functionalized with chloride, carbazole, and *tert*-butyl carbazole ligands

1D.4. Carbene gold complexes as emitters.

The preparation of luminescent CAAC-gold complexes is similar to that of their copper analogues. The only difference is the use of gold(I) halide instead of copper(I) halide. Complex **1D.51** shows PL in a solid polycrystalline state in the visible range at 298 K.¹²⁸ These emissions were assigned to phosphorescence based on the emission decay profile, which is in microseconds. In these complexes **1D.52** and **1D.53**, aurophilic interaction is observed between two individual molecules in a head-to-tail manner with Au $\cdots$ Au distance of 3.407 Å.¹⁰⁵ **1D.52** and **1D.53** show PL in DCM solution at room temperature with PLQY of 0.01 % (for **1D.52**) and 0.29 % (for **1D.53**). The emission bands for them were observed in the range of 426–451 nm. In 2019, Razali and co-workers reported two-coordinate Au(I) complexes (**1D.54** and **1D.55**) with a benzimidazolium moiety.¹²⁹ They were synthesised by the reaction of benzimidazolium salts with Ag₂O, followed by transmetallation with Au(SMe₂)Cl. Complexes **1D.54** and **1D.55** possess intramolecular aurophilic interaction with Au $\cdots$ Au distances of 3.564 Å and 3.520 Å, respectively. The emission spectra of **1D.54** and **1D.55** display dual emission (high-energy band and low-energy band), which significantly depends upon the temperature. The HE fluorescence emission bands are assigned due to the ¹XLCT mixed with ¹MLCT, whereas the LE band is due to the thermal-assisted phosphorescence. Further, Ohshita and co-workers used bis(diphenylphosphinyl)-functionalized dipyrrodo-annulated NHC to isolate the complexes **1D.56**.¹³⁰ Complex **1D.56** displays an aurophilic interaction, which is mainly due to the rigid ligand framework. Further, Prabusankar and co-workers reported a gold complex (**1D.57**) that undergoes Au $\cdots$ H–C(sp³) hydrogen bonding interaction (Figure 1D.2).¹³¹ **1D.57** was synthesised by the transmetallation method. In complex **1D.57**, HOMO is located on anthracene groups with low contribution from NHC and Au(I) moieties, and LUMO orbital contribution arises from anthracene. In solution, the emission spectrum of **1D.57** displays a band from 375 nm to 500 nm and exhibits a blue emission, but the solid-state emission ranges from 400 to 500 nm. The stronger luminescence in the crystalline form is triggered by aggregation-induced emission and gives a significant fluorescence PLQY (the Φ_F value of 8.8 % ($\lambda_{\text{max}} = 446$ nm)). The fluorescence emission of **1D.57** is mainly due to an S₁→S₀ transition, which is affirmed by the nanosecond lifetime. The major contribution in the emission spectrum is attributed to the anthracene orbitals, along with minimal contributions from NHC and Au metal.

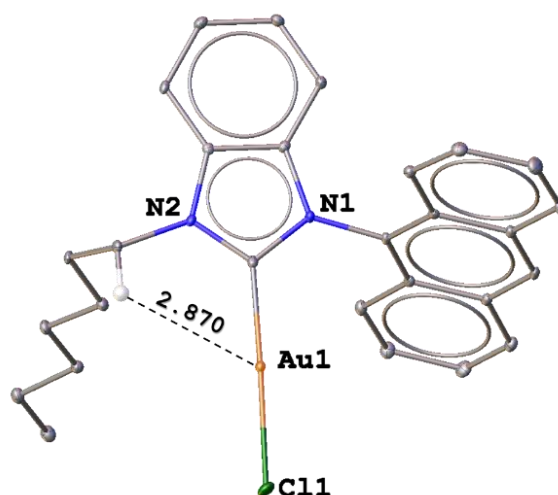


Figure 1D.2. The molecular structure of **1D.57** displaying Au $\cdots$ H interaction. Hydrogen atoms are omitted for clarity, and the structure is reproduced from the CIF file.¹³¹

Very simple linear CAAC-gold-halide complexes **1D.58** and **1D.59** were synthesised by Romanov *et al.* with less PLQY (<5%) that depict emission at 438 and 528 nm.^{122, 125} The UV/Vis spectra of **1D.58** display an absorption band centred at 350 nm, arising due to the LMCT. The complex **1D.60** by Thompson and co-workers revealed a radiative rate controlled via TADF.¹¹¹ The luminescence studies of **1D.60** in methylcyclohexane solution reveal an energy difference between the lowest singlet and triplet excited states of 920 cm⁻¹. An organic light-emitting diode (OLED) was fabricated using **1D.60** as a luminescent dopant that has an external quantum efficiency of 12% and narrow, deep-blue emission (CIE = 0.16, 0.06). Dinda and co-workers reported **1D.61** and **1D.62** and studied their photophysical properties.^{126, 132} It was observed that the ancillary ligands can influence the photophysical properties in solution and the solid state. **1D.61** and **1D.62** display absorption bands around 255-370 nm, which are assigned for MLCT and ILCT. **1D.61** emits at 360 nm with a lifetime in nanoseconds. Emission bands exhibited by **1D.62** were measured at 523 nm in the solid state and 422 nm in the solution state. The origin of the emissions observed at 523 nm was assigned to metal perturbed IL transitions, whereas the high-energy emission at ~430 nm was from IL π - π^* transitions. Thompson and co-workers synthesised **1D.63**, which shows emission maxima at 650 nm in 2Me-THF with 0.37 μ s lifetime and 75 % PLQY.¹³³ Che and coworkers reported compound **1D.64-1D.67** with emission maxima between 510-520 nm and PLQY near 91 %.¹³⁴ Di *et al.* opened a new avenue by synthesising high-performance OLEDs based on linear carbene-metal-amide (CMA) complexes (**1D.68-1D.69**) with near 100% internal quantum efficiency (IQE), and their application in high-performance OLEDs.^{117, 135} In these complexes, the LUMO is

mostly localised on CAAC (behaves as an acceptor) and the HOMO resides mostly on amide (behaves as a donor). To explain the luminescence properties of the complexes, they hypothesised a rotationally assisted spin-state inversion (RASI) mechanism. According to this mechanism, the T_1 is higher in energy compared to S_1 (i.e. negative energy gap, $\Delta E < 0$) upon intermolecular rotation of the carbazole (Cz) ligand about N(Cz)-Au-C(CAAC) axis, which promotes fast and efficient reverse intersystem crossing (RISC), enhancing the high-performance solution-processed OLEDs. Also, Hall et al. discovered an ultrafast dynamic in the TADF of **1D.68**. Later, Conaghan et al. utilised **1D.68** for the fabrication of OLEDs using an efficient vacuum process. In the solution process, Di et al. reported that a device based on **1D.68** shows EL quantum efficiency ($\eta_{\text{EQE,EL}}$) up to 27.5 %, whereas Conaghan *et al.* revealed its ELQE greater than 23 % in the vacuum process. Very recently, the same group, Di and co-workers, further utilised **1D.68** and demonstrated the highly efficient solution-processed LEDs by using a dual-dopant device (**1D.68**:TBRb) with >20 % EQE in electroluminescence, where TBRb (2,8-di-tert-butyl-5,11-bis(4-tert-butyl-phenyl)-6,12-diphenyltetracene) is a simple yellow fluorescent rubrene derivative. Following this, Credgington and co-workers also studied the influence of different parameters on the photophysical properties of **1D.68**. Usually, **1D.68** shows mid-green emission in solution as well as in amorphous thin film. However, by varying the host material emission of 240 can be tuned from green to blue, which is majorly influenced by the intermolecular interactions and CT-CT coupling. They further explored the method of CMAs crystallisation for **1D.68** using polar and low glass-transition-temperature matrix and unveiled the significant impact of molecular conformations on the photophysical processes. Credgington and co-workers also studied **1D.68** to see the effect of a heavy atom on coinage-metal bridged CMAs and revealed that the ISC rate follows the order of CMA(Cu) > CMA(Au) > CMA(Ag), which results from the stronger ^1CT - ^3CT coupling in the case of copper than gold. Penfold and co-workers also reported that there is an emulation between direct ISC happening between ^3CT - ^1CT and indirect ways, which couple with ^3LE (intermediate locally-excited triplet state) on their donor or acceptor ligands and the energy of the ^3LE decreases by decreasing the metal size. So, the indirect path plays a significant role for the lighter metals instead of the heavier metals. Similarly, **1D.70** was also found to be very emissive ($\Phi_{\text{PL}} = 95\%$), displaying an emission band at λ_{max} 502 nm with a lifetime of 1.20 μs .¹²⁰ Upon cooling **1D.70** to 77 K, a hypsochromic shift (426 nm λ_{max}) was observed with increased lifetime (530 μs), which is a confirmation of a thermally promoted emission process at room temperature. Similar to copper complexes, gold isomers were synthesised **1D.71**-**1D.72**, which show λ_{max} at 523 and 490 nm with PLQY of 54 % and 100 %.¹⁰⁹ Thompson and coworkers further isolated the **1D.73**-

1D.74 depicts λ_{max} at 479 and 484 nm with PLQY of >95 % in both cases.¹¹⁹ MAC-based analogous of gold (I) complex **1D.75** was also probed for the emission properties and OLED fabrication. The OLEDs fabrication using **1D.75** as a dopant emitted green light (λ_{max} = 510 nm) with an external quantum efficiency (EQE) of 18 %.¹²⁷ Thompson and coworkers further isolated the **1D.76-1D.77** depicts λ_{max} at 554 and 528 nm in the Ps film with PLQY of 77 and 50 %.¹²¹ However, there is only one report on mesoionic gold complexes, which show a TADF mechanism and were synthesised by Yan and coworkers¹²³. The compounds **1D.78** and **1D.79** show intermolecular charge transfer with emission maxima at 580 and 555 nm, with around ~55 % PLQY. This is an open domain for future device fabrication by changing the ligand and metal scaffold.

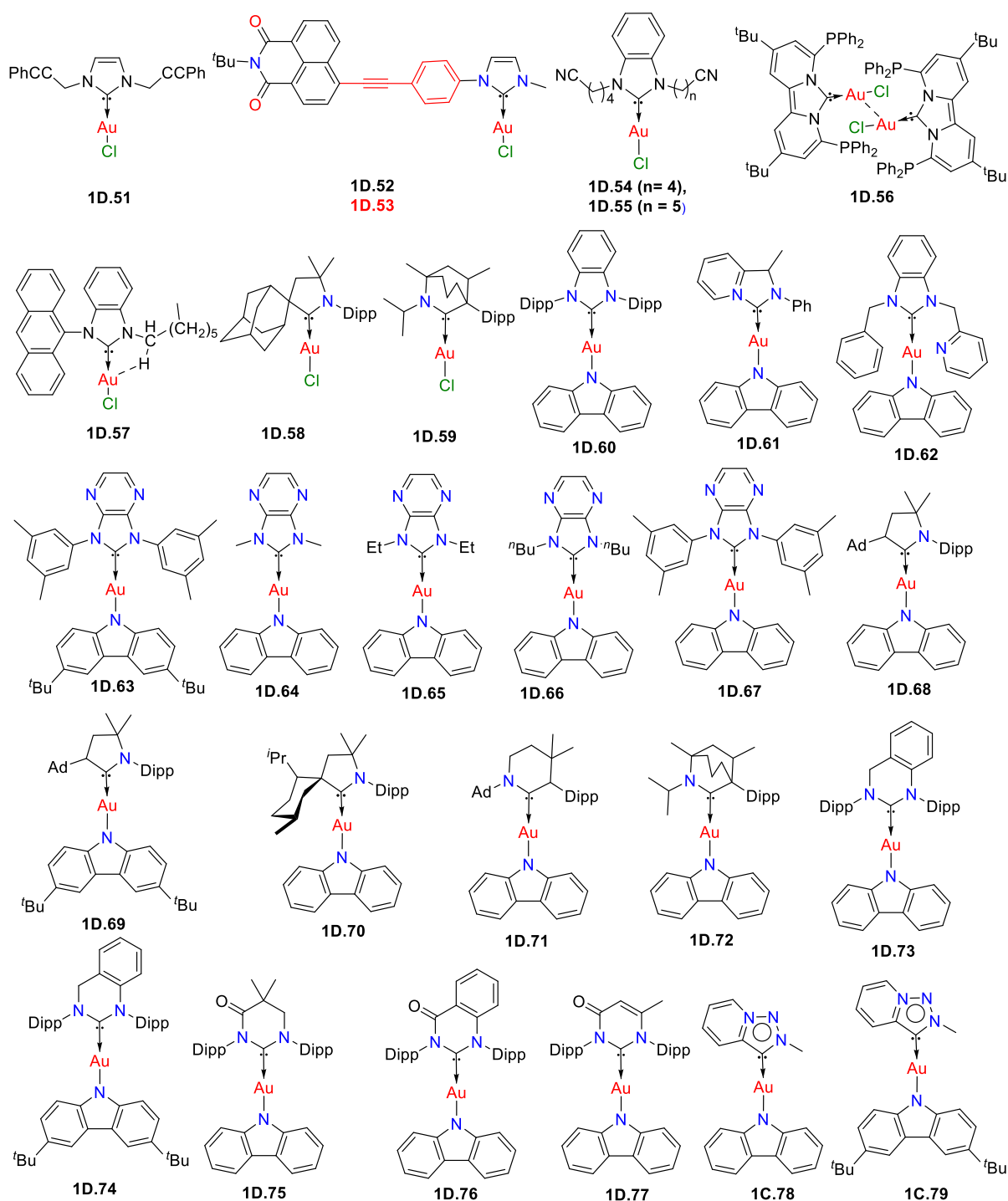


Chart 1D.3: Reported examples of carbene-gold complexes (NHC, CAAC, MAC, DAC, *a*NHC) functionalized with chloride, carbazole, and *tert*-butyl carbazole ligands.

1E. Carbenes in the coordination sphere of group-6 carbonyls.

A wide range of highly stable, neutral NHC-borane adducts, in which boron exists in the +3 oxidation state, have been reported (Figure 1E.1).^{4, 136} Owing to their versatile reactivity, these adducts have been widely utilised as reagents and catalysts in organic synthesis.¹³⁷ The

complementary interaction between the strong Lewis basicity of NHCs and the Lewis acidity of boranes underpins the ease of adduct formation, analogous to classical borane complexes with ethers, amines, sulfides, or phosphines.¹³⁶ However, the exceptionally strong σ -donor ability of NHC ligands imparts far greater stability to NHC-borane adducts compared with those formed from conventional donors. Importantly, many of these complexes can be synthesised on a multigram scale and exhibit excellent solubility in common organic solvents. Their practical utility has been demonstrated in diverse transformations, including serving as co-initiators in radical polymerisations and as stoichiometric reducing agents for aryl, alkyl, and alkenyl halides, triflates, and carbonyl derivatives. Steric and bulk play a huge role while isolating the BH_3 adduct, due to the side carbene insertion reaction into the B-H bond upon complex formation ($^{\text{Me}_2}\text{CAAC}$, MAC).¹³⁸ In this section, we aim to highlight the isolated NHC-stabilised BH_3 complexes (Chart 1E.2).

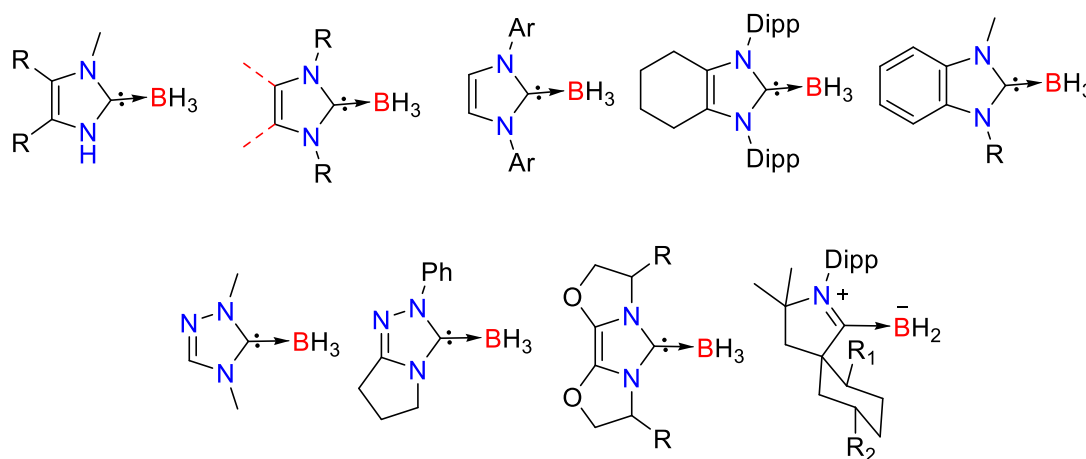


Chart 1E.1. Reported examples of NHC-borane complexes.

Electron-rich NHC-boranes can donate two electrons *via* their B-H bonds to form transition-metal complexes.¹³⁹ Braunschweig and co-workers reported species such as $[\text{M}(\text{CO})_5(\eta^1\text{-H}_3\text{B}(\text{IME}_2))]$ ($\text{M} = \text{Cr}$ (**4B.I**), Mo (**4B.II**), W (**4B.III**)) and $[\text{CpMn}(\text{CO})_2(\eta^1\text{-H}_3\text{B}(\text{IME}_2))]$ (**4B.IV**), generated by irradiating the corresponding metal carbonyls with $(\text{IME}_2)\text{BH}_3$ (Chart 4B.2). In these, borane coordinates through a B-H-M three-centre two-electron bond, as confirmed by ^{11}B NMR (δ -42 to -47 ppm) and single crystal X-ray diffraction. Tobita's group later showed that $(\text{NHC})\text{BH}_3$ ($\text{NHC} = \text{IME}_4$, $\text{I}^t\text{Pr}_2\text{Me}_2$) reacts with $\text{Cp}^*(\text{CO})_2\text{W}(\text{py})\text{Me}$ to yield hydrido(hydroborylene)tungsten complexes $\text{Cp}^*(\text{CO})_2\text{W}(\text{H})[\text{BH}(\text{NHC})]$ (**4B.V** and **4B.VI**), with characteristic ^{11}B signals ($\delta \sim 74$ ppm).¹⁴⁰ X-ray studies revealed short W-B bonds (2.174 Å) and a W-H-B three-centre two-electron interaction (Chart 1E.2). These complexes further undergo hydroboration with terminal alkynes to give NHC-stabilised η^3 -boraallyl species, e.g.,

$\text{Cp}^*(\text{CO})_2\text{W}[\eta^3\text{-PhHCCHBH-(NHC)}]$ (**4B.VII** and **4B.VIII**; $\delta^{11}\text{B} = -9.5$ and -8.9 ppm). In contrast, Shimoi and co-workers extensively explored the reactivity of phosphine- and amine–borane adducts with carbonyl complexes, resulting in the isolation and characterization of several novel compounds.¹⁴¹⁻¹⁴⁴

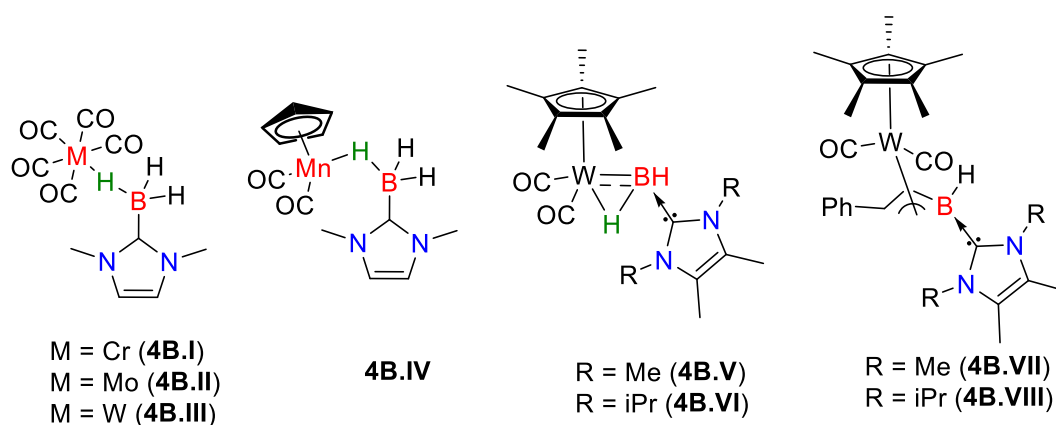


Chart 1E.2: Reported examples of NHC-borane reactivity with group-6 carbonyl complexes.

1D.5 Motivation and objectives.

Coinage metal complexes (Cu, Ag, Au) supported by N-heterocyclic carbenes are widely recognised for their diverse luminescent properties and applications in optoelectronics, sensors, and catalysis. However, abnormal carbenes (*a*NHCs) remain less explored in this context. In contrast, *a*NHCs are explored in the area of organic transformations, small molecule activation, reactive species, anti-cancer activity, and photophysical properties (very preliminary) (Figure 1D.3). The stronger σ -donor capacity and altered orbital orientation of *a*NHCs can substantially tune metal-ligand charge transfer, ligand-centred states, and metallophilic interactions. By introducing an *a*NHC ligand into coinage metal systems, one can probe new emissive pathways, enhance stability under ambient conditions, and potentially access solvatochromic or mechanochromic responses. In recent years, there has been rapid progress in carbene-based (NHC, CAAC, DAC, MAC) coinage metal amide complexes, driven by their straightforward synthesis and remarkable emissive behaviour. In contrast, abnormal carbene-stabilised coinage metal amides remain scarcely explored. Existing synthetic strategies often fail to yield such complexes, highlighting the need for rational ligand design. Tailoring abnormal carbene frameworks for coordination to coinage metals is expected to open avenues for unprecedented optical and electronic features.

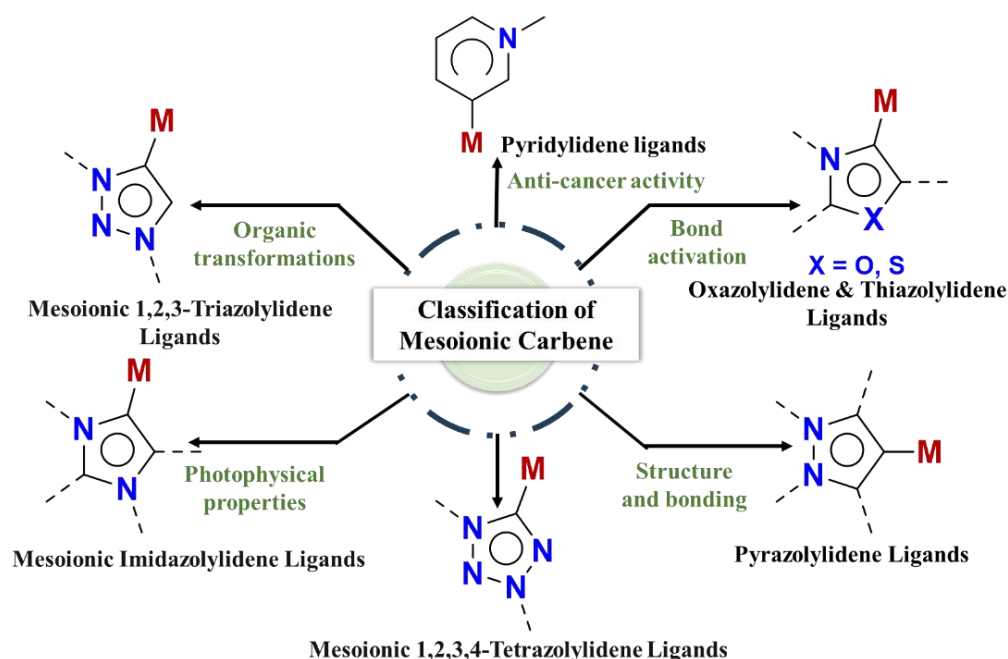


Figure 1D.3: Isolated abnormal carbenes and their application in different domains. ¹⁰¹

The work described in Chapter 4.1 addresses this gap by establishing a viable synthetic entry into these inaccessible *a*NHC-coinage metal-amide systems (*a*CMA). With continued development, *a*CMA complexes hold the promise of evolving from being largely academic curiosities into commercially relevant photoactive materials.

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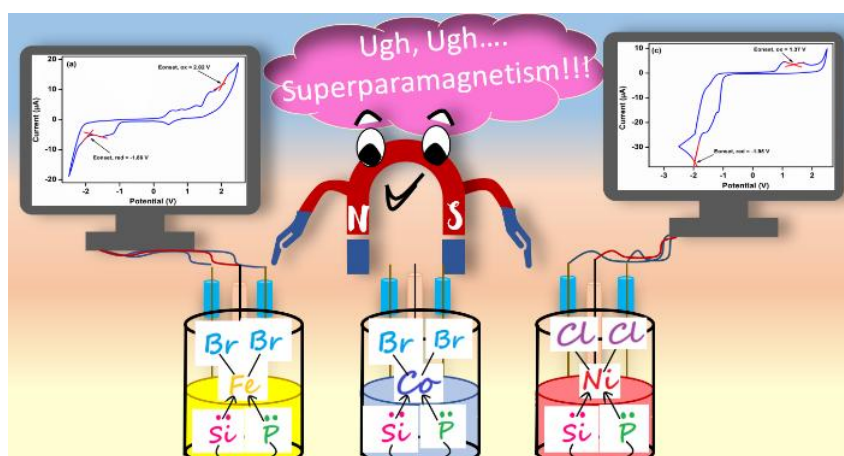
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Chapter 2: Synthesis and Coordination of Phosphine-Silylene-Based Hybrid Ligand Towards 3d-Transition and Coinage Metals

Chapter 2A: First Row Transition Metal Complexes of Phosphine-Silylene-based Hybrid Ligand



Adapted from: **R. Akhtar**,[#] S. H. Kaulage,[#] M. P. Sangole, S. Tothadi, P. Parvathy, P. Parameswaran, K. Singh, S. Khan* First Row Transition Metal Complexes of Phosphine-Silylene based Hybrid Ligand. [*Inorg. Chem.* **2022**, *61*, 34, 13330-13341.](#)

2A.1 Objective of this work.

We have prepared two new silylene-phosphine-based hybrid ligands $[\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN}(\text{R})\text{C}_6\text{H}_4(\text{PPh}_2)]$ ($\text{R} = \text{TMS}$ {trimethylsilyl} (**2A.1**), TBDMS {*tert*-butyldimethylsilyl} (**2A.2**)), which possess two donor sites. Further, the treatment of the bidentate ligand **2A.1** with base metal halides (FeBr_2 , CoBr_2 , $\text{NiCl}_2\cdot\text{dme}$ (Nickel chloride(II) ethylene glycol dimethyl ether)) and **2A.2** with $\text{NiBr}_2\cdot\text{dme}$ (Nickel bromide(II) ethylene glycol dimethyl ether) afforded four-coordinate six-membered metal complexes **2A.3-2A.6** respectively, which feature coordination from both Si(II) and P(III) sites. Subsequently, complexes **2A.3** $[\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN}(\text{SiMe}_3)\text{C}_6\text{H}_4(\text{PPh}_2)(\text{FeBr}_2)]$, **2A.4** $[\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN}(\text{SiMe}_3)\text{C}_6\text{H}_4(\text{PPh}_2)(\text{CoBr}_2)]$, **2A.5** $[\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN}(\text{SiMe}_3)\text{C}_6\text{H}_4(\text{PPh}_2)(\text{NiCl}_2)]$ and **2A.6** $[\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN}(\text{Si}^t\text{BuMe}_2)\text{C}_6\text{H}_4(\text{PPh}_2)(\text{NiBr}_2)]$ are studied for their redox and magnetic properties with the help of UV-Vis spectroscopy, cyclic voltammetry, and SQUID magnetometry. Complexes **2A.3-2A.6** were found to display paramagnetic behaviour. All the compounds are well established by single-crystal X-ray diffraction studies.

2A.2 Introduction

N-heterocyclic silylenes have recently attracted significant attention and demonstrated their potential as excellent ligands in various metal-catalysed organic transformations.¹ Several donor-stabilised silylenes have been synthesised to date and examined for their coordination toward transition metals, especially metal carbonyl complexes.^{2,3} Considering the bidentate ligand can provide a greater degree of stability than monodentate ligands, a substantial number of bidentate silylene ligands have been reported, representing the backbone of N,N'-{bis(*tert*-butyl)amidinate}chlorosilylene $[\text{PhC}(\text{N}^t\text{Bu})_2\text{SiCl}]$.^{2h,3} Apart from these, there are several bidentate silylene-based ligands where different donor atoms (e.g., N, C, Si, P) are combined with the Si(II) centre.⁴ These bidentate systems have shown their potential for stabilising many reactive species and transition metal complexes.^{3,5} The concept of hybrid ligands has increased acceptance in designing new strategies for molecular activation, homogeneous catalysis, functional materials, or small-molecule sensing.^{3,4} In 2016, we reported a hybrid $[\text{PhC}(\text{N}^t\text{Bu})_2]\text{SiN}(2,6\text{-}^i\text{Pr}_2)\text{PPh}_2$ (**2A.A**) ligand, which was further utilised to isolate a dimeric dinuclear Au(I) complex with $\text{Au}\cdots\text{Au}$ interaction.^{5a} Following this work, a few new silylene-phosphine-based hybrid ligands (**2A.B-D**) were synthesised and probed for the metal complexation reactions (Chart 2A.1).^{5c-e}

Although there are some reports on bidentate silylene ligands supported first-row transition metal halide complexes (**2A.i-ix**, Chart 2A.2), they are only limited to structural authentication.⁶ Surprisingly, there is no report on the complexes of first-row transition metal halides (MX_2 ; $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$; $\text{X} = \text{Cl}, \text{Br}$) with such a hybrid $\text{Si(II)}\text{-P}$ system. The base metal complexes (Fe, Co , and Ni) supported by silylene ligands are of significant interest due to their immediate application in catalysis, and the additional phosphine donor can fine-tune their reactivity. Considering the fact that the first-row transition metal halides are highly sought after in catalysis, the synthesis and in-depth understanding of the silylene-phosphine ligated MX_2 complexes ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$) is deemed desirable. We made our initial efforts with our previously reported $\text{Si(II)}\text{-P}$ ligand **2A.A**, but could not isolate the expected complexes so far. Therefore, we designed a new backbone and prepared two novel $\text{Si(II)}\text{-P(III)}$ based hybrid silylenes [$\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN(R)C}_6\text{H}_4(\text{PPh}_2)$] ($\text{R} = \text{TMS}$ {trimethylsilyl} (**2A.1**), TBDMS {*tert*-butyldimethylsilyl} (**2A.2**)). The hybrid silylene **2A.1** was further treated with FeBr_2 , CoBr_2 , and $\text{NiCl}_2(\text{dme})$ salts, which afforded complexes **2A.3-2A.5**. Similarly, **2A.2** was reacted with $\text{NiBr}_2(\text{dme})$ salt, which afforded complex **2A.6**. These complexes were further studied for their redox and magnetic properties. Our results are discussed in detail as follows.

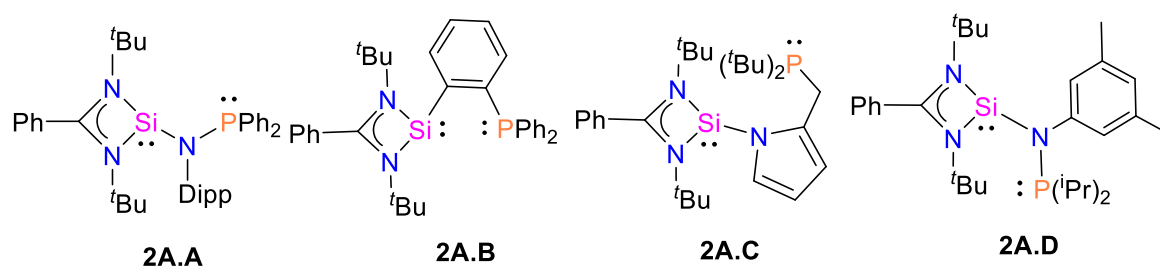


Chart 2A.1: Previously reported silylene-phosphine-based hybrid ligands.

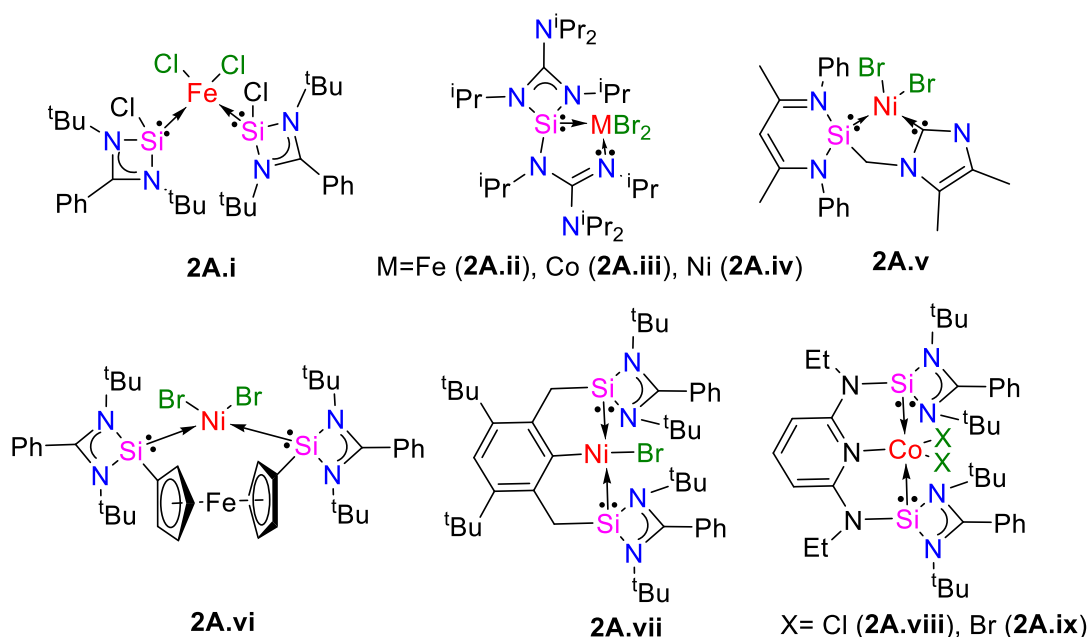


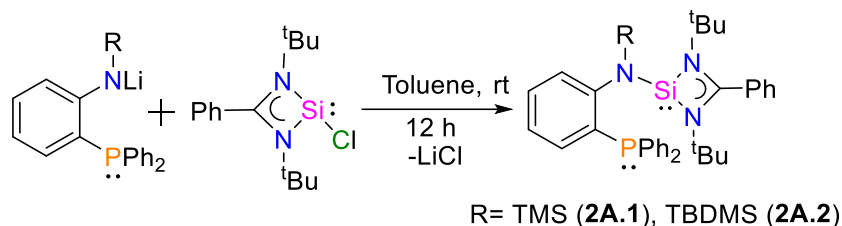
Chart 2A.2: Previous reports on silylene-Fe(II), Co(II), and Ni(II) halide complexes.

2A.3 Results and Discussion.

2A.3.1 Structural elucidation.

The treatment of $[\text{PhC}(\text{N}^t\text{Bu})_2]\text{SiCl}$ with $\text{LiN}(\text{R})(\text{C}_6\text{H}_4)\text{PPh}_2$ ($\text{R} = \text{TMS}$, TBDMS) in toluene at room temperature afforded the silylene-phosphine-based hybrid ligands $[\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN}(\text{R})(\text{C}_6\text{H}_4)\text{PPh}_2]$ ($\text{R} = \text{TMS}$ (**2A.1**), TBDMS (**2A.2**) in good yield (Scheme 2A.1).⁷ Colorless crystals of **2A.1** and **2A.2** suitable for single-crystal X-ray analysis were obtained after storing their concentrated solutions for 24 hours. The ^{31}P NMR spectra of **2A.1** and **2A.2** display a single peak at δ -22.75 and -27.21 ppm, respectively. The ^{29}Si NMR spectra of **2A.1** and **2A.2** exhibit a doublet (for Si(II) center) at δ -13.11 and -13.92 ppm with the $J_{\text{Si-P}}$ coupling constant of 21.6 Hz and 30.2 Hz, respectively. The ^{31}P and ^{29}Si NMR signals for **2A.1** and **2A.2** are upfield-shifted compared to the hybrid silylenes (Chart 2A.1), indicating that **2A.1** and **2A.2** are good ligands due to the strong electron-donating ability of the TMS and TBDMS groups. **2A.1** crystallizes in the triclinic $P\bar{1}$ space group, while **2A.2** crystallises in the monoclinic $P2_1/n$ space group. The molecular structure of **1** show that the Si(II) atom is in the vertex of a trigonal pyramid connected to the three N atoms (Figure 2A.1). Due to the poor-quality crystal data, we refrain from discussing the bonding parameter of **2A.2**. The molecular structures of **2A.1** and **2A.2** confirm the presence of two donating sites, Si(II) and P(III), leading to the anticipation that **2A.1** and **2A.2** can behave as a bidentate ligand. To gain further insight into the coordination behaviour of **2A.1** and **2A.2**, we expanded our investigation

towards 3d-transition metals [FeBr₂, CoBr₂, NiCl₂(dme), NiBr₂(dme)] as they are highly sought after in catalysis due to their cost-effectiveness and environmentally friendly nature.⁸



Scheme 2A.1. Synthesis of **2A.1** and **2A.2**.

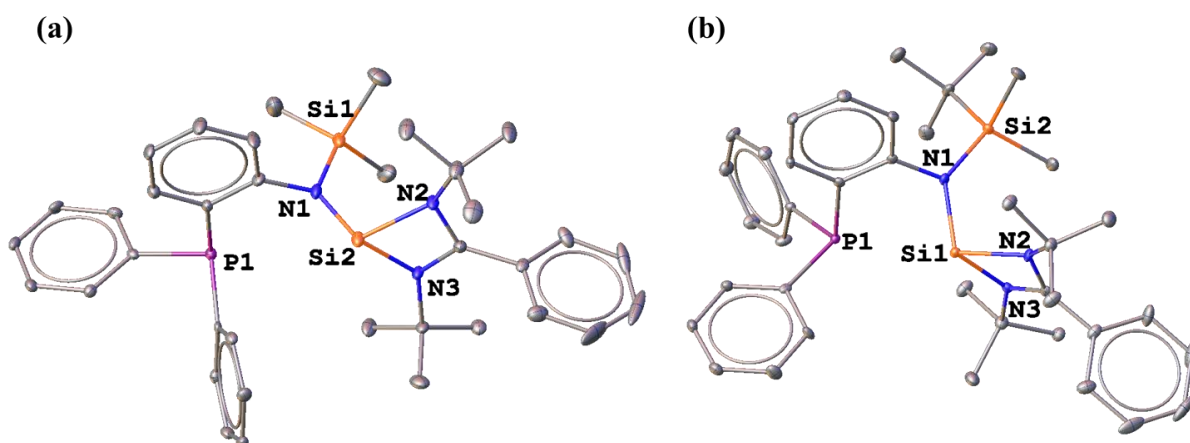
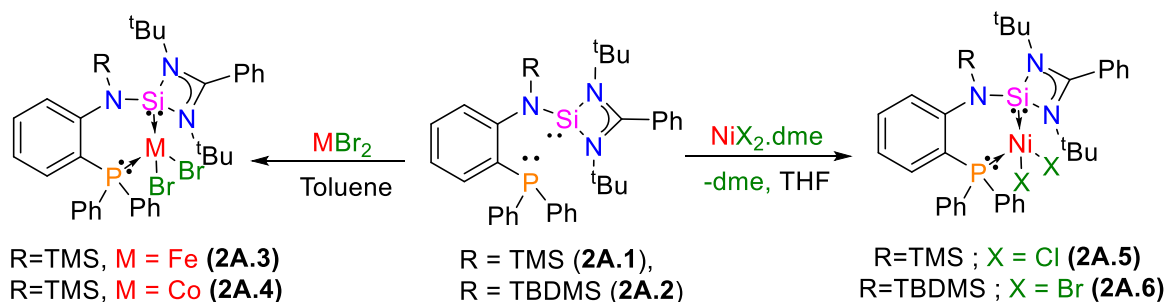


Figure 2A.1. (a) The molecular structure of **2A.1**. The anisotropic displacement parameters are depicted at the 50 % probability level. Hydrogen atoms and solvents are omitted for clarity. Selected bond distances (Å) and angles (°): N3-Si2 1.880(3), N2-Si2 1.920(3), Si2-N1 1.804(3), Si1-N1 1.758(3), C6-N1 1.446(5), C5-C6 1.407(5), P1-C5 1.845(4); C14-P1-C5 103.3(2), P1-C5-C6 120.5(3), N1-C6-C5 121.9(3), Si2-N1-Si1 131.3(2), N1-Si2-N2 108.3(1), N1-Si2-N3 106.5(1), N2-Si2-N3 68.8(1), N2-C30-N3 105.6(3). (b) The molecular structure of **2A.2**. The anisotropic displacement parameters are depicted at the 50 % probability level. Hydrogen atoms and solvents are omitted for clarity.

Treatment of **2A.1** with one equivalent of FeBr₂ and CoBr₂ in toluene furnished the respective transition metal complexes **2A.3** and **2A.4** as yellow and blue solids, respectively. However, a similar methodology did not work for the NiCl₂/NiBr₂ salts and led to the formation of decomposed products, which could not be identified. Therefore, another nickel source, NiCl₂(dme) (dme = 1,2-dimethoxyethane), was employed to prepare the desired nickel complex **2A.5** (Scheme 2A.2). Red-colored crystals of **2A.5** suitable for single-crystal X-ray analysis were isolated by storing a concentrated solution at room temperature for 24 hours. We further

explored the reactivity pattern of ligand **2A.2** by treating it with one equivalent of $\text{NiBr}_2(\text{dme})$ and isolated the red colored crystals of **2A.6** at room temperature.



Scheme 2A.2. Synthesis of complexes **2A.3-2A.6**.

The X-ray diffraction studies and NMR spectroscopic techniques established the constitution of complexes **2A.3-2A.6**. The ^1H NMR spectra of **2A.3-2A.6** showed the broadening of the signals. Moreover, we could not obtain ^{29}Si and ^{31}P NMR spectra (solution state) of **2A.3** and **2A.4**, but **2A.5** and **2A.6** were further characterised by ^{29}Si and ^{31}P NMR spectroscopy. Tacke and co-workers reported a similar observation that they could not characterise their Fe- and Co-silylene complexes by solution-state NMR spectroscopic technique.^{5b} We further recorded the solid-state ^{29}Si and ^{31}P NMR spectra of complexes **2A.3** and **2A.4** and observed a characteristic peak in the ^{31}P NMR spectra for both the complexes. Complexes **3** and **4** display a peak at δ 20.91 ppm and at δ 22.53 ppm in ^{31}P NMR spectra, respectively. However, we could not get any satisfactory data from the solid-state ^{29}Si NMR spectra.

The ^{29}Si NMR spectrum of **2A.5** displays two resonances at δ 1.02 ppm (Si(II)) and δ 9.29 ppm (SiMe₃), respectively, and they are downfield shifted as compared to those in **2A.1** [δ -13.11 ppm (Si(II)) and δ 5.00 ppm (SiMe₃)]. The ^{31}P NMR spectrum of **2A.5** reveals a similar observation, where the phosphorus peak appears at δ 16.85 ppm (^{31}P NMR peak of **2A.1**: δ -22.75 ppm). In the case of complex **2A.6**, ^{29}Si NMR spectrum displays two resonances at δ 6.11 ppm (Si(II)) and δ 16.11 ppm (SiMe₃), respectively, and they are also downfield shifted as compared to **2** [δ -14.05 ppm (Si(II)) and δ 9.17 ppm (SiMe₃)]. The ^{31}P NMR spectrum of **2A.6** shows a peak at δ 17.99 ppm (^{31}P NMR peak for **2**: δ -27.21 ppm). This downfield shift of ^{31}P NMR and ^{29}Si NMR signals in **2A.5** and **2A.6** is due to the coordination of P and Si atoms to the Ni(II) centre, which decreases the electron density on P and Si centres. To get further insight into the magnetic behaviour of **2A.3-2A.6**, we measured the magnetic susceptibility using SQUID magnetometry (*vide infra*).

Complexes **2A.3**, **2A.4**, **2A.5**, and **2A.6** crystallise in the orthorhombic $Pna2_1$, the triclinic $P-1$, the monoclinic $C2/c$, and the triclinic $P-1$, space groups, respectively. The molecular structure of **2A.3** displays a four-coordinate Fe(II) centre ligated to silicon and phosphorus donor sites. The Fe(II) centre in **2A.3** attains a distorted tetrahedral geometry with the Br1-Fe1-P1 and Si2-Fe1-Br2 bond angles of $113.92(4)^\circ$ and $113.75(4)^\circ$, which closely matches with those reported in **2A.ii** by Tacke and co-workers.^{5b} The Si2-Fe1 bond length in **2A.3** is 2.441(2) Å, which is longer than the Fe-Si bond length in **2A.ii** (2.3876(7) Å) (Figure 2A.2),^{5b} but matches well with the Fe-Si bond lengths in **2A.i** (2.442(2) Å and 2.445(2) Å).^{6a} It should be noted that **2A.3** crystallises in the $Pna2_1$ space group, which is a ferroelectric active space group.^{6a,9} This unnoticed property of the silylene-supported Fe(II) complex of **2A.3** might lead to a new application of such complexes.

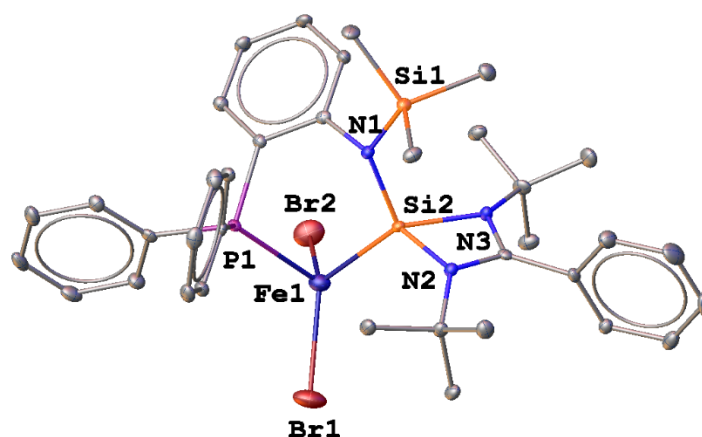


Figure 2A.2. The molecular structure of **2A.3**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and solvents are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Br2-Fe1 2.388(1), Br1-Fe1 2.361(1), P1-Fe1 2.428(2), Si2-Fe1 2.441(2), N3-Si2 1.849(4), N2-Si2 1.849(4), N1-Si2 1.759(4), Si1-N1 1.779(4); and Si2-Fe1-P1 $86.01(5)^\circ$, Br2-Fe1-P1 $101.87(4)^\circ$, Br1-Fe1-P1 $113.92(4)^\circ$, Si2-Fe1-Br2 $113.75(4)^\circ$, Si2-Fe1-Br1 $120.63(4)^\circ$, Br1-Fe1-Br2 $115.20(3)^\circ$, N1-Si2-Fe1 $113.5(1)^\circ$, Si2-N1-Si1 $126.8(2)^\circ$.

The solid-state structure of cobalt complex **2A.4** is similar to those observed for **2A.iii** and **2A.viii**.^{5b,6f} The Co(II) centre in **4** attains a distorted square planar geometry (Figure 2A.3) with bond angles P1-Co1-Br2 and Br1-Co1-Si2 of $96.88(3)^\circ$ and $93.64(5)^\circ$, slightly deviating from the ideal square planar angles. Conversely, similar complex **2A.iii** shows a distorted tetrahedral geometry with Si-Co-Br and N-Co-Br bond angles of $109.01(4)^\circ$ and $119.46(5)^\circ$, respectively.^{5b} The Co1-Si2 bond distance in **2A.4** is 2.1903(8) Å, which is significantly shorter than the Si-

Co bond distance in **2A.iii** (2.3245(13) Å)^{5b}, but it is in good agreement with that in **2A.viii** (2.1949 and 2.2244(11) Å) and (LSiCl)₂CoBr₂ [L= PhC(N^tBu)₂, 2.1949(5) Å and 2.1793(5) Å].^{6f} Similarly, complex **2A.5** shows a distorted square planar geometry with the bond angles P1-Ni1-Cl2, P1-Ni1-Si2, Cl2-Ni1-Cl1, and Cl2-Ni1-Si2 of 93.88(4)°, 88.64(4)°, 96.08(4)° and 156.06(4)°, respectively (Figure 2A.3). Analogous Ni(II) complex **2A.6** also shows a distorted square planar geometry with the bond angles P1-Ni1-Si2, P1-Ni1-Cl2, Cl1-Ni1-Si2, and Cl2-Ni1-Cl1 of 88.64(4)°, 93.88(4)°, 87.83(4)°, and 96.08(4)°, respectively (Figure 2A.4). A similar kind of distortion in square planar geometry of the Ni(II) centre was also observed in the complexes **2A.iv** and **2A.v**.^{5b,6b} The Ni1-Si2 bond length in **2A.5** is 2.162(1) Å, which is marginally longer than those in **2A.iv** (2.118 Å),^{5b} but closely matches with the Ni-Si bond distance of **2A.v** (2.1553(8) Å).^{6b} It is always difficult to predict the possible geometries (tetrahedral and square planar) for the tetra-coordinated complexes. Hence, we used geometry index (τ_4) to calculate the possible geometries of the complexes **2A.3-2A.6**.^{6a,9b,9c} Based on the calculated τ_4 values of **2A.3-2A.6**, we can propose that **2A.3** has a distorted tetrahedral geometry, while **2A.4-2A.6** display distorted seesaw geometries (Appendix section 2A.A.3).

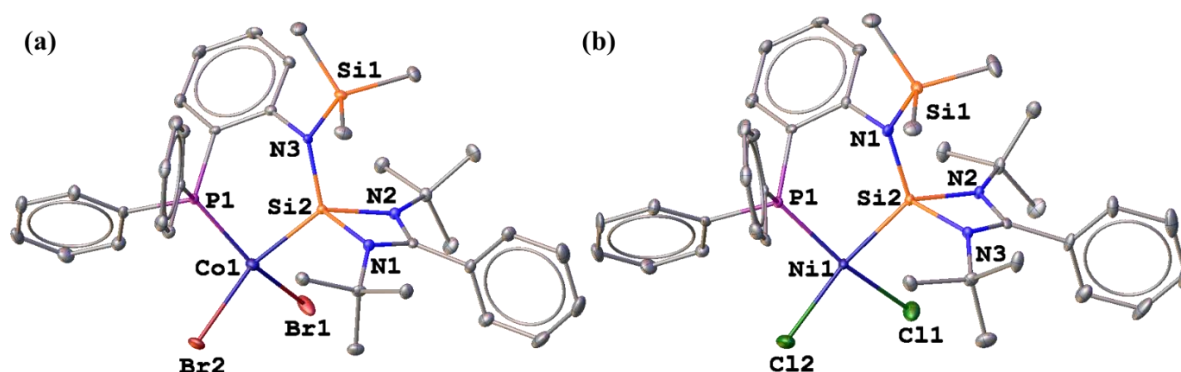


Figure 2A.3. The molecular structure of **2A.4**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and solvents are omitted for clarity. Selected bond distances (Å) and angles (°): Br2-Co1 2.3764(6), Br1-Co1 2.315(2), Co1-P1 2.1561(9), Co1-Si2 2.1903(8), Si2-N1 1.842(3), Si2-N3 1.739(3), Si2-N2 1.866(3), Si1-N3 1.786(2); and P1-Co1-Si2 87.91(3), P1-Co1-Br2 96.88(3), P1-Co1-Br1 119.19(3), Br1-Co1-Si2 93.64(5), Br2-Co1-Si2 141.52(4), Br2-Co1-Br1 100.42(4), N1-Si2-Co1 112.6(1), N3-Si2-Co1 119.7(1), Si1-N3-Si2 129.5(2), N2-Si2-N1 71.3(1). (b) The molecular structure of **2A.5**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ni1-Cl1 2.201(1), Ni1-Cl2 2.229(1), Ni1-P1 2.138(1), Ni1-Si2 2.162(1), Si2-N2 1.832(3), Si2-N3 1.833(3), Si2-

N1 1.741(3), Si1-N1 1.781(3); and P1-Ni1-Si2 88.64(4), P1-Ni1-Cl2 93.88(4), P1-Ni1-Cl1 162.99(5), Cl1-Ni1-Si2 87.83(4), Si2-Ni1-Cl2 156.06(5), Cl2-Ni1-Cl1 96.08(4), N3-Si2-N2 72.0(1), Si2-N1-Si1 129.02(2).

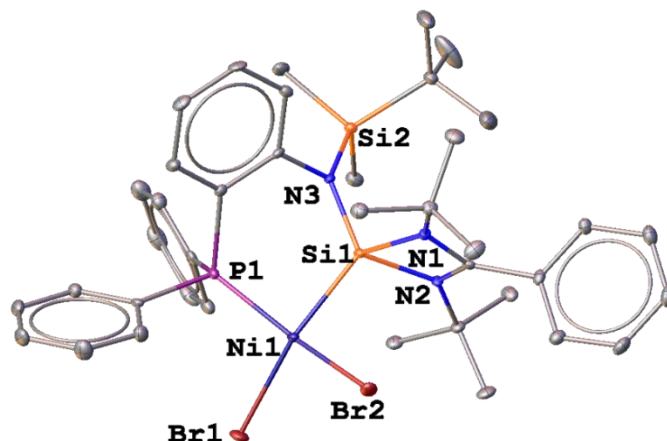


Figure 2A.4. The molecular structure of **2A.6**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and solvent are omitted for clarity. Selected bond distances (Å) and angles (°): Br1-Ni1 2.3798(8), Br2-Ni1 2.3359(8), Si1-Ni1 2.176(1), P1-Ni1 2.125(1), Si1-N1 1.812(3), Si1-N2 1.828(2), N3-Si1 1.758(2), N3-Si2 1.788(3); and Br1-Ni1-Br2 96.05(2), P1-Ni1-Br1 94.91(3), P1-Ni1-Br2 156.62(3), Br2-Ni1-Si1 91.90(3), Br2-Ni1-Si1 153.01(3), Si1-Ni1-P1 87.58(4), N1-Si1-N2 72.6(1), Si1-N3-Si2 135.0(2).

2A.3.2 Electrochemical and optical studies

We have performed cyclic voltammetry studies to understand the redox properties of complexes **2A.3-2A.6**. Cyclic voltammetry was performed in a non-aqueous electrolyte medium (*t*-butyl-ammonium-hexafluorophosphate used as electrolyte). The solution of **2A.3** and **2A.4** were prepared in tetrahydrofuran (THF), while dichloromethane (DCM) was used for **2A.5**. The glassy carbon electrode was used as a working electrode, and platinum was used as a counter electrode. All the experiments were carried out with respect to a pseudo-reference electrode (platinum wire).¹⁰ The slow scan rate (50 mV s⁻¹) in the potential window of 3 to -3 V was employed to scrutinise the electrochemical oxidation-reduction of **2A.3**, **2A.4**, and **2A.5**. The distinct redox peaks in the cyclic voltammogram (CV) (Figure 2A.5) of **2A.3-5** suggest an electroactive nature.¹¹ In the case of iron complex **2A.3** (Figure 6a), a reversible redox peak is visible with an anodic peak at $E_{pa} = 506$ mV, which is attributed to Fe(I)→Fe(II), and its corresponding reduction peak appears at $E_{pc} = 436$ mV. Another reduction peak at $E_{pc} = -1250$ mV is attributed to Fe(I)→Fe(0), while the oxidation peak appears at a more positive potential,

$E_{pa} = 1644 \text{ mV}$ ($\text{Fe(II)} \rightarrow \text{Fe(III)}$).¹² To verify that these peaks correspond to the metal centre, we carried out the same experiments with ligand **2A.1**, which did not show any redox features in the potential window of 3V to -3V (see Appendix section Figure 2A.A.21). In the case of cobalt complex **2A.4** (Figure 2A.5b), three redox peaks were observed.

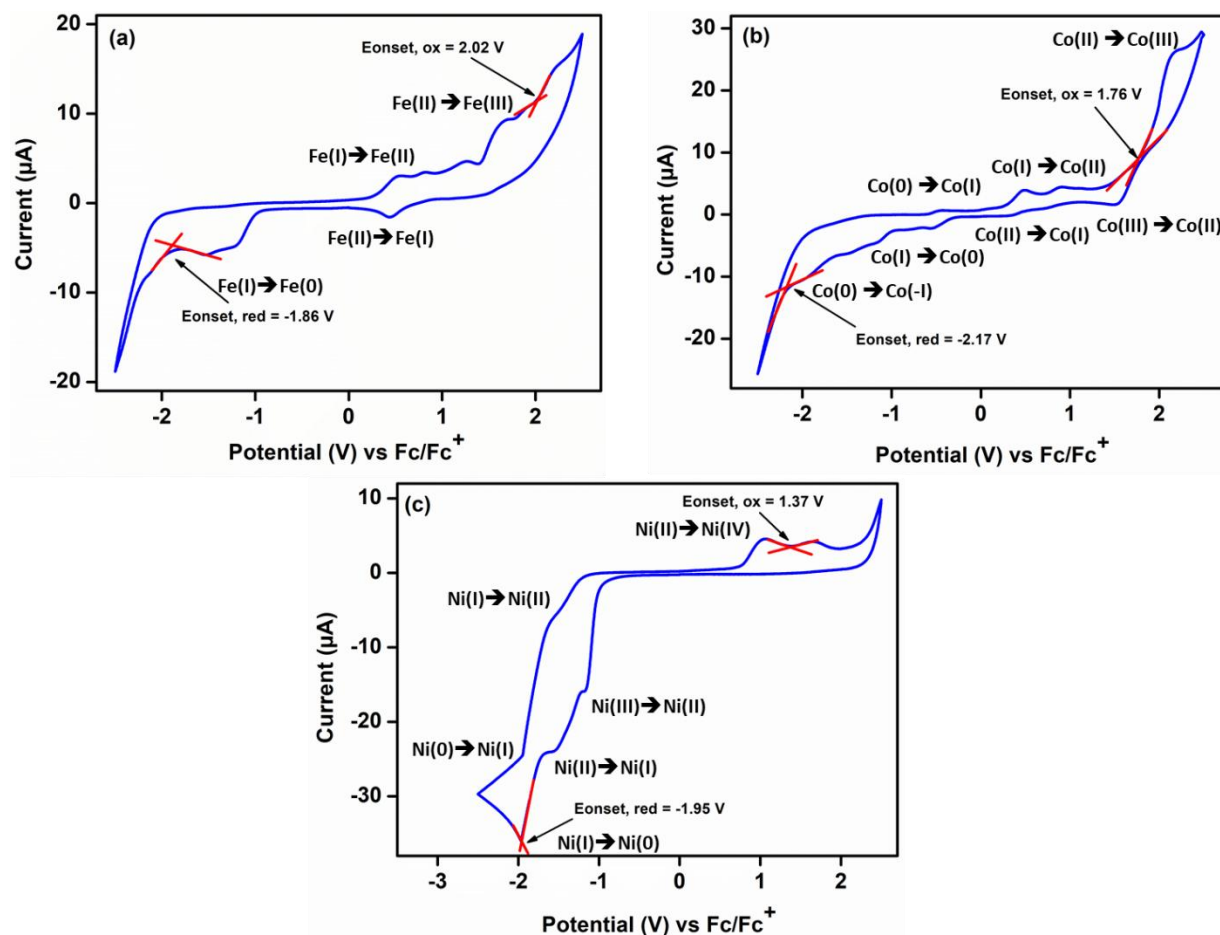


Figure 2A.5. Cyclic voltammogram of complex **2A.3** (a), **2A.4** (b) in THF and **2A.5** (c) in DCM with 0.05 M *t*-butyl-ammonium-hexafluorophosphate. All potentials were referenced to the Fc/Fc⁺ couple. Scan rate = 50 mVs⁻¹. Schematic of complexes, showing structural changes that occur upon oxidation/reduction.

The assignment of these peaks is as follows; $E_{pc} = -551 \text{ mV}$ for $\text{Co(I)} \rightarrow \text{Co(0)}$, $E_{pc} = 400 \text{ mV}$, and 753 mV for $\text{Co(II)} \rightarrow \text{Co(I)}$ (this dual peak is because of some intermediate state in the solution), and the third peak at $E_{pc} = 1519 \text{ mV}$ for $\text{Co(II)} \rightarrow \text{Co(III)}$. The corresponding oxidation peak of these three reversible reductions appeared at $E_{pa} = -458 \text{ mV}$ for $\text{Co(0)} \rightarrow \text{Co(I)}$, $E_{pa} = 483 \text{ mV}$ and 919 mV for $\text{Co(I)} \rightarrow \text{Co(II)}$ and the third one at 2141 mV for $\text{Co(II)} \rightarrow \text{Co(III)}$. The reduction trace at extreme negative potential $E_{pa} = -1927 \text{ mV}$ was assigned to $\text{Co(0)} \rightarrow \text{Co(-I)}$.¹³ For nickel complex **2A.5**, CV was performed in dichloromethane (Figure 6c). Two reversible redox events with reduction peaks at $E_{pc} = -1522 \text{ mV}$ and $E_{pc} = 1960 \text{ mV}$ were

assigned to Ni(II)→Ni(I) and Ni(I)→Ni(0) with corresponding oxidation peaks at $E_{pa} = -1950$ mV and $E_{pa} = -1611$ mV for Ni(0)→Ni(I) and Ni(I)→Ni(II), respectively.¹⁴ The reduction peak at $E_{pa} = -1172$ mV is assigned to Ni(III)→Ni(II) electron transfer event. The broad oxidation peak at extreme positive potential corresponds to Ni(II)→Ni(IV) two-electron oxidation with $E_{pa} = 1054$ mV and 1708 mV, respectively. The standard oxidation potential of Ni(II) to Ni(IV) is $E_{pa} = 1590$ mV, but when Ni(II) directly oxidises to Ni(IV), it shows dual peak behaviour. Similar redox behaviour was observed for **2A.6** (see Appendix section Figure 2A.A.22).

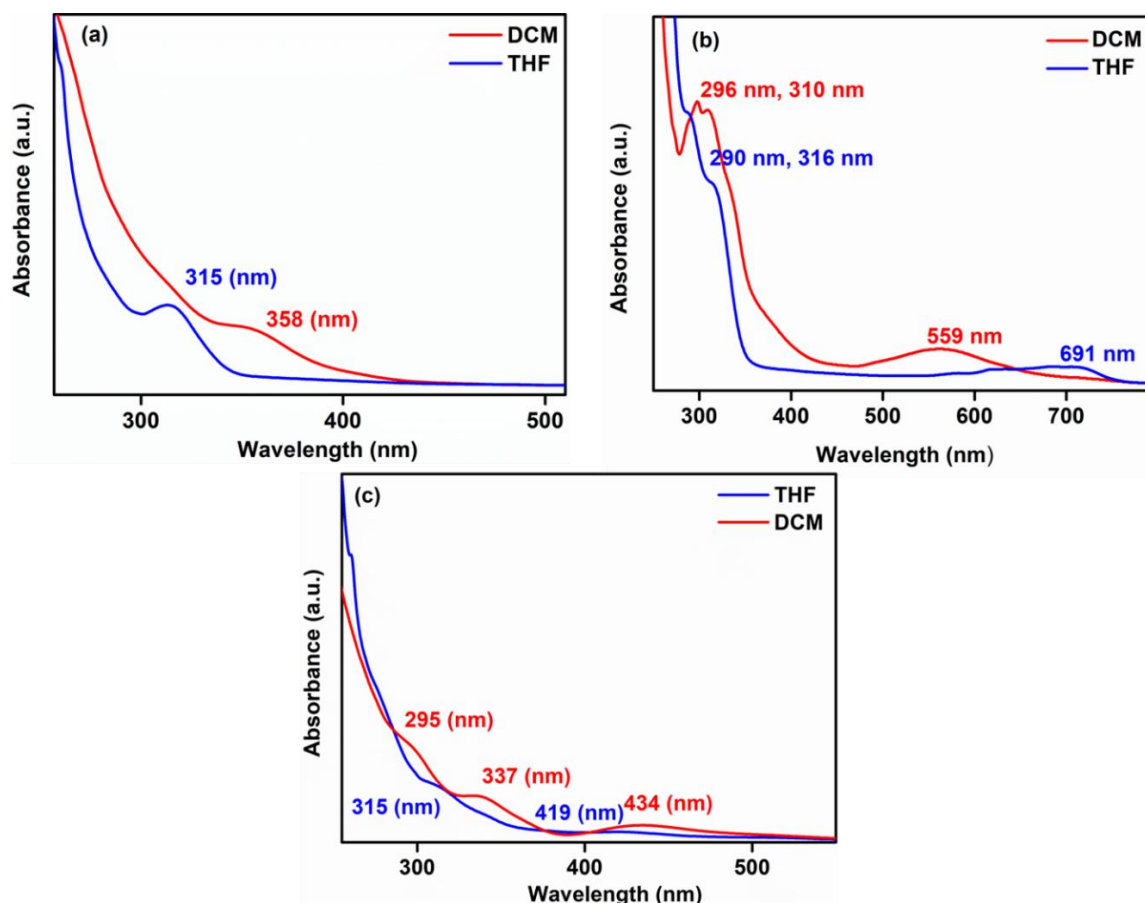


Figure 2A.6. UV-vis absorption spectra of **2A.3** (a), **2A.4** (b), and **2A.5** (c) in THF (blue) and DCM (red) solvents.

Further, we recorded the UV-vis absorption spectra of all the complexes. The colour of the **2A.3** and **2A.4** complexes is faint yellow and ink blue, respectively, and for **2A.5** and **2A.6**, it is displaying a deep red colour. The UV-vis absorption spectrum of **2A.3** exhibits a peak at 315 nm in THF and 358 nm in DCM, which could be attributed to the MLCT transition (Figure 2A.6). A similar peak in the ligand is observed for the $n \rightarrow \pi^*$ transition (see Appendix section Figure 2A.A.23). Similarly, for **2A.4**, a peak at 559 nm in DCM and 691 nm in THF originated due to the d-d transition, and another peak between 290-320 nm (in THF and DCM) could be

assigned due to the $n \rightarrow \pi^*$ transition. Two peaks are observed for **2A.5** as well due to MLCT and $n \rightarrow \pi^*$ transitions (Figure 2A.6c). Similar transitions are also observed for the complex **2A.6** (see Appendix section Figure 2A.A.24).¹⁶ These proposed transitions are further supported by the TDDFT calculations (*vide infra*).

The thermal stability of all the complexes and weight loss was checked by thermogravimetric analysis (TGA) (see Appendix section Figure 2A.A.25). We observed that **2A.3** is stable up to 255 °C, **2A.4** is steady at 210 °C, but **2A.5** and **2A.6** are stable up to 290 °C, hinting at the more stable nature of **2A.5** and **2A.6**.

2A.3.3 Magnetic properties studies:

The magnetic properties of complexes **2A.3-2A.5** were studied by recording the temperature-dependent magnetisation (M–T) data in the 5 K–300 K temperature range and isothermal magnetisation (M–H) curves in a cyclic ± 6 Tesla magnetic field. The M–H curve was recorded at 5 K and 300 K to study the nature of the complexes.¹⁸ An increasing linear trend of magnetisation with the magnetic field at 300 K, i.e., a straight line with a positive slope (Figures 2A.7a and 2A.7b) depicts that samples **2A.3** and **2A.4** are paramagnetic at room temperature. In contrast, the sigmoidal curve in Figure 8c shows the superparamagnetic nature of sample **2A.5** at room temperature. At lower temperatures (5 K), all the complexes (**2A.3-2A.5**) show S-shaped M–H curves with negligible coercivity and remanence magnetisation values (Figure 2A.7d–2A.7f). The negligible coercivity (H_c) and remanence (M_r) values indicate that the received materials are soft magnetic materials and may be like superparamagnetic materials. It has been further concluded from M–H loops that magnetisation of **2A.3** is higher than that of **2A.4** and **2A.5**. M–T curves of the complexes are composed of zero-field cooled (ZFC) and field-cooled (FC) curves.¹⁹ For the zero-field-cooled measurement (ZFC), the samples were cooled to 5 K without an external magnetic field. A field of 100 Oe was then applied, and simultaneously, the magnetisation was measured with increasing temperature. In the field-cooled (FC) measurement, the sample is subjected to the same field, but the magnetic moment is recorded with decreasing temperature (from 300 K to 5 K). The following observations were made from the M–T plots of all three samples:

- (i) For **2A.3** & **2A.4**, the ZFC and FC magnetisation curves continuously decrease with the measurement temperature increase.
- (ii) ZFC and FC curves overlap in **2A.3** & **2A.4**.
- (iii) There is a bifurcation in the ZFC and FC magnetisation curves for **2A.5**.

(iv) The ZFC magnetisation initially increases with the increase in temperature and shows a maximum at $T_{\max} = 8.2$ K in sample **2A.5**. On the contrary, the FC magnetisation decreases with an increase in temperature.

The continuous increase in magnetisation with the decrease in measurement temperature for samples **2A.3** & **2A.4** (ZFC and FC magnetisation curves) suggests that these samples are soft magnetic. In addition, the overlapping of ZFC and FC magnetisation curves in the case of complexes **2A.3** & **2A.4** is due to the paramagnetic tail and paramagnetic contributions (Figure 2A.8).²⁰ The bifurcation between ZFC and FC plots generally shows the presence of spin glass, cluster glass, exchange bias, and superparamagnetic behaviour (Figure 2A.8c).^{19a} The visible divergence in the ZFC and FC curves is due to the superparamagnetic contribution for sample **2A.5**.

To find out the preferred electronic state of all the samples, the effective paramagnetic moment (μ_{eff}) was calculated. To determine the μ_{eff} , we have adopted two approaches: a) fitting of magnetic susceptibility (χ) derived from the M-T data ($\chi = M/H$) with the Curie–Weiss law: $\chi = C/(T - \Theta)$, in which C is the Curie constant and Θ is the Curie–Weiss temperature. Afterwards, the μ_{eff} for all the samples is obtained using $\mu_{\text{eff}} = \sqrt{8C}\mu_B$. b) Fitting of M-H data with the Langevin equation (see Appendix Figure 2A.A.26). The effective magnetic moment of **2A.3** was found at 5.3 BM (Linear fit) and 5.5 BM (Langevin fit), corresponding to 4 unpaired electrons. Hence, we can conclude that **2A.3** is a high-spin complex.^{5b} Similarly, μ_{eff} for **2A.4** was found at 4.7 BM, reflecting a high-spin complex nature, as it corresponds to 3 unpaired electrons. The slight increment in μ_{eff} values of **2A.3** and **2A.4** from the theoretically calculated values can be attributed to the orbital mixing^{5b}

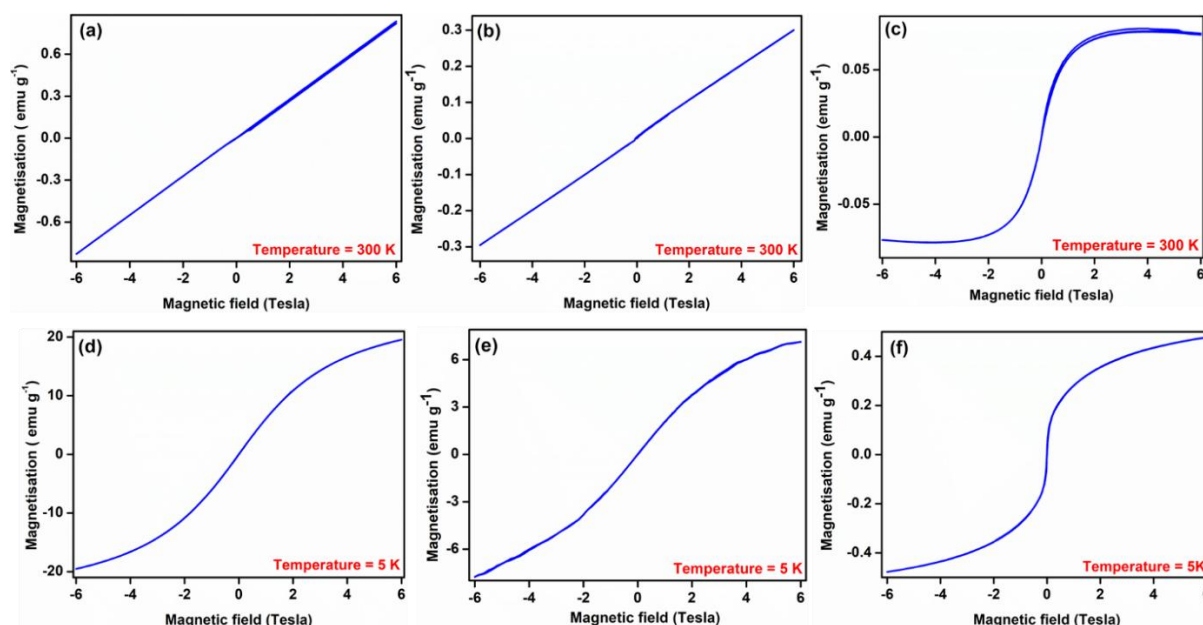


Figure 2A.7. Field-dependent magnetization curve measured by applying external magnetic field at 5 K and 300 K. M vs. H plot (a) and (d) for complex **2A.3**, (b) and (e) for complex **2A.4**, (c) and (f) for complex **2A.5**. {M = Applied magnetic field, M = Magnetization}.

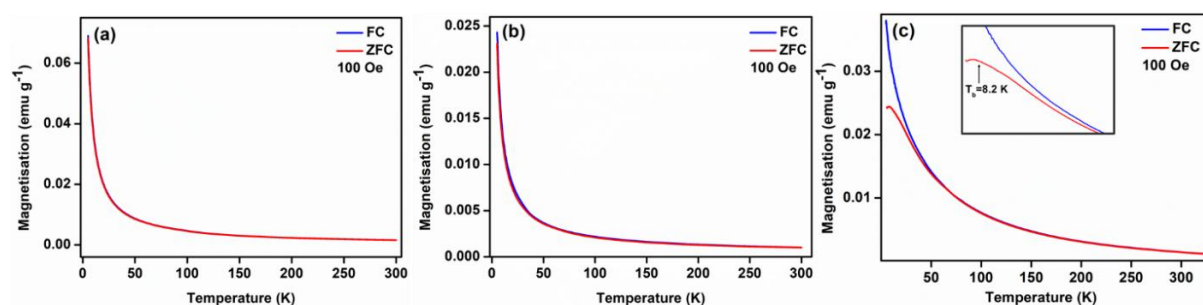


Figure 2A.8. Zero-field cooled (ZFC) and Field-cooled (FC) magnetisation curves as a function of temperature for the complexes **2A.3**, **2A.4**, and **2A.5** measured with an applied field of 100 Oe between 5 K and 300 K.

The SQUID data of the nickel complex **2A.5** indicate its superparamagnetic nature, which is not a common phenomenon for four-coordinate Ni(II) complexes. However, due to the poor data fitting (approaches 1 and 2), we could not obtain the value of the effective magnetic moment for **2A.5**. Hence, we used Evan's method (NMR Method) to calculate the magnetic moment of **2A.3-2A.6**, which revealed the magnetic moment of 5.1 BM (**2A.3**), 4.08 BM (**2A.4**), 1.75 BM (**2A.5**), and 1.4 BM (**2A.6**), respectively (Figure 2A.9).^{21,5b} We performed the variable temperature (238-298 K) ¹H NMR spectroscopy to see the changes in magnetic properties at variable temperatures (see Appendix Figure 2A.A.28-2A.A.30). The magnetic moment of **2A.3** is slightly decreased (4.9 BM) at low temperature, while complexes **2A.4-**

2A.5 show a slight enhancement in the magnetic moments (4.4 BM (**2A.4**) and 1.9 BM (**2A.5**)). The magnetic moment of a four-coordinate Ni(II) complex with square planar geometry is expected to be zero. However, a significant distortion in this geometry can cause the magnetisation of the complex.²² Consequently, **2A.5** and **2A.6** display a magnetic moment of 1.75 BM and 1.4 BM, confirming the paramagnetic behaviour revealed by SQUID measurements. We presume that the magnetisation in **2A.5** and **2A.6** is due to the distortion in the bite angle and square planar geometry.²² However, no such magnetic properties of silylene-Ni(II) complexes have been reported thus far.

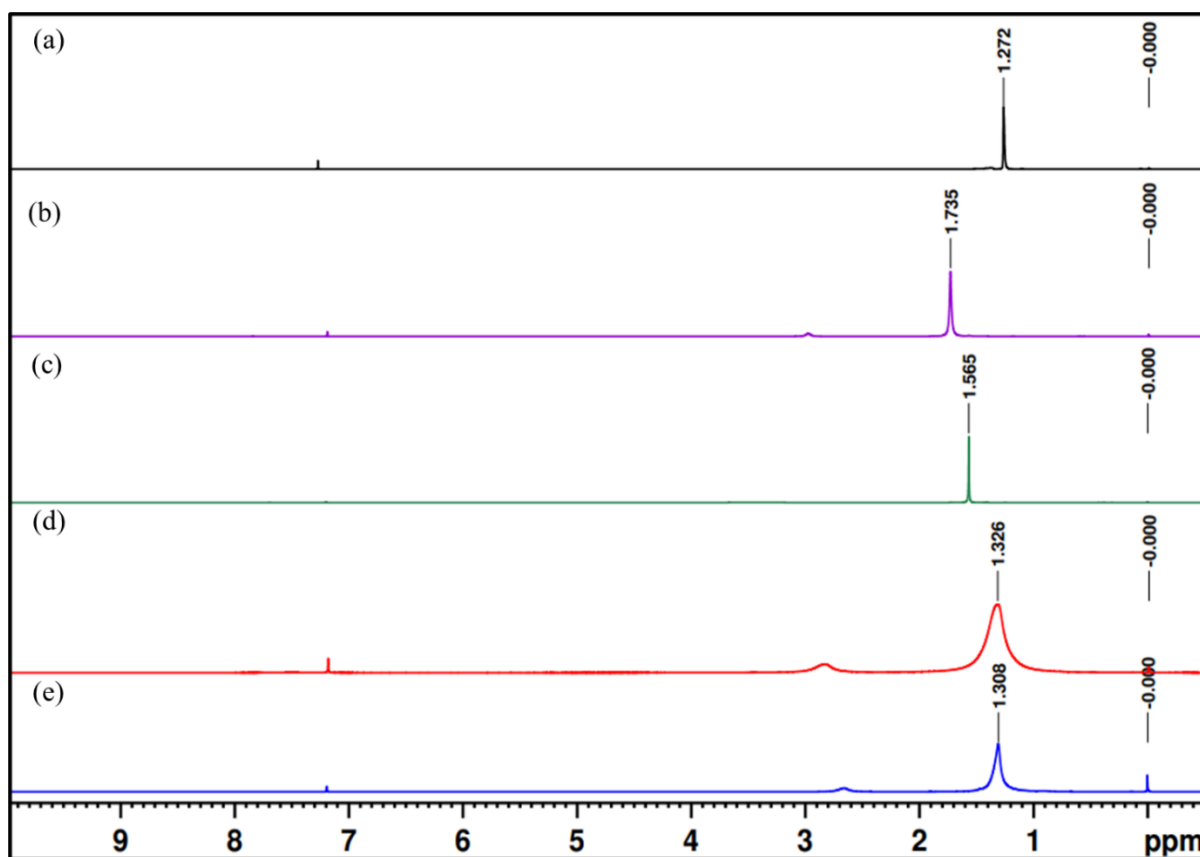


Figure 2A.9. (a) ^1H NMR spectrum of the capillary tube filled with the Reference solution (tert-butanol) and CDCl_3 . (b) Capillary filled with complex **2A.3** dissolved in the Reference solution and CDCl_3 . (c) Capillary filled with complex **2A.4** dissolved in the Reference solution and CDCl_3 . (d) Capillary filled with complex **2A.5** dissolved in the Reference solution and CDCl_3 . (e) Capillary filled with complex **2A.6** dissolved in the Reference solution and CDCl_3 . The peaks are labelled in ppm. Inset: NMR tubes with the capillary tubes used for the Evans method.

2A.3.4 Computational Quantum Mechanical Studies:

Quantum mechanical calculations were carried out at the M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level to understand the geometries of the complexes **2A.3-2A.5** in different spin states and their relative stabilities. The geometrical optimizations at the B3LYP/def2-TZVPP level and energetic evaluations at the M06/def2-TZVPP//B3LYP/def2-TZVPP level of theory show a similar trend.²³

We have calculated each complex in two different initial geometries, viz., tetrahedral and square planar arrangement, and each geometry in two possible spin states, viz., low spin state and high spin state (Figure 2A.10). The geometrical optimisation converges into two minima for each complex. Among the two minima located for iron complex **2A.3**, the high spin state **⁵2A.3** is energetically low-lying than the low spin state **³2A.3** by 21.0 kcal mol⁻¹. The corresponding free energy difference in chloroform solvent is 20.75 kcal mol⁻¹. The high spin state complex **⁵2A.3** adopts a distorted tetrahedral arrangement around the metal center and is much closer to experimental geometry, whereas the low spin state complex **³2A.3** adopts a distorted square planar arrangement. The root means square deviation (RMSD) of experimental geometry from the low spin and high spin geometries are 0.971 Å and 0.284 Å, respectively. The geometric data and relative energy indicate that the iron complex **2A.3** exists in the high spin state with four unpaired electrons. The calculated spin-only magnetic moment is 4.9 BM, which matches quite well with the observed magnetic moment of 5.1 BM from the magnetic experiments using the NMR-Evans method.

On the other hand, among the two minima located for the cobalt complex, the high spin state **⁴2A.4** is more stable than the low spin state **²2A.4** by 2.6 kcal mol⁻¹. The corresponding free energy difference in chloroform solvent is 2.26 kcal mol⁻¹. Note that, the experimental geometry obtained from the X-ray crystallographic data is closer to the low spin state **²2A.4**. On the other hand, the RMSD of experimental geometry from the low spin and high spin geometries are 0.547 Å and 0.475 Å, respectively. Since the energy difference between the two spin states is less, it is expected that these two spin states will coexist in solution. The calculated spin-only magnetic moment is 3.9 BM for the high spin state and the observed magnetic moment is 4.08 BM. The observed magnetic moment is higher than the spin-only magnetic moment and can be attributed to two factors viz., strong spin-orbital coupling and the significant presence of the high spin complex in solution. The reports of Co(II) complexes in pseudo-tetrahedral geometry show a range of magnetic moments up to 5 BM.²⁴

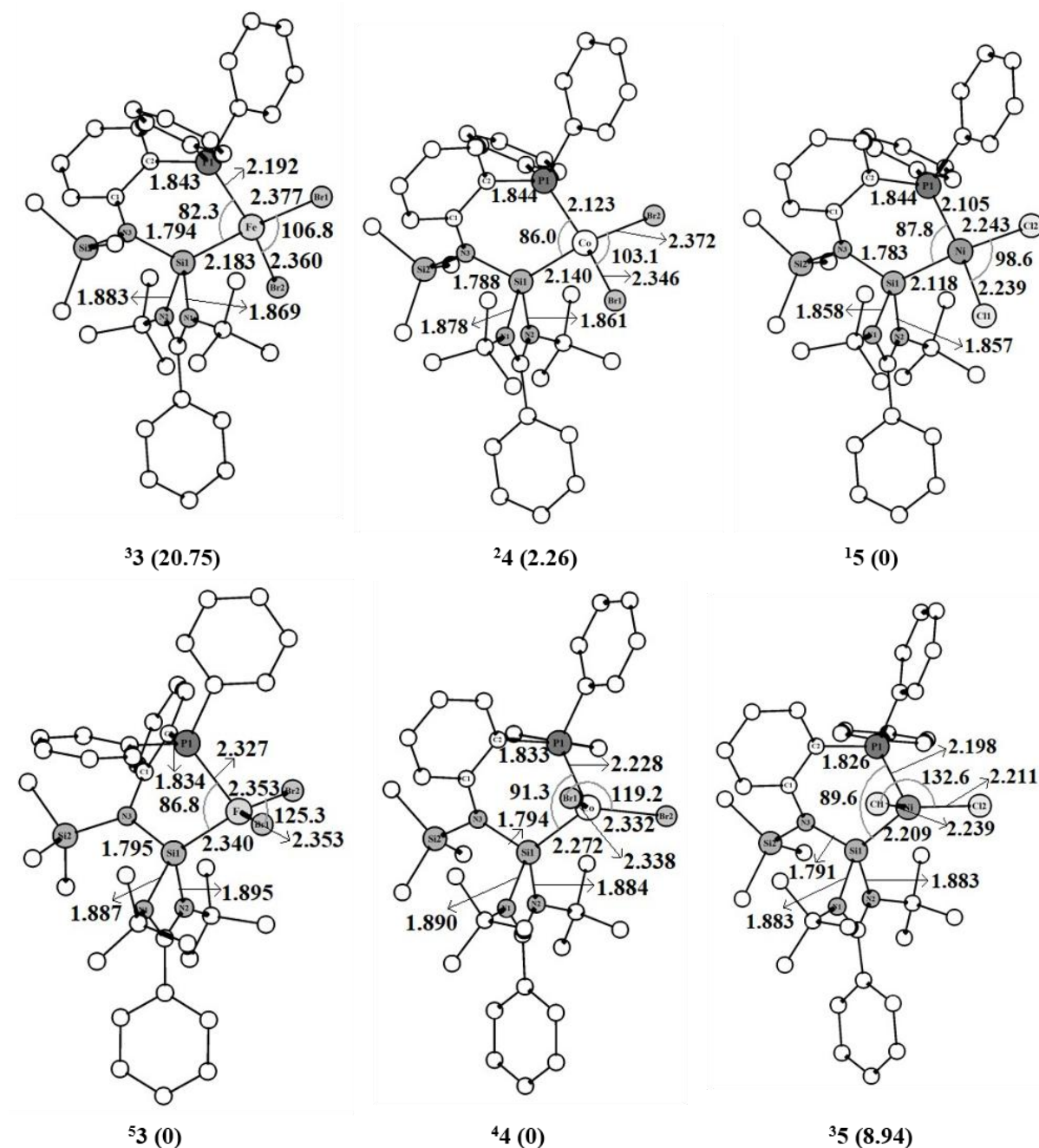


Figure 2A.10. Equilibrium geometries of compounds **2A.3-2A.5** in their respective low and high spin states at the BP86-GD3BJ/def2-SVP level of theory. The relative free energies in kcal mol⁻¹ with respect to the most stable spin states in chloroform solvent are given in parenthesis. All hydrogen atoms are removed for clarity. The left superscript of the structural number indicates the spin multiplicity.

In contrast, among the two minima located for the nickel complex, the high spin state **32A.5** is less stable than the low spin state **15** by 7.9 kcal mol⁻¹. The corresponding free energy difference in chloroform solvent is 8.94 kcal mol⁻¹. The high spin state exists in a distorted tetrahedral

geometry, whereas the low spin state exists in a distorted square planar geometry. Here also, the experimental geometry obtained from the X-ray crystallographic data is much closer to the low spin state **12A.5**. The RMSD of experimental geometry from the geometry of low spin state is only 0.260 Å, whereas that from the geometry of high spin state is 0.666 Å. The observed magnetic moment of the complex is very low (1.75 BM), which clearly suggests that compound **2A.5** mainly exists in a low-spin state in solution.

The energetics associated with the formation of these complexes **2A.3-2A.5** by the reaction of ligand **2A.1** with MX_2 ($\text{M} = \text{Fe-Ni}$, $\text{X} = \text{Cl/Br}$) is found to be exothermic and exergonic. The reaction energy for the high-spin complexes falls in the range -59.90 to -70.17 kcal mol⁻¹, while the Gibbs free energy change is between -49.23 to -59.60 kcal mol⁻¹ (Table S6).

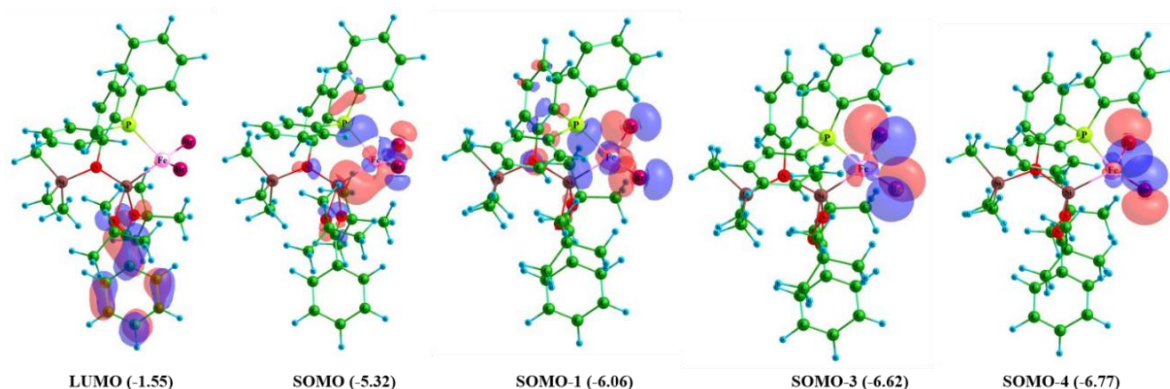


Figure 2A.11. Singly occupied molecular orbitals (SOMO) and lowest unoccupied molecular orbital (LUMO) of iron complex in its high spin state **52A.3** at the M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory. Eigenvalues in eV are given in parenthesis. Isosurface value is 0.045.

The singly-occupied molecular orbitals (SOMOs) of the high spin complexes are metal-ligand anti-bonding orbitals, which are majorly localized on the metal centre, while the lowest unoccupied molecular orbital (LUMO) is a π^* -orbital on the benzamidinate ligand moiety. The SOMOs and LUMOs of **52A.3** are given in Figure 2A.11. The frontier molecular orbitals of **42A.4** and **32A.5** are similar to those of **52A.3** (Figure S7). The spin density values on the metal centre for the high spin complexes are 3.20 for **52A.3**, 2.22 for **42A.4** and 1.23 for **32A.5**. The spin density values confirm that the unpaired electron density is localised largely on the metal centres.

The absorption properties of ligand **2A.1** and complexes **2A.3-2A.5** were studied using time-dependent density functional theory (TD-DFT) analysis at the M06/def2-TZVPP//BP86-

GD3BJ/def2-SVP level of theory using the polarized continuum model (PCM) model in solvent DCM for **2A.3-2A.5** and in solvent THF for **2A.1**. The calculated absorption spectrum of ligand **2A.1** shows two peaks in the range of 299-318 nm (expt. $\lambda_{\text{max}} = 317$ nm) which are attributed to $n \rightarrow \pi^*$ transitions. The absorption peak at 299 nm ($f = 0.095$) is due to the transition from the lone pair of electrons from P to π^* -molecular orbitals on the phenyl ring, whereas the absorption peak at 318 nm ($f = 0.075$) is attributed to the transition from the lone pair of electrons from Si to π^* -orbitals on the phenyl ring (Figure 2A.12).

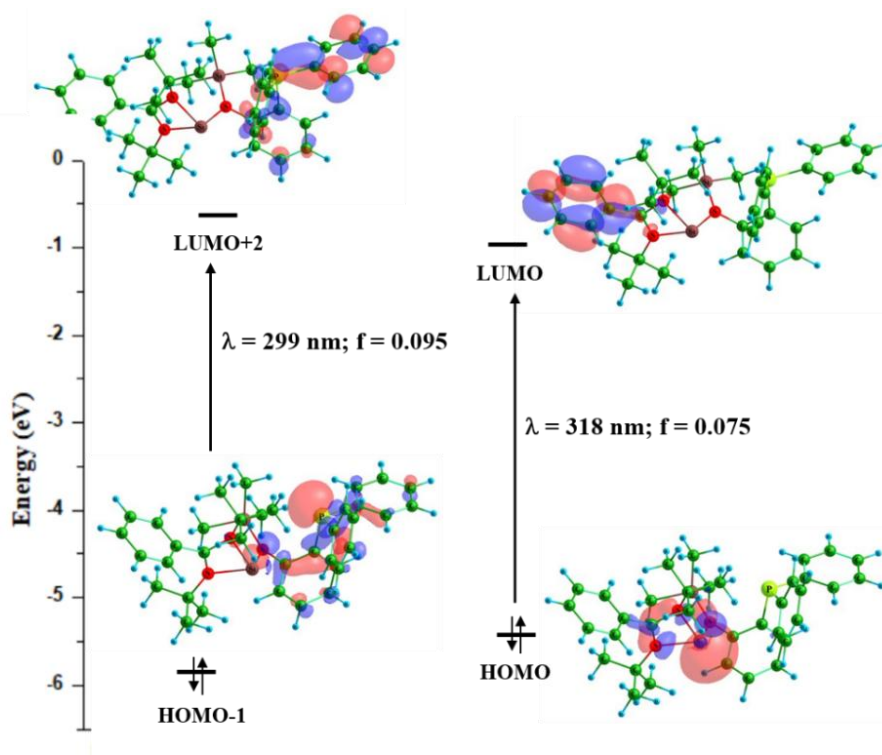


Figure 2A.12. The important molecular orbitals (MO) of ligand **2A.1** involved in the electronic transition at the M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory. The isosurface value of MO plots is 0.045. The corresponding absorption wavelength (λ in nm) and oscillator strength (f) are given.

The absorption peak of high-spin complex **⁵2A.3** at 394 nm ($f = 0.033$, expt. $\lambda_{\text{max}} = 358$ nm) can be assigned to a transition from the metal-centered d-orbital (SOMO) to the π^* -molecular orbital of the phenyl ring (LUMO) and hence, can be considered as metal to ligand charge transfer (MLCT) band (Figure 2A.11). It is noteworthy that the low-spin complex **³2A.3** does not show any peak in this region with significant transition probability. This is corroborated well with the energetics that the iron complex exists in a high-spin state.

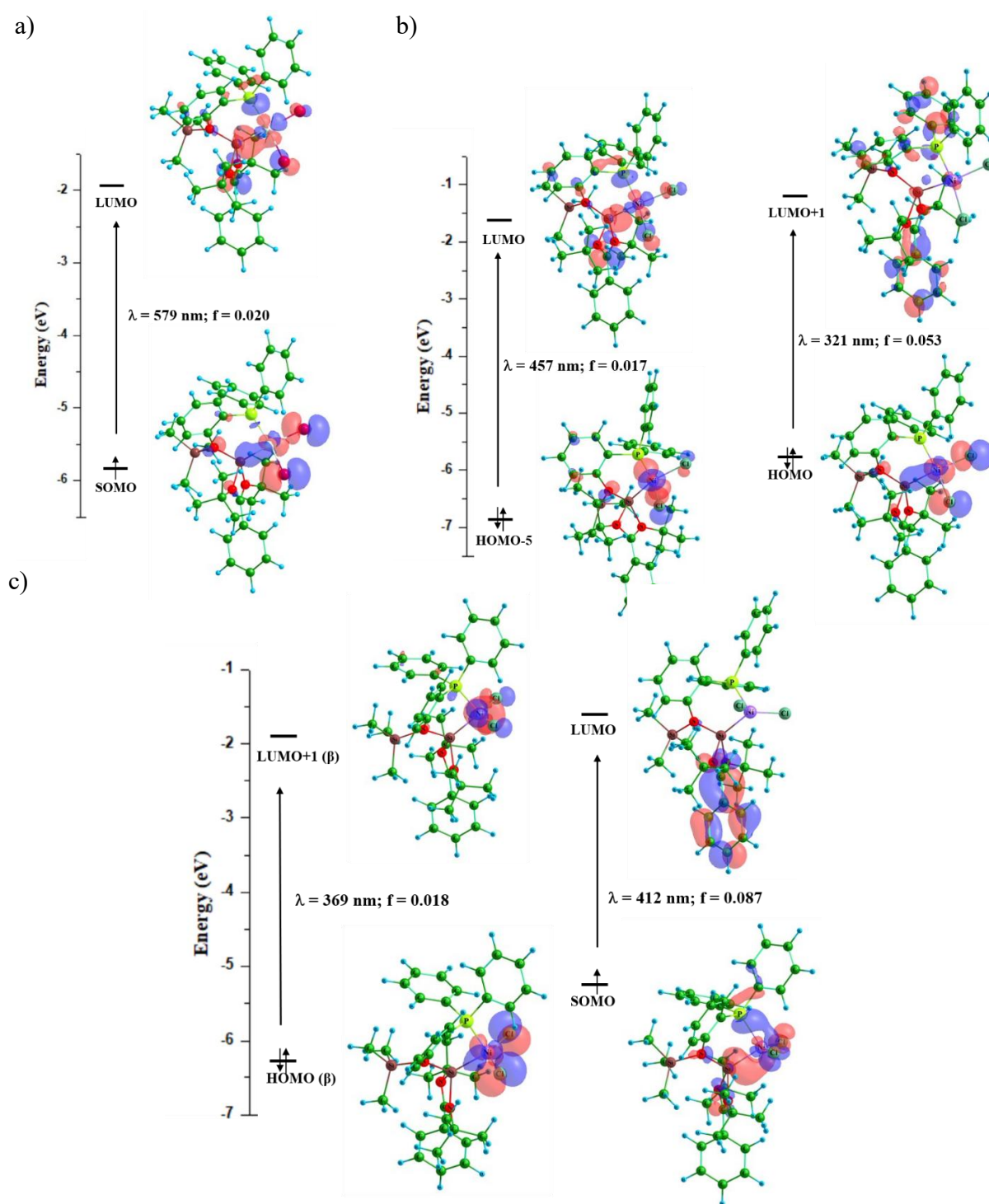


Figure 2A.13. The important molecular orbitals (MO) of (a) low spin cobalt complex $^2\mathbf{2A.4}$, (b) low spin nickel complex $\mathbf{2A.15}$ and (c) high spin nickel complex $^3\mathbf{2A.5}$ involved in the electronic transition at the M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory. The isosurface value of MO plots is 0.045. The corresponding absorption wavelength (λ in nm) and

oscillator strength (f) are given. All singly occupied levels correspond to alpha orbitals unless mentioned otherwise in parenthesis (β).

On the other hand, the low spin complex **2A.4** shows an absorption peak at 579 nm ($f = 0.02$, expt. $\lambda_{\text{max}} = 559$ nm) which can be attributed to d-d transition, viz., a transition from the metal-centred d-orbital (SOMO) to the empty metal d-orbital (LUMO) (Figure 2A.13a). The high spin complex **4A.4** shows no peak in this region with significant transition probability. The low-spin complex **15** shows absorption peaks at 321 nm ($f = 0.053$) and 457 nm ($f = 0.017$) with significant transition probability. On other hand, the high spin complex **3A.5** shows absorption peaks at 369 nm ($f = 0.018$) and 412 nm ($f = 0.087$). The absorption bands in the experimentally recorded spectrum of complex **2A.5** appear as merged peaks at 337 and 434 nm. The absorption observed for **1A.5** at 321 nm ($f = 0.053$) can be assigned as an MLCT band originating from the metal-centred d-orbital (HOMO) to the π^* -molecular orbital of the phenyl ring (LUMO+1), while that at 457 nm ($f = 0.017$) can be attributed to a d-d transition from metal-centred d-orbital (HOMO-5) to empty metal d-orbital (LUMO) (Figure 2A.13b). Likewise, the absorption observed for **3A.5** at 412 nm ($f = 0.087$) can be assigned as an MLCT band from singly occupied metal d-orbital (SOMO) to the π^* -molecular orbital of the phenyl ring (LUMO), while that at 369 nm ($f = 0.018$) can be assigned as a d-d transition from β -set of occupied metal d-orbital (HOMO) to unoccupied metal d-orbital (LUMO+1) (Figure 2A.13c).

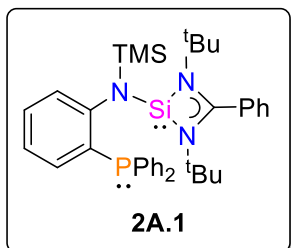
2A.4 Conclusion:

We have synthesised two novel phosphine-silylene-based hybrid ligands (**2A.1** and **2A.2**), whose coordination abilities are studied with 3d transition metal halides (Fe(II), Co(II), Ni(II)). All the compounds are well characterised by single-crystal X-ray diffraction studies and multinuclear NMR spectroscopic studies. The electrochemical analysis confirmed the redox-active nature of all the complexes (**2A.3-2A.6**), and the nickel complexes **2A.5** and **2A.6** were found to be thermally more stable than the others. All the metal complexes show magnetisation in an external magnetic field and display paramagnetic behaviour at room temperature. Computational quantum mechanical studies also supported the redox and magnetic nature of the complexes. However, all of them are superparamagnetic at low temperatures. This is the first report of a silylene-supported nickel(II) complex exhibiting superparamagnetic behaviour originating from the distorted square planar geometry. This interesting magnetic behaviour of silylene-supported first-row transition metal complexes implicates that the role of the ligand is

vital in determining the properties of the derived metal complexes. We hope that tunable silylene ligands could provide a vast area for future studies in material science.

2A.5 Synthesis of 2A.1-2A.6.

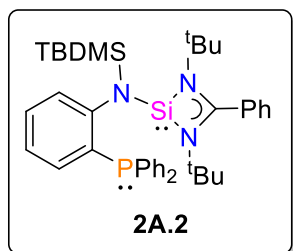
2A.5.1. Synthesis of 2A.1: N,N'-{bis(*tert*-butyl)amidinate}chlorosilylene (295 mg, 1 mmol)



and LiN(PPh₂)(Ph)(SiMe₃) (355 mg, 1 mmol) taken in Schlenk flask, to which 30 mL of toluene was added at room temperature and stirred for overnight. The resulting solution was filtered off using sintered glass frit under argon atmosphere and solvent was removed under vacuum to yield pale yellow solid. Single crystals suitable for X-ray

analysis were grown in toluene at -30 °C. Yield: 90% (548 mg). M.p. 190-195 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K, TMS): δ 0.39 (s, 9H, (SiCH₃)₃), 1.25 (s, 9H, (CH₃)₃C), 1.42 (s, 9H, (CH₃)₃C), 6.84-6.96 (m, 5H, Ph), 7.03-7.14 (m, 7H, Ph), 7.28-7.30 (m, 1H, Ph), 7.36-7.40 (m, 1H, Ph), 7.49-7.50 (m, 1H, Ph), 7.58-7.61 (m, 2H, Ph), 7.78-7.75 (m, 2H, Ph) ppm; ¹³C {¹H} NMR (100.613 MHz, C₆D₆, 298 K) δ 159.6 (NCN), 155.8, 141.1, 139.9, 138.4, 135.0, 134.6, 132.4, 130.3, 129.4, 128.7, 128.1, 127.7, 124.2, 54.1 [C(CH₃)₃], 53.3 [C(CH₃)₃], 33.4 [C(CH₃)₃], 32.3 [C(CH₃)₃], 3.15 [Si(CH₃)₃] ppm; ³¹P {¹H} NMR (C₆D₆, 161.97 MHz, 298 K): δ -22.75 ppm (s); ²⁹Si {¹H} NMR (C₆D₆, 79.49 MHz, 298 K): δ 5.00 ppm (s, SiMe₃) δ -13.10 ppm (d, J_{Si-P} = 21.6 Hz). HRMS C₃₆H₄₆N₃PSi₂: Calculated *m/z* 607.2968; Observed *m/z* 606.4788 [M-1]⁺.

2A.5.2. Synthesis of 2A.2: 2.5 M *n*-BuLi solution in hexane (1.6 mL, 4 mmol) was added to

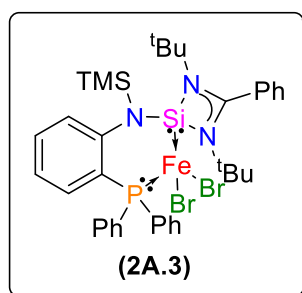


the solution of 2-(diphenylphosphanyl)aniline (1 g, 4 mmol) in THF (60 mL) and kept in stirring at room temperature for 3-4 hours and then *tert*-butyldimethylsilylchloride (470 mg, 4 mmol) was added. The reaction mixture was refluxed for 12 h in THF, followed by complete evaporation of THF under vacuum. Then 30 ml DCM was

added to the reaction mixture and filtration was done by using sintered glass frit under argon atmosphere. This solution was concentrated under vacuum and then kept at -30 °C to afford pale yellow crystals. Second lithiation of [C₆H₄NH(Si(*t*Bu)Me₂)(PPh₂)] was done in Et₂O at 0 °C for 5 h, and lithium salt of [C₆H₄NH(Si(*t*Bu)Me₂)(PPh₂)] was isolated. N,N'-{bis(*tert*-butyl)amidinate}chlorosilylene (295 mg, 1 mmol) and [C₆H₄NLi(Si(*t*Bu)Me₂)(PPh₂)] (355 mg, 1 mmol) were taken in a Schlenk flask, 30 mL of toluene was added at room temperature to the reaction mixture and stirred overnight. The resulting solution was filtered off using a sintered glass frit under argon atmosphere, and the solvent was removed under vacuum to yield

yellow solid. Single crystals suitable for X-ray analysis were grown in toluene at $-30\text{ }^{\circ}\text{C}$. Yield: 83 % (439 mg). M.p. $195\text{--}200\text{ }^{\circ}\text{C}$. ^1H NMR (C_6D_6 , 400 MHz, 298 K, TMS): δ 0.49 (s, 3H, $(\text{CH}_3)\text{Si}$), 0.57 (s, 3H, $(\text{CH}_3)\text{Si}$), 0.75 (s, 9H, $(\text{CH}_3)_3\text{N}$), 1.08 (s, 9H, $(\text{CH}_3)_3\text{N}$) 1.36 (s, 9H, $(\text{CH}_3)_3\text{C}$), 6.70–6.76 (m, 3H, Ph), 6.83–6.85 (m, 2H, Ph), 6.90–6.88 (m, 2H, Ph), 6.96–7.00 (m, 5H, Ph), 7.16–7.18 (m, 1H, Ph), 7.36–7.40 (t, 1H, Ph), 7.48–7.49 (m, 1H, Ph), 7.54–7.58 (t, 2H, Ph), 7.79–7.95 (t, 2H, Ph) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100.613 MHz, C_6D_6 , 298 K) δ 158.4 (NCN), 157.7, 157.4, 141.7, 140.6, 139.6, 135.1, 134.8, 134.5, 133.9, 133.7, 130.0, 125.7, 123.4, 54.5 [C(CH_3)₃], 53.0 [C(CH_3)₃], 34.4 [$\text{Si}(\text{CH}_3)_2(\text{C}(\text{CH}_3)_3)$], 33.5 [C(CH_3)₃], 32.3 [C(CH_3)₃], 28.2 [$\text{Si}(\text{CH}_3)_2(\text{C}(\text{CH}_3)_3)$], 22.7 [$\text{Si}(\text{CH}_3)_2(\text{C}(\text{CH}_3)_3)$], 14.2 [$\text{Si}(\text{CH}_3)_2\text{Bu}$], -2.6 [$\text{Si}(\text{CH}_3)_2\text{Bu}$] ppm; ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6 , 161.97 MHz, 298 K) : δ -27.21 ppm (s) ; ^{29}Si $\{^1\text{H}\}$ NMR (C_6D_6 , 79.49 MHz, 298 K): δ 9.17 ppm (s, SiMe_2Bu) δ -14.05 ppm (d, $J_{\text{Si-P}} = 30.2\text{ Hz}$). HRMS: $\text{C}_{39}\text{H}_{52}\text{N}_3\text{PSi}_2$ Calculated m/z 649.3437; Observed m/z 649.9080 $[\text{M}]^+$.

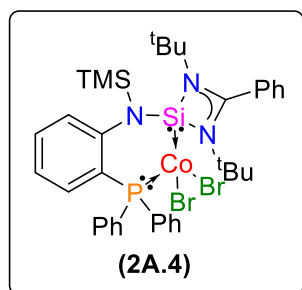
2A.5.1. Synthesis of 2A.3: Compound **2A.1** (304 mg, 0.5 mmol), FeBr_2 (107 mg, 0.5 mmol)



and toluene (20 mL) were added in a Schlenk flask. The mixture was stirred at room temperature for 12 h. Then the reaction mixture was filtered off, reduced to 4–5 mL under vacuum, and kept for crystallisation at room temperature. Suitable crystals were obtained in pale yellow colour. Yield: 60% (221 mg); M.p. $225\text{--}230\text{ }^{\circ}\text{C}$. ^{31}P MAS NMR (300 Hz, 298 K): δ 20.91 ppm. Magnetic moment: [5.6

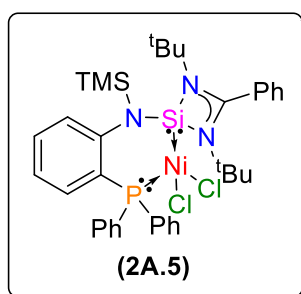
BM (300 K–5 K, field constant 100 Oe), 5.5 BM (at 5 K temperature) {using SQUID magnetometry}, 5.004 BM at 298 K {using Evans method}. HRMS: $\text{C}_{36}\text{H}_{46}\text{Br}_2\text{FeN}_3\text{PSi}_2$ Calculated m/z 821.0684; Observed m/z 820.2173 $[\text{M}-1]^+$.

2A.5.4. Synthesis of 2A.4: Compound **2A.1** (304 mg, 0.5 mmol) and CoBr_2 (109 mg, 0.5 mmol)



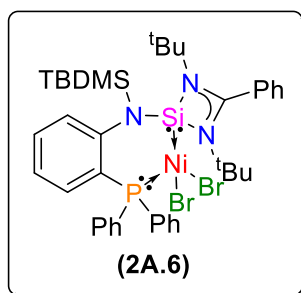
were taken in a Schlenk flask, and 30 mL toluene was added to it. The solution was stirred overnight. After filtration, the filtrate was concentrated to 4–5 mL under vacuum and kept at $-30\text{ }^{\circ}\text{C}$ in a freezer. After a day, ink blue-colored crystals were obtained. Yield: 58% (180 mg); M.p. $210\text{--}215\text{ }^{\circ}\text{C}$. ^{31}P MAS NMR (300 Hz, 298 K): δ 22.53 ppm. Magnetic moment: [4.73 BM (at 5 K temperature)

{using SQUID magnetometry}, 4.132 BM at 298 K {using Evans method}. HRMS: $\text{C}_{36}\text{H}_{46}\text{Br}_2\text{CoN}_3\text{PSi}_2$ Calculated m/z 824.0667; Observed m/z 824.0726 $[\text{M}]^+$.

2A.5.5. Synthesis of 2A.5: Compound **2A.1** (304 mg, 0.5 mmol), NiCl₂(dme) (110 mg, 0.5

mL), and dry THF (20 mL) were added in a Schlenk flask. The reaction mixture was stirred at room temperature for 6 h. Then, filtration was done using sintered glass frit under an argon atmosphere, and the solvent was removed in a vacuum. Then the solvent was reduced to 5-7 mL and kept for recrystallization at room temperature. After 12 h, red-colored crystals were obtained. Yield:

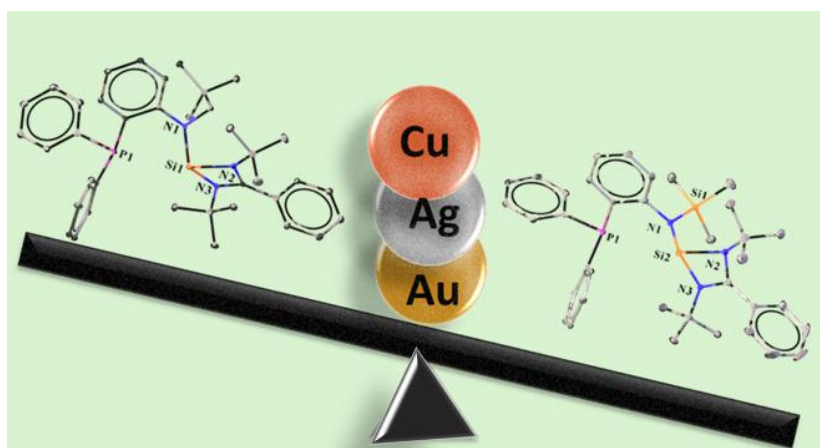
67% (276 mg); M.p. 225-235 °C. ³¹P {¹H} NMR (CDCl₃, 161.97 MHz, 298 K): δ 16.85 ppm (s); ²⁹Si {¹H} NMR (CDCl₃, 79.49 MHz, 298 K) δ 9.45 ppm (s, SiMe₃), δ 1.02 ppm (d, 2J_{Si-P} = 101.9 Hz). Magnetic moment: 1.30 BM at 298 K {using Evans method}. HRMS: C₃₆H₄₆Br₂NiN₃PSi₂ Calculated m/z 735.1698; Observed m/z 736.2664 [M+1]⁺.

2A.5.6. Synthesis of 2A.6: Compound **2A.2** (324 mg, 0.5 mmol), NiBr₂(dme) (154 mg, 0.5

mL), to which THF (20 mL) was added in a Schlenk flask. The reaction mixture was stirred at room temperature for 6 h. Then filtration was done using sintered glass frit under an argon atmosphere, and the solvent was removed to 5-7 ml in a vacuum and kept for crystallization at room temperature. After 12 h, red-colored crystals were obtained. Yield: 67% (276 mg); M.p. 225-235 °C. ³¹P

{¹H} NMR (CDCl₃, 161.97 MHz, 298 K): δ 17.99 ppm (s); ²⁹Si {¹H} NMR (CDCl₃, 79.49 MHz, 298 K) δ 16.11 ppm (s, SiMe₃), δ 6.11 ppm (d, 2J_{Si-P} = 89.2 Hz). Magnetic moment: 1.30 BM at 298 K {using Evans method}. HRMS: C₃₉H₅₂Br₂NiN₃PSi₂ Calculated m/z 865.1158; Observed m/z 866.1220 [M+1]⁺.

Chapter 2B: Synthesis and Coordination of Phosphine-Silylene-Based Hybrid Ligand Towards Coinage Metals



Adapted from: **R. Akhtar**, R. Panday, S. Khan* Synthesis and Coordination of Phosphine-Silylene-Based Hybrid Ligand Towards Coinage Metals (*Manuscript under permission*)

2B.1 Objective of the work

This work presents the diverse coordination nature of the bidentate ligand (phosphine-based hybrid amidinosilylene) toward group 11 metal precursors to access a series of coinage metal complexes (**2B.3-2B.11**). The previously synthesised phosphine-based hybrid silylene (**2B.1**), along with the synthesis and characterisation of a new phosphine-based hybrid amidinosilylene (**2B.2**), is explored to isolate the coinage metal complexes **2B.3-2B.11**. Reaction of hybrid amidinosilylene (**2B.1** and **2B.2**) with CuSCN and CuBr yielded dimeric copper(I) complexes stabilised by bridging anions (**2B.3** and **2B.4**), respectively. In contrast, reaction with AgCl, AgBr, and AgCN afforded monomeric coordinated silver(I) halide (**2B.6-2B.7**) and cyanide derivatives (**2B.8** and **2B.9**). Similarly, treatment with AuCl in 1:1 yielded monomeric gold(I) complexes (**2B.10** and **2B.11**), where coordination occurs exclusively through the silylene centre, while the phosphine donor remains non-coordinated. The solid-state structures of compounds **2B.2-2B.11** were confirmed by single-crystal X-ray diffraction, NMR spectroscopy, and mass spectrometry.

2B.2 Introduction

Over the past few decades, N-heterocyclic silylene has witnessed remarkable progress.^{1c, 4d, 25-31} The derivatisation and incorporation of diverse functionalities at the Si(II) centre become increasingly accessible after the isolation of three-coordinate benzamidinato silylene $\text{SiCl}\{\text{PhC}(\text{N}^t\text{Bu})_2\}$ by using a facile synthetic route.^{7a,32} To date, a wide range of benzamidinato silylene variants have been documented, showcasing diverse structural modification and coordination behaviour that highlights their versatility as a ligand.^{21,33-40} Literature studies reveal that changes in the substituents at the Si(II) centre directly modulate the HOMO-LUMO gap, thereby influencing its σ -donor strength.³⁵ The ability of silylenes to donate their lone pair to functionalized transition metal centres has enabled the isolation of a wide variety of silylene-transition metal complexes.^{9a,41-45} Compared to monodentate analogues, bidentate ligands often impart enhanced stability, and numerous bidentate silylenes incorporating diverse donor atoms (e.g., N, C, Si, and P) in conjunction with the Si(II) centre have also been synthesised.^{4d,4c,46,47} These ligands have proven effective in stabilising reactive species and various transition metal complexes.^{5b,6a,6f,42,48-53} Despite notable progress in the chemistry of $\text{NHSi} \rightarrow \text{coinage metal}$ complexes in recent years, the scope of hybrid silylene chemistry remains rather limited.⁵⁴⁻⁶⁰ Meanwhile, hybrid silylene ligands have further gained attention as a powerful design strategy for molecular activation, homogeneous catalysis, functional materials, and small-molecule

sensing.⁶¹⁻⁶⁸ In this context, in 2016, a phosphine-silylene hybrid ligand, $\text{Si}\{\text{N}(\text{Dipp})\text{PPh}_2\}\{\text{PhC}(\text{N}^t\text{Bu})_2\}$ (**2B.A**) was reported by our group, which showed the coordination with AuCl .^{5a} Subsequently, a few new phosphine-based hybrid silylene ligands (**2B.B-2B.E**) were synthesised and investigated for the synthesis of metal complexes (Chart 2B.1).^{5a,5d, 69}

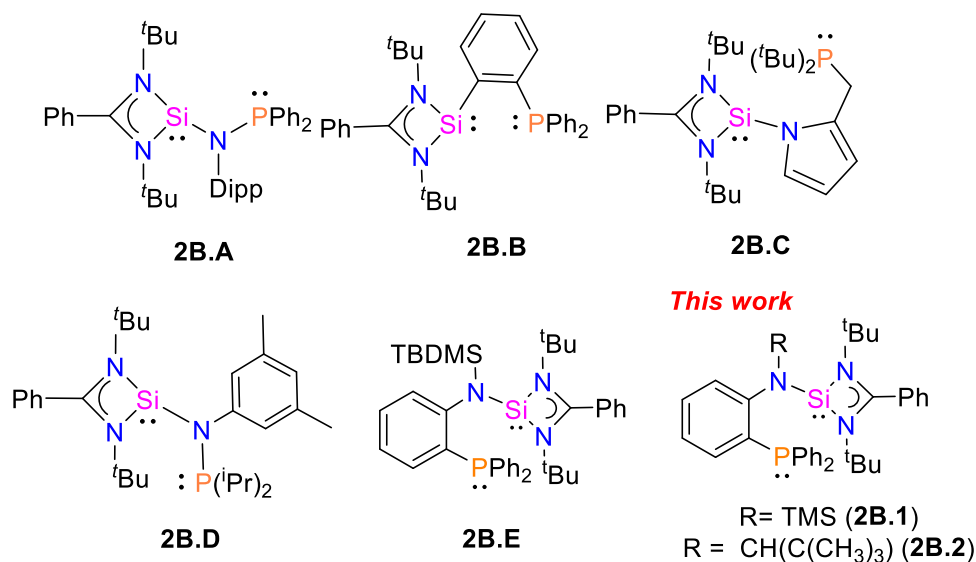


Chart 2B.1. Previously reported silylene-phosphine-based hybrid ligands

Among the synthesised ligands, only **2B.A** and **2B.B** were explored for their reactivity toward group 11 metal salts (CuCl and AuCl).^{5a,5c,70} Treatment of **2B.A** with $\text{AuCl} \cdot \text{SMe}_2$ in 1:1 enabled the isolation of a monomeric $\text{Au}(\text{I})\text{Cl}$ complex (**2B.I**) along with a dimeric $\text{Au}(\text{I})$ species (**2B.II**) featuring an intramolecular $\text{Au} \cdots \text{Au}$ interaction. In contrast, the reaction of ligand **2B.B** with CuCl and AuCl leads to the formation of the diamagnetic complex $[\text{2B.B}_2\text{Cu}]^+[\text{CuCl}_2]^-$ (**2B.III**), and a six-membered $\text{C-P-Au} \cdots \text{Au-Si-C}$ ring (**2B.IV**), respectively (Chart 2B.2).

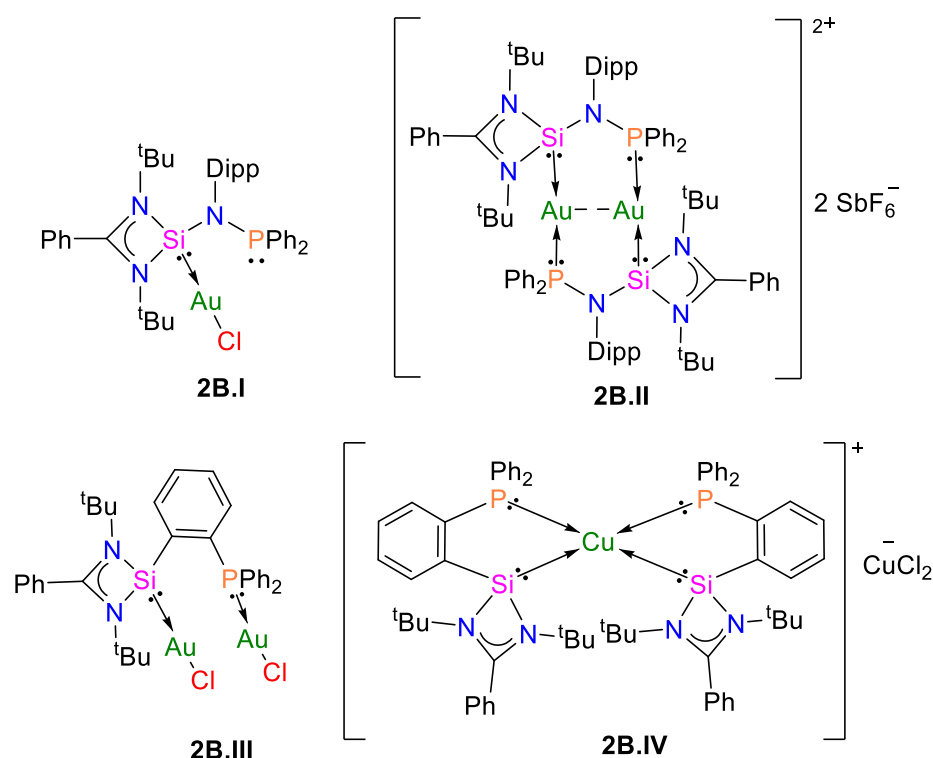


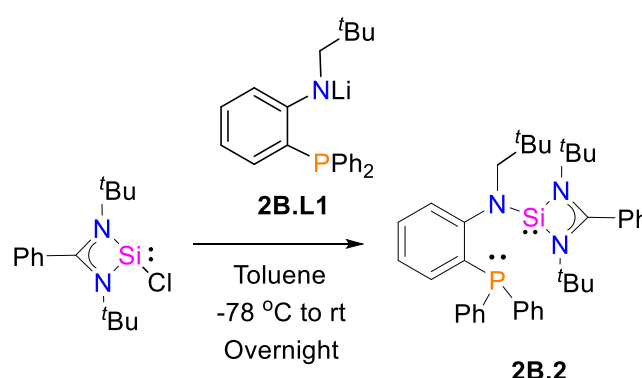
Chart 2B.2. Previously reported phosphine-based hybrid silylene group 11 complexes.

The limited number of reports (**2B.I-2B.IV**, Chart 2B.2) on bidentate phosphine-based silylene complexes with Group 11 metals illustrates the rarity and unexplored nature of this ligand system. The defining structural characteristic of this type of ligand is the simultaneous presence of the Si: and P: donor sites. Owing to the scarcity of reported hybrid NHSi-coinage metal complexes, we investigated the previously reported ligand Si{N(TMS)C₆H₄(PPh₂)}{PhC(N^tBu)₂} {trimethylsilyl} (**2B.1**) for its reactivity towards coinage metal precursors (CuCSN, AgBr, AgCN, AuCl.SMe₂).⁶⁹ In parallel, we designed a new hybrid silylene with a more robust Si(II)-P(III) backbone Si{N(CH(C(CH₃)₃)C₆H₄(PPh₂))}{PhC(N^tBu)₂} (**2B.2**). Further, **2B.1** and **2B.2** were treated with group 11 metal precursors (CuCl, CuSCN, AgX (X = Cl, Br, CN), and AuCl.SMe₂) to generate Si(II)→coinage metal complexes (**2B.3-2B.11**). These studies highlight the influence of substituents on the benzamidinato-phosphine-based silylene framework in modulating the coordination behaviour toward coinage metals, and the results are presented herein.

2B.3 Result and discussion

To explore the new coordination modes, we employed the previously reported phosphine functionalized amidinato silylene Si{N(CH₂C(CH₃)₃)C₆H₄(PPh₂))}{PhC(N^tBu)₂} (**2B.1**) toward coinage metal salts.⁶⁹ To widen the ligand scope of this hybrid system, we also prepared

another analogue with a $-\text{CH}_2\text{C}(\text{CH}_3)_3$ group. The reaction of $\text{SiCl}\{\text{PhC}(\text{N}^t\text{Bu})_2\}$ with $\text{LiN}(\text{CH}_2\text{C}(\text{CH}_3)_3)(\text{C}_6\text{H}_4)\text{PPh}_2$ in toluene at room temperature afforded the silylene-phosphine-based hybrid ligand $\text{Si}\{\text{N}(\text{CH}_2\text{C}(\text{CH}_3)_3)\text{C}_6\text{H}_4(\text{PPh}_2)\}\{\text{PhC}(\text{N}^t\text{Bu})_2\}$ (**2B.2**) in good yield (Scheme 2B.1). Yellow crystals of **2B.2** suitable for single-crystal X-ray analysis were obtained after storing their concentrated solutions for 24 h at room temperature. The ^{31}P NMR spectra of **2B.2** display a single peak at δ -23.64 ppm, which is comparable to **2B.1** (-22.75). The ^{29}Si NMR spectra of **2B.1** and **2B.2** exhibit a doublet [for Si(II) center] at δ -13.11 and -7.76 ppm with the $J_{\text{Si-P}}$ coupling constants of 21.6 and 32.8 Hz, respectively. The ^{29}Si NMR signal for **2B.1** is more upfield-shifted compared to the ligand **2B.2**, which might be due to the strong electron-donation of the TMS (trimethylsilyl) group and the coupling between the silicon-phosphorus center. Ligand **2B.1** crystallises in the triclinic $P\bar{1}$ space group, while **2B.2** crystallizes in the $I41/a$ tetragonal space group (Figure 1). The molecular structure of **2B.1** and **2B.2** shows that the Si(II) atom is at the vertex of a trigonal pyramid, connected to the three N atoms (Figure 2B.1). The molecular structures of **2B.1** and **2B.2** confirm the presence of two donating sites, Si(II) and P(III), leading to the anticipation that **2B.1** and **2B.2** can behave as bidentate ligands. The Si1-N1 bond distance is 1.788(2) Å, whereas the Si1-N2 and Si1-N3, are 1.904(2) Å and 1.903(2) Å, respectively. Compared to the previously reported ligand (**2B.1**), the Si2-N1 bond length is slightly longer (1.804(3) Å), while for the other two bonds, one is shorter (N3-Si2 1.880(3) Å) and the other is slightly elongated (N2-Si2 1.920(3) Å).



Scheme 2B.1: Synthesis of **2B.1** and **2B.2**.

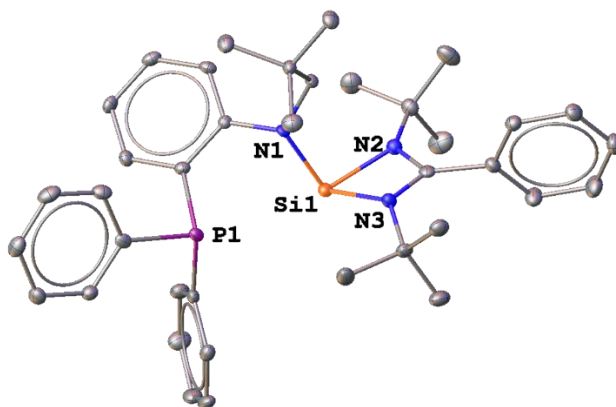
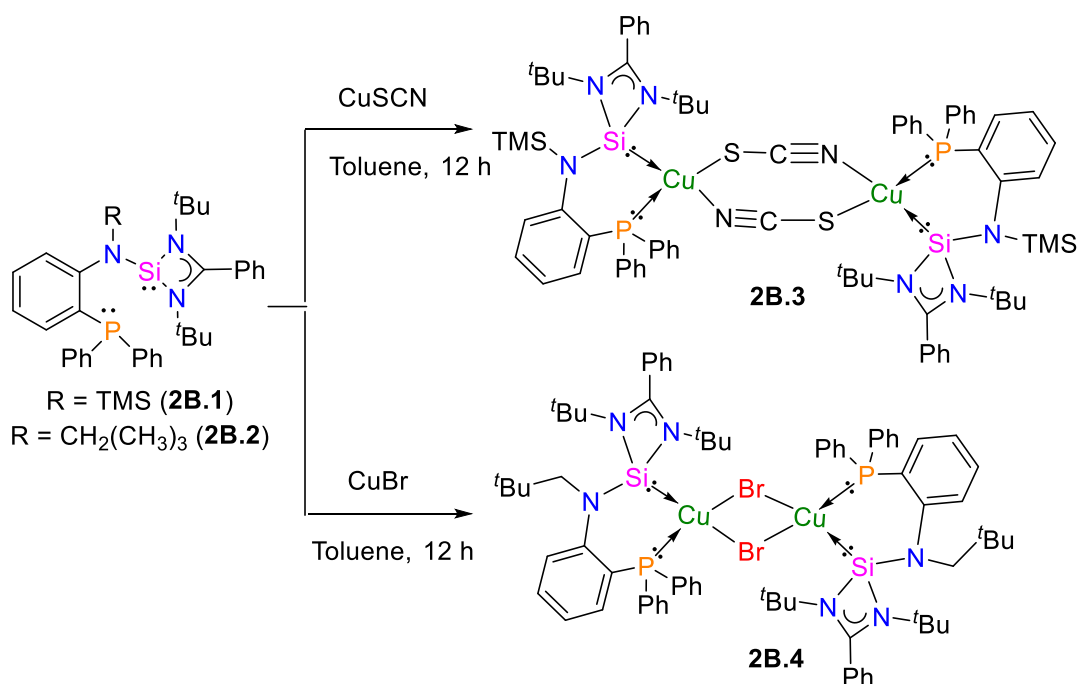


Figure 2B.1. Molecular structure of **2B.2**. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): N1-Si1 1.788(2), Si1-N2 1.904(2), Si1-N3 1.903(2), Si1-P1 3.319(1); N1-Si1-N3 103.39(8), P1-C7-C12 119.9(2), Si1-N1-C12 116.8(1).

To gain further insights into the coordination behaviour of ligands **2B.1** and **2B.2**, we examined their reactivity with group 11 metal precursors. Attempts to react ligand **2B.1** with copper halides consistently resulted in decomposition and black metal deposition at the bottom of the flask. In contrast, treatment of **2B.1** with one equivalent of CuSCN in toluene afforded complex **2B.3** as a yellow solid. However, ligand **2B.2** reacted cleanly with CuBr to furnish complex **2B.4** (yellow crystals), without any sign of decomposition or metal leaching (Scheme 2B.2). Complexes **2B.3** and **2B.4** crystallises in $P2_1/n$ monoclinic space group (Figure 2B.2). The molecular structure of **2B.3** and **2B.4** reveals a dimeric structure where the copper(I) centre is four-coordinated (Figure 2B.2). In complex **2B.3**, copper centre is coordinated with the N-atom of one thiocyanate group, the S-atom of another thiocyanate group, and the Si, P-atom of the ligand. However, complex **2B.4**, copper centre displays coordination with two Br-atoms and the Si, P-atom of the ligand. The complex **3** is the second report on the NHSi-supported copper(I) thiocyanate complex, which displays a structure similar to the previously documented NHSi-supported copper(I) thiocyanate complex.⁶⁶ For complex **2B.3**, the ^{29}Si NMR spectrum displays two resonances at δ 4.15 ppm [Si(II)] and δ 8.02 ppm (SiMe₃), respectively, and they are downfield shifted as compared to those in **2B.1** { δ -13.11 ppm [Si(II)] and δ 5.00 ppm (SiMe₃)}. The ^{31}P NMR spectrum of **2B.3** reveals a similar observation, where the phosphorus peak appears at δ -7.34 ppm (^{31}P NMR peak of **2B.1**: δ -22.75 ppm). However, the ^{29}Si NMR and ^{31}P NMR spectrum of **2B.4** displays a doublet at δ 6.45 (d, J = 110.1 Hz) and a singlet at δ -12.64 ppm, respectively, both of which are downfield shifted compared to **2** { δ -7.76 ppm [Si(II)] and δ -23.64 ppm [P(III)]}.



Scheme 2B.2: Synthesis of **2B.3** and **2B.4** via the reaction of **2B.1** with CuSCN afforded **2B.3**, and the reaction of **2B.2** with CuBr afforded **2B.4**.

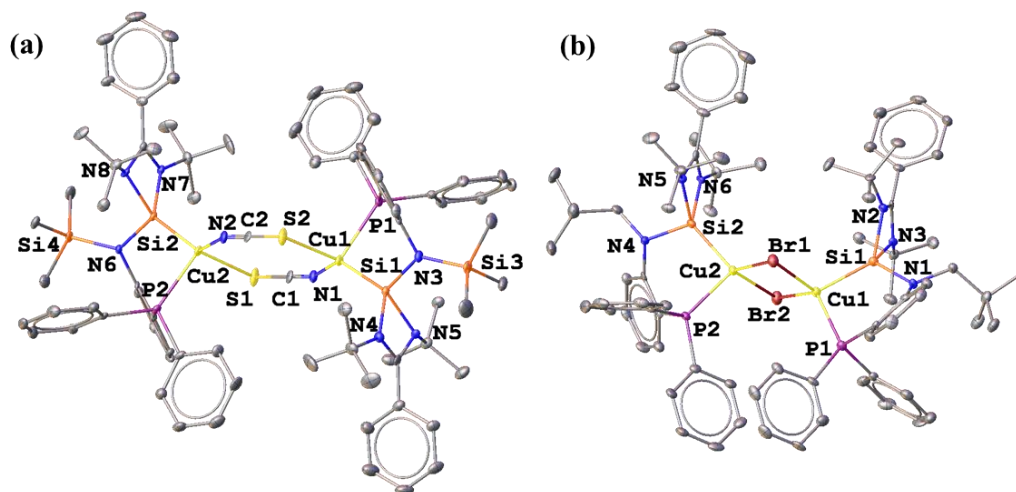
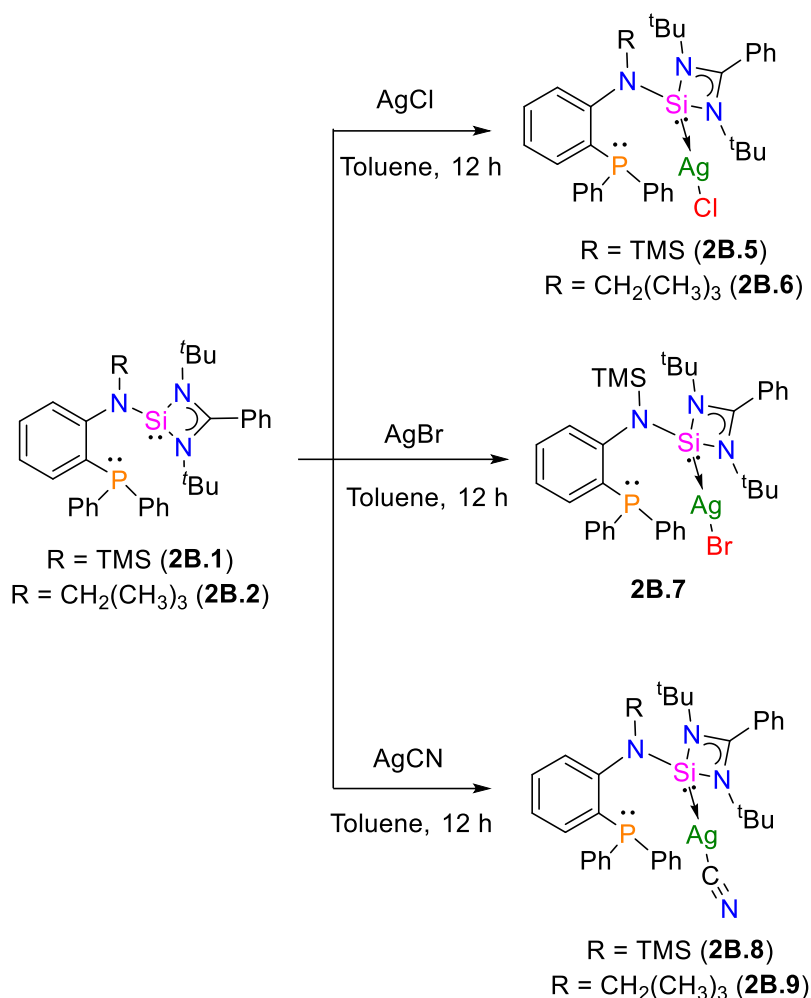


Figure 2B.2. Molecular structure of **2B.3** and **2B.4**. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): (a) For **2B.3**, Cu1-N1 1.957(3), N1-C1 1.167(5), C1-S1 1.646(4), P1-Cu1 2.333(1), Si1-Cu1 2.228(1); S2-C2-N2 178.0(4), C2-N2-Cu2 159.5(3), P1-Cu1-Si1 91.14(4), S2-Cu1-N1 103.0(1). (b) For **2B.4**, Cu1-Br1 2.5024(8), Cu1-Br2 2.4713(9), Si1-Cu1 2.226(2), P1-Cu1 2.252(2), Si2-Cu2 2.226(2).

The bond lengths and bond angles of **2B.3** are comparable with those reported for the NHC-copper(I) thiocyanate complex ($[\{\text{PhC}(\text{N}^t\text{Bu})_2\}\text{Si}\{\text{N}(\text{SiMe}_3)_2\}]_2\text{Cu}_2\text{SCN}_2$ [Cu1-N1, N1=C1,

C1=S1 and Si1-Cu1 bond lengths of **2B.3** are 1.957(3), 1.167(5), 1.646(4) and 2.228(1) Å, respectively, and the C2-N2-Cu2 and S2-C2-N2 bond angles are 159.5(3) and 178.0(4)°, respectively; Cu-N, N=C, C=S and Cu-Si bond lengths of ([{PhC(N^tBu)₂}Si{N(SiMe₃)₂}]₂Cu₂SCN₂) are 1.938(5), 1.155(7), 1.646(5), and 2.224(2) Å, respectively, and the N-C-S and Cu-N-C bond angles are 177.7(5) and 161.5(4)°, respectively]. However, complex **2B.4** is isostructural to our previously reported [PhC(N^tBu)₂Si{N(Cbz)₂}CuBr]₂ and [PhC(N^tBu)₂Si{N(TMS)₂}CuBr]₂.^{57,66} The central copper atom adopts a distorted tetrahedral geometry, likely arising from the steric influence of the phosphine donor and the *tert*-butyl substituents (Figure 2). The Si1-Cu1 and Si2-Cu2 bond lengths (2.226(2) and 2.226(2) Å) in **2B.4** are similar than those in [PhC(N^tBu)₂Si{N(Cbz)₂}CuBr]₂ (2.203(2) and 2.212(2) Å) and shorter to [PhC(N^tBu)₂Si{N(TMS)₂}CuBr]₂ (2.243(3) and 2.250(3) Å).

Although in a recent development, our group has isolated the benzamidinato silylene coordinated silver(I) halide and cationic silver(I) complexes. The cationic silver(I) complexes were further explored in a three-component A³-coupling reaction; however, the structural validation of the silver(I) halide complex with a bidentate ligand is still missing.⁷¹ To address this, we examined the reactivity of ligands **2B.1** and **2B.2** with silver precursors (AgCl, AgBr, and AgCN). Treatment of AgCl with ligands **2B.1** and **2B.2** afforded complexes **2B.5** and **2B.6**, respectively, exhibiting a similar linear bonding geometry (Scheme 2B.3). Compound **5** crystallises in the *P*2₁/*c* monoclinic space group, and complex **6** crystallises in the triclinic *P* $\bar{1}$ space group. For complex **2B.5**, the ²⁹Si NMR spectrum displays two resonances; two doublet of doublet δ 13.63 (d), 13.17 (d), 7.33 (d), 6.88 (d) ppm [Si(II)] and δ 10.09 (d) ppm (SiMe₃), respectively, and they are downfield shifted as compared to those in **2B.1** { δ -13.11 ppm [Si(II)] and δ 5.00 ppm (SiMe₃)}. The ³¹P NMR spectrum of **2B.5** shows a signal at δ -20.01 ppm, representing a slight downfield shift compared to the free ligand [δ -22.75 ppm], consistent with the lack of phosphorus involvement in coordination with AgCl. However, the ²⁹Si NMR and ³¹P NMR spectrum of **6** displays a doublet at δ 15.45 (d, *J* = 110.1 Hz) and a singlet at δ -17.59 ppm, respectively, both of which are downfield shifted compared to **2B.2** { δ -7.76 ppm [Si(II)] and δ -23.64 ppm [P(III)]}. The Si1-Ag1 and Ag1-Cl1 bond distance in complex **2B.5** is 2.356(1) and 2.375(1) Å, respectively, with a Si1-Ag1-Cl1 bond angle of 173.96(4)°. In complex **2B.6**, the bond lengths are slightly shorter [Si1-Ag1, 2.352(1) Å and Ag1-Cl1, 2.337(1) Å], and the Si1-Ag1-Cl1 bond angle is more bent (171.78(4)°) compared to **2B.5** (Figure 2B.3).



Scheme 2B.3: Synthesis of **2B.5-2B.9**.

A similar reactivity pattern of ligand **2B.1** was observed while treating with AgBr (**2B.7**) (Scheme 2B.3). Complex **2B.7** is isostructural to **2B.5**, which crystallises in the same $P2_1/c$ monoclinic space group. For complex **2B.7**, the ^{29}Si NMR spectrum displays two resonances: two broad peaks at δ 14.52 (b), 8.32 (b) ppm for Si(II) and δ 10.12 (s) ppm for SiMe₃, respectively. In complex **2B.7**, the Si1-Ag1 and Ag1-Br1 bond distance is 2.3576(8) and 2.4739(6) Å, respectively whereas the Si1-Ag1-Br1 bond angle is 172.84(2)° (Figure 2B.3).

Further, we investigated the reaction of **2B.1** and **2B.2** with silver cyanide (AgCN), which showed a reactivity pattern similar to their corresponding halide complexes (Scheme 2B.3). Compound **2B.8** crystallises in the monoclinic space group $P2_1/c$, whereas complex **2B.6** crystallises in the orthorhombic $Pca2_1$ space group. However, the complex **2B.8** and **2B.9** is the first report on the NHSi-supported silver(I) cyanide complexes. The ^{29}Si NMR spectrum of **2B.8** exhibits two broad peaks at δ 15.14 (b), 8.32 (b) ppm assigned to Si(II), along with a sharp signal at δ 10.07 (s) ppm for SiMe₃, respectively. The ^{31}P NMR spectrum of **2B.8** shows a

signal at δ -19.72 ppm, consistent with the absence of phosphorus coordination with AgCl. Similarly, the ^{29}Si NMR and ^{31}P NMR spectrum of **2B.9** displays a broadening at δ 17.27 (d, J = 110.1 Hz) and a singlet at δ -18.75 ppm, respectively. The molecular structure of complex **2B.8** shows the Si1-Ag1 and Ag1-C1 bond distances are 2.372(1) and 2.169(5) Å, respectively, while the C1-N1 bond length is 0.976(7) Å, characteristic of a triple bond. The bond angle for Si1-Ag1-C1 is 173.5(1)° and near to linearity for Ag1-C1-N1 178.0(5)°. In complex **2B.9** the Si1-Ag1 and Ag1-C1 bond length (2.366(4) Å, 2.11(2) Å, respectively), are comparable to those in complex **2B.8**, whereas the C1-N4 bond length is slightly elongated (1.11(2) Å) (Figure 2B.3). The bond angles Ag1-C1-N4 (174(1)°) and Si1-Ag1-C1 (173.2(4)°) indicate a nearly linear, but slightly deviated, coordination environment around the silver centre.

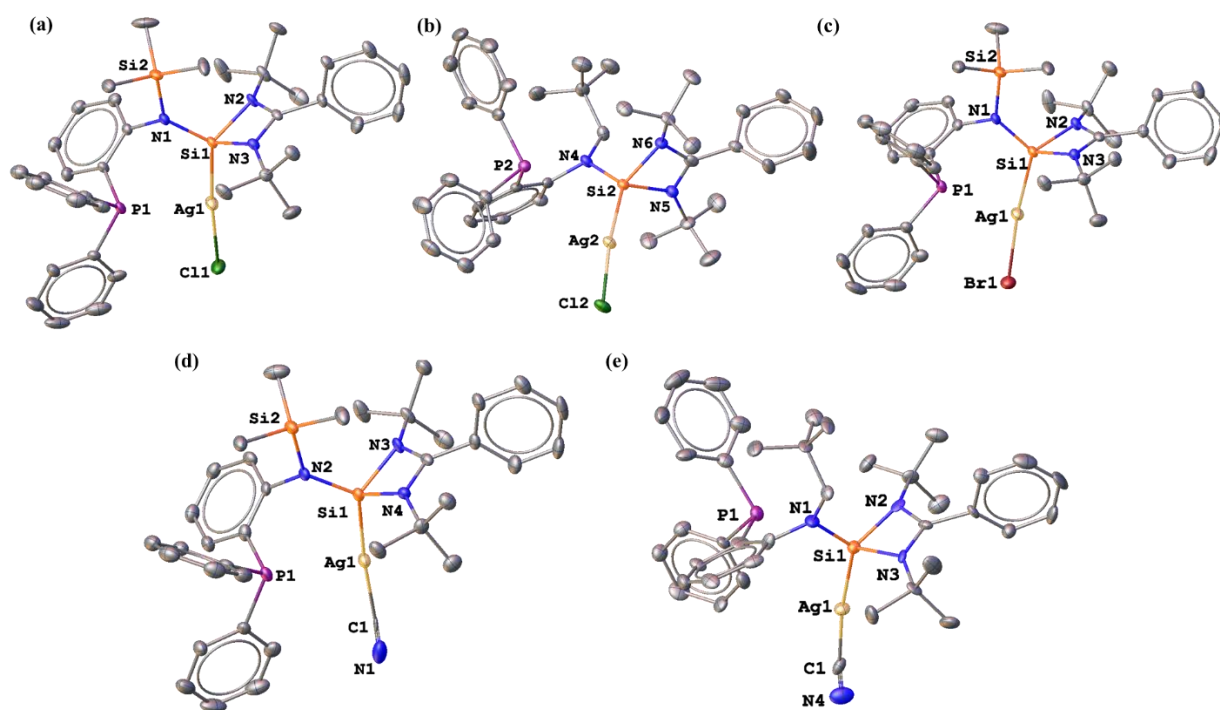
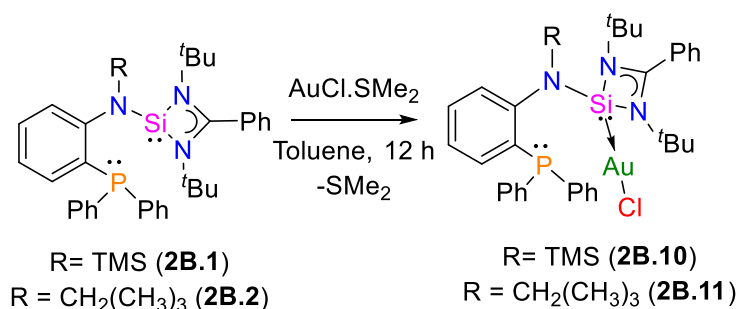


Figure 2B.3. Molecular structure of **2B.5-2B.9**. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms and solvent are omitted for clarity. Selected bond distances (Å) and angles (deg): (a) For **2B.5**, Si1-Ag1 2.356(1), Ag1-Cl1 2.375(1), P1-Ag1 3.805(1); Si1-Ag1-Cl1 173.96(4). (b) For **2B.6**, Si1-Ag1 2.337(1), Ag1-Cl1 2.352(1), Ag1-P1 3.556(2); Si1-Ag1-Cl1 is 171.78(4). (c) For **7**, Si1-Ag1 2.3576(8), Ag1-Br1 2.4739(6), Ag1-P1 3.800(1); Si1-Ag1-Br1 172.84(2). (d) For **2B.8** Si1-Ag1 2.372(1), Ag1-C1 2.169(5), C1-N1 0.976(7), Ag1-P1 3.772(1); Si1-Ag1-C1 173.5(1), Ag1-C1-N1 178.0(5). (e) For **9** Si1-Ag1 2.366(4), Ag1-C1 2.11(2), C1-N4 1.11(2), Ag1-P1 3.798(4); Ag1-C1-N4 174(1), Si1-Ag1-C1 173.2(4).

After this, we reacted **2B.1** and **2B.2** with $\text{AuCl}\cdot\text{SMe}_2$ and isolated the complexes **2B.10** and **2B.11** as colourless crystals, respectively (Scheme 2B.4). The ^{29}Si NMR spectrum of **10** exhibits two peaks at δ 11.95 (d, $J = 4.5$ Hz) ppm for Si(II) and 10.09 (s) ppm for SiMe_3 . The ^{29}Si NMR spectrum of **2B.11** displays only one sharp doublet at δ 15.78 (d, $J = 3.9$ Hz) ppm. The ^{31}P NMR spectrum of **2B.10** and **2B.11** shows a signal at δ -19.63 and -17.52 ppm, consistent with the absence of phosphorus coordination with AuCl . Complexes **2B.10** and **2B.11** crystallise in the Cc and $P2_1/c$ monoclinic space groups (Figure 2B.4). The molecular structure of complex **2B.10** shows that the Si1-Au1 and Au1-Cl1 bond distances are 2.241(2) and 2.320(2) Å, respectively, while the bond angle for Si1-Au1-Cl1 is $175.99(7)^\circ$. In complex **2B.11**, the Si1-Au1 and Au1-Cl1 bond lengths (2.252(1) and 2.336(1) Å, respectively) are slightly longer than in complex **2B.10**, but interestingly, the Si1-Au1-Cl1 angle is linear with a bond angle of $179.18(3)^\circ$. The bond distance and bond angle are comparable to the previously reported phosphine-silylene-based hybrid ligand.^{5a,70} For the complex reported by Roesky and co-workers (**2B.III**), the Au-Si bond length is 2.238(3) Å with an Au-Si-Cl bond angle of $173.86(13)^\circ$, while in the work of Khan and co-workers (**2B.I**), the corresponding Au-Si bond length is 2.246(2) Å and the Au-Si-Cl bond angle is $177.39(9)^\circ$.^{5a,70}



Scheme 2B.4: Synthesis of **2B.10-2B.11**.

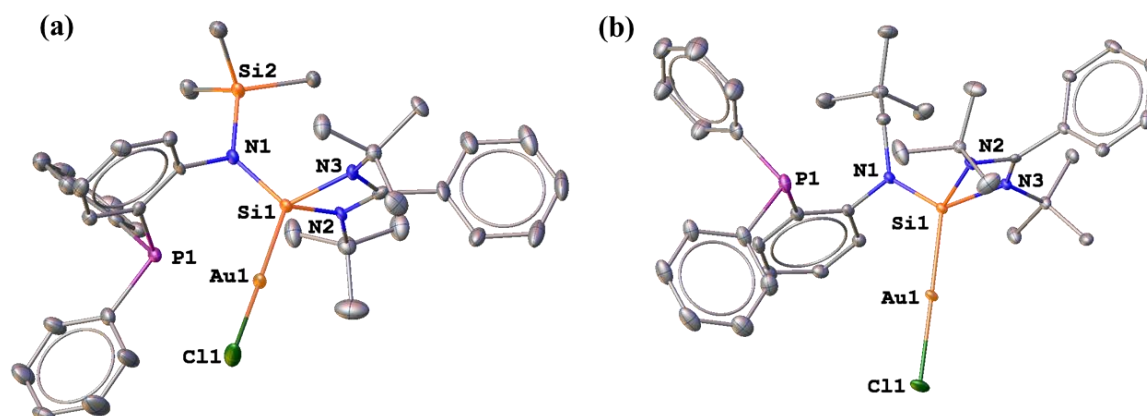


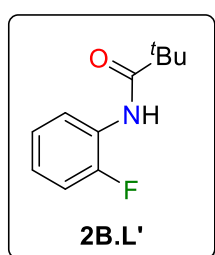
Figure 2B.4. Molecular structure of **2B.10-2B.11**. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms and solvent are omitted for clarity. Selected bond distances (Å) and angles (deg): (a) For **2B.10**, Si1-Au1 2.241(2), Au1-Cl1 2.320(2), P1-Au1 3.746(2); Si1-Au1-Cl1 175.99(7). (b) For **2B.11**, Si1-Au1 2.252(1), Au1-Cl1 2.336(1), P1-Au1 4.670(2); Si1-Au1-Cl1 179.18(3).

2B.4 Conclusion

In summary, we have synthesised a new phosphine-based hybrid ligand by utilising amidinato backbone. Further, the $\text{Si}\{\text{N}(\text{R})\text{C}_6\text{H}_4(\text{PPh}_2)\}_2\{\text{PhC}(\text{N}^t\text{Bu})_2\}$ [$\text{R} = \text{TMS}$ {trimethylsilyl}] (**2B.1**) and $\text{CH}(\text{C}(\text{CH}_3)_3)$ (**2B.2**) was employed to isolate several silylene-supported group 11 metal complexes. Copper(I) precursors afforded dimeric complexes stabilised by bridging anions, silver(I) and gold(I) salts yielded monomeric species with exclusive silylene coordination, leaving the phosphine donor non-coordinated. Thus, the overall reactivity of the phosphine silylene-based hybrid toward group 11 elements indicates that the silylene is a better σ -donor than the phosphine. Single-crystal X-ray diffraction studies and multinuclear NMR spectroscopic studies characterise all the compounds. These results provide valuable insights for the design of new hybrid silylenes, which can be further employed to access a broader range of coinage metal complexes with strong potential to serve as highly efficient catalysts in diverse organic transformations.

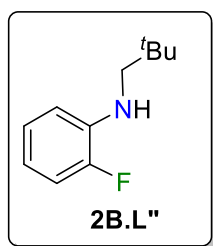
2B.5. Synthesis of 2A.2-2A.11.

2B.5.1. Synthesis of 2B.L': Fluoroaniline (2 ml, 20.71 mmol) reacted with trimethylacetyl

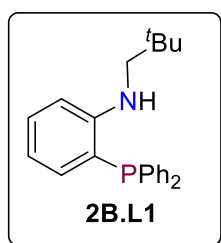


chloride (2.5 ml, 20.71 mmol) and triethylamine (2.8 ml, 20.71 mmol) in 250 ml diethyl ether, and the mixture was stirred overnight. This resulted in the formation of a white precipitate of $\text{NEt}_3 \cdot \text{HCl}$, after an aqueous workup, the ether-soluble compound, N-(2-(diphenylphosphanyl)phenyl)pivalamide (**2B.L'**) was isolated as white

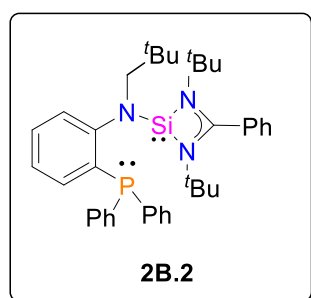
needle-shaped crystals in 98% yield (**Scheme 2B.1**). M.P. 80 °C ^1H NMR (CDCl_3 , 400 MHz, 298 K, TMS): δ 1.32 (s, 9H, $\text{C}(\text{CH}_3)_3$), 7.17-6.98 (m, 3H, Ph), 7.63 (s, 1H, Ph), δ 8.33 (t, 1H, Ph) ppm. ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100.613 MHz, 298 K): δ 175.60 (s, $\text{C}=\text{O}$), 152.75 (s, Ph), 150.34 (s, Ph), 125.60 (s, Ph), 123.53 (d, Ph), 123.02 (d, Ph), 120.62 (s, Ph), 113.58 (d, Ph), 38.94 (s, $\text{C}(\text{CH}_3)_3$), 26.52 (s, $\text{C}(\text{CH}_3)_3$) ppm. ^{19}F $\{^1\text{H}\}$ NMR (CDCl_3 , 376.49 MHz, 298 K): δ -132.11 (s) ppm.

2B.5.2. Synthesis of 2B.L'': The N-(2-(diphenylphosphaneyl)phenyl)pivalamide (**2B.L'**) (4 g,

20.5 mmol) was treated with LiAlH_4 (2.3 g, 61.5 mmol) in 150 ml of tetrahydrofuran (THF) and refluxed for 2 days. After reflux, an aqueous workup was performed, and the desired **2B.L''** ligand was obtained as a liquid in 60% yield (**Scheme 2B.2**). ^1H NMR (CDCl_3 , 400 MHz, 298 K, TMS): δ 1.12 (s, 9H, $\text{C}(\text{CH}_3)_3$), 3.02 (s, 2H, CH_2), 4.02 (s, 1H, NH), 6.68 (s, 1H, Ph), 6.81 (t, 1H, Ph), 7.12-7.02 (m, 2H, Ph) ppm. ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100.613 MHz, 298 K): δ 151.62 (s, Ph), 149.26 (s, Ph), 136.52 (d, Ph), 123.48 (s, Ph), 114.87 (s, Ph), 113.19 (d, Ph), 110.79 (s, Ph), 54.26 (s, $\text{CH}(\text{CH}_3)_3$), 30.91 (s, $\text{C}(\text{CH}_3)_3$), 26.47 (s, $\text{C}(\text{CH}_3)_3$) ppm. ^{19}F $\{^1\text{H}\}$ NMR (CDCl_3 , 376.49 MHz, 298 K): δ -137.24 ppm.

2B.5.3. Synthesis of 2B.L1: **2B.L''** (2 g, 11.04) was treated with KPh_2 (22.08 ml, 11.04, 0.5

molar solution in THF) in dioxane and refluxed for 5 days. After the reflux, a workup was performed with DCM under an inert atmosphere, and crystallisation was carried out in ethanol, yielding white block-shaped crystals at -30°C in 72% yield (**Scheme 2B.3**). M.P. 89.5°C ^1H NMR (CDCl_3 , 400 MHz, 298 K, TMS): δ 0.82 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.87 (d, 2H, CH_2), 4.54 (s, 1H, NH), 6.62 (d, 2H, Ph), 6.81 (s, 1H, Ph), 7.23 (s, 1H, Ph), 7.35 (s, 10H, Ph) ppm. ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100.613 MHz, 298 K): δ 150.14 (d, Ph), 134.32 (d, Ph), 133.20 (d, Ph), 132.73 (d, Ph), 129.49 (s, Ph), 127.74 (s, Ph), 127.51 (d, Ph), 117.73 (s, Ph), 115.52 (s, Ph), 108.77 (s, Ph), 54.54 (s, $\text{CH}(\text{CH}_3)_3$), 30.68 (s, $\text{C}(\text{CH}_3)_3$), 26.43 (s, $\text{C}(\text{CH}_3)_3$) ppm. ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3 , 161.97 MHz, 298 K): δ -20.17(s) ppm.

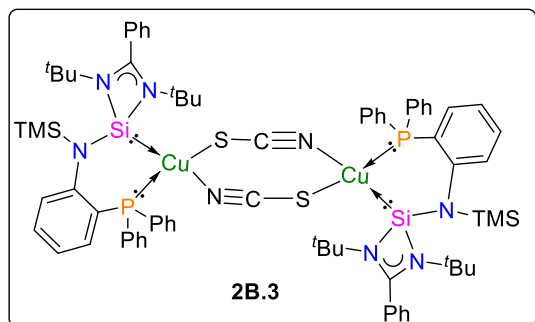
2B.5.4. Synthesis of 2B.2: N,N'-{bis(tert-butyl)amidinate}chlorosilylene (295 mg, 1 mmol)

and $\text{LiN}\{\text{CH}_2(\text{CH}_3)_3\}\{(\text{PPh}_2)\text{C}_6\text{H}_4\}$ (427 mg, 1 mmol) were taken in a Schlenk flask, to which 30 mL of toluene was added at room temperature and stirred for overnight. The resulting solution was filtered off using sintered glass frit under an argon atmosphere, and the solvent was removed under vacuum to yield pale yellow solid.

Single crystals suitable for X-ray analysis were grown in toluene at -30°C . Yield: 77.5 % (470 mg). M.p. $190\text{--}195^\circ\text{C}$. ^1H NMR (C_6D_6 , 400 MHz, 298 K, TMS): δ ^1H NMR (400 MHz, C_6D_6) δ 0.73 (s, 9H, $\text{CH}(\text{CH}_3)_3$), 1.03 (s, 18H, $\text{C}(\text{CH}_3)_3$), 2.70 (d, 2H, $\text{CH}(\text{CH}_3)_3$), 6.67-6.59 (m, 2H, Ph), 6.81 (t, 2H, Ph), 6.97-6.94 (m, 4H, Ph), 7.04 (d, $J = 6.1$ Hz, 9H, Ph), 7.45-7.42 (m, 3H, Ph), ppm; ^{13}C $\{^1\text{H}\}$ NMR (100.613 MHz, C_6D_6 , 298 K) δ 163.20 (s, NCN), 157.82 (s, Ph), 157.59 (s, Ph), 138.43 (s, Ph), 134.04 (s, Ph), 133.57 (d, Ph), 130.64

(d, Ph 130.25-130.01 (m, Ph), 129.18 (s, Ph), 128.82 (s, Ph), 123.05 (s, Ph), 121.14 (s, Ph), 56.31 (s $\underline{\text{CH}}(\text{CH}_3)_3$), 52.91 (s, $\underline{\text{C}}(\text{CH}_3)_3$), 52.03 (s, $\underline{\text{C}}(\text{CH}_3)_3$), 34.76 (s, $\text{C}(\underline{\text{CH}}_3)_3$), 29.85 (s, $\text{C}(\underline{\text{CH}}_3)_3$) ppm; ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6 , 161.97 MHz, 298 K): δ -23.64 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 79.49 MHz, 298 K): δ -7.76 ppm (d, $J_{\text{Si-P}} = 32.8$ Hz).

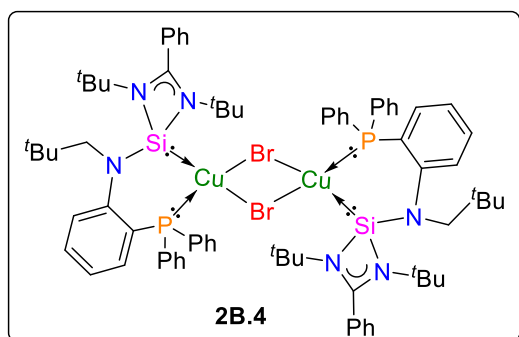
2B.5.5. Synthesis of 2B.3: **2B.1** (304 mg, 0.5mmol) and CuBr_2 (60.81 mg, 0.5 mmol) were



taken in a flask, and 40 mL of toluene was added to the reaction mixture. After overnight stirring at room temperature, the reaction mixture was filtered off, and toluene was concentrated. The yellow crystals suitable for X-ray analysis were obtained from a toluene and n-pentane mixture after 1 day at room temperature. Yield: 79.6 % (290 mg). M.p.

210-225 °C ^1H NMR (400 MHz, CDCl_3) δ 0.07 (d, 18H, $(\text{SiCH}_3)_3$), 1.05 (b, 36H, $(\text{CH}_3)_3\text{C}$), 2.35 (s, 6H, $\underline{\text{CH}}_3$), 6.68-6.57 (m, 3H, Ph), 6.76 (dd, 1H, Ph), 7.00-6.93 (m, 4H, Ph), 7.17 (dt, 6H, Ph), 7.24 (d, 3H, Ph), 7.30-7.27 (m, 4H, Ph), 7.37 (t, 14H, Ph), 7.55-7.42 (m, 12H, Ph), 7.72-7.60 (m, 1H, Ph), ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 170.13 (s, $\text{N}\underline{\text{C}}\text{N}$), 149.80 (d, $J = 11.0$ Hz), 136.85 (s), 134.62 (s), 134.42 (s), 132.98 (d, $J = 15.3$ Hz), 131.85 (d, $J = 4.8$ Hz), 130.95 (s), 129.56 (s), 128.30 (s), 128.01 (s), 127.29 (d, $J = 18.5$ Hz), 126.86 (s), 124.27 (s), 122.47 (d, $J = 2.7$ Hz), 53.95 (s, $\underline{\text{C}}(\text{CH}_3)_3$), 52.77 (s, $\underline{\text{C}}(\text{CH}_3)_3$), 30.96 (s, $\text{C}(\underline{\text{CH}}_3)_3$), 29.92 (s, $\text{C}(\underline{\text{CH}}_3)_3$), 20.43 (s, $\text{C}(\underline{\text{CH}}_3)_3$), 3.28 (s, $\text{Si}(\underline{\text{CH}}_3)_3$) ppm; ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3 , 161.97 MHz, 298 K): δ -7.34 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.49 MHz, 298 K): δ 8.02 ($\underline{\text{Si}}\text{Me}_3$), 4.15 (b) ppm.

2B.5.6. Synthesis of 2B.4: **2** (303 mg, 0.5mmol) and CuBr_2 (71.7 mg, 0.5 mmol) were taken

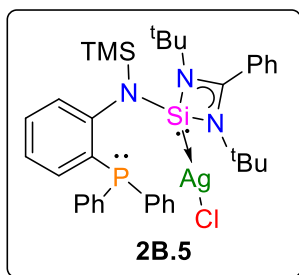


in a flask, and 40 mL of toluene was added to the reaction mixture. After overnight stirring at room temperature, the reaction mixture was filtered off, and toluene was concentrated. The yellow crystals suitable for X-ray analysis were obtained from toluene after 1 day at room temperature. Yield: 66.7 % (250 mg). M.p. 220-225 °C ^1H NMR (400

MHz, CDCl_3) δ 0.49 (s, 18H, $\text{CH}(\text{CH}_3)_3$), 1.05 (s, 36H, $\text{C}(\text{CH}_3)_3$), 3.11 (s, 4H, $\underline{\text{CH}}(\text{CH}_3)_3$), 6.73-6.63 (m, 4H, Ph), 7.23-7.14 (m, 5H, Ph), 7.31-7.24 (m, 11H, Ph), 7.34 (dd, 3H, Ph), 7.42-7.37 (m, 4H, Ph), 7.47-7.42 (m, 3H, Ph), 7.57-7.48 (m, 8H, Ph) ppm; ^{13}C NMR (101 MHz,

CDCl_3) δ 164.70 (s, $\text{N}\equiv\text{N}$), 134.66-133.67 (m), 131.35 (s), 129.61 (s), 128.01 (s), 127.24 (dd), 126.63-126.54 (m), 120.48 (s), 55.06 (s, $\text{C}(\text{CH}_3)_3$), 52.56 (s, $\text{C}(\text{CH}_3)_3$), 33.61 (s, $\text{C}(\text{CH}_3)_3$), 33.28 (s, $\text{C}(\text{CH}_3)_3$), 33.05 (s, $\text{C}(\text{CH}_3)_3$), 30.52 (d, $\text{C}(\text{CH}_3)_3$), 30.21-30.00 (m, $\text{C}(\text{CH}_3)_3$), 29.95 (s, $\text{C}(\text{CH}_3)_3$), 28.96 (s, $\text{C}(\text{CH}_3)_3$), 28.36 (s, $\text{C}(\text{CH}_3)_3$), 27.71 (s, $\text{C}(\text{CH}_3)_3$), 26.47 (d, $\text{C}(\text{CH}_3)_3$) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.97 MHz, 298 K): δ -12.64 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.49 MHz, 298 K): δ 6.45 (d, $J = 110.1$ Hz) ppm.

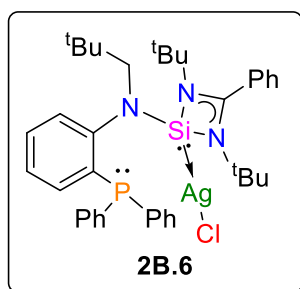
2B.5.7. Synthesis of 2B.5: **1** (304 mg, 0.5mmol) and AgCl (71.6 mg, 0.5 mmol) were taken in



a flask, and 40 mL of toluene was added to the reaction mixture. After overnight stirring at room temperature, the reaction mixture was filtered off, and toluene was concentrated. The colourless crystals suitable for X-ray analysis were obtained from toluene after 1 day at room temperature. Yield: 82.8 % (310 mg). M.p. 225-233 °C ^1H NMR (401 MHz, CDCl_3) δ 0.12 (s, 9H, (SiCH_3)₃), 1.29 (d,

18H, (CH_3)₃C), 7.18-7.05 (m, 3H, Ph), 7.25-7.22 (m, 2H), 7.32-7.27 (m, 5H), 7.35 (dd, 2H), 7.44-7.37 (m, 4H), 7.58-7.45 (m, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 169.39 (d, $\text{N}\equiv\text{N}$), 150.21 (s, Ph), 149.96 (s, Ph), 136.84 (d, Ph), 136.59-135.77 (m, Ph), 135.28 (d, Ph), 132.94 (dd, Ph), 131.28 (d, Ph), 129.95 (d, Ph), 128.88 (s, Ph), 128.14-127.70 (m, Ph), 127.70-126.98 (m, Ph), 126.14 (s, Ph), 124.89 (s, Ph), 54.14 (s, $\text{C}(\text{CH}_3)_3$), 53.79 (s, $\text{C}(\text{CH}_3)_3$), 31.64 (d, $\text{C}(\text{CH}_3)_3$), 31.17 (s, $\text{C}(\text{CH}_3)_3$), 1.55 (d, $\text{Si}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.97 MHz, 298 K): δ -20.01 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.49 MHz, 298 K): δ 13.63 (d), 13.17 (d), 10.09 (d, $\text{Si}(\text{CH}_3)_3$), 7.33 (d), 6.88 (d).

2B.5.8. Synthesis of 2B.6: **2B.2** (303 mg, 0.5mmol) and AgCl (71.6 mg, 0.5 mmol) were taken

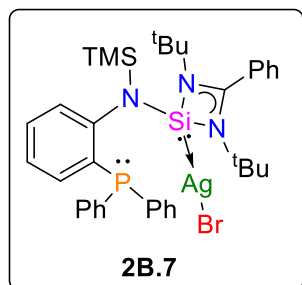


in a flask, and 40 mL of toluene was added to the reaction mixture. After overnight stirring at room temperature, the reaction mixture was filtered off, and toluene was evaporated. The colourless crystals suitable for X-ray analysis were obtained from a DCM and pentane mixture after 1 day at room temperature. Yield: 80.2 % (300 mg). M.p. 220-230 °C ^1H NMR (401 MHz, CDCl_3) ^1H NMR (401 MHz, CDCl_3)

δ 0.65 (s, 8H, $\text{CH}(\text{CH}_3)_3$), 1.26 (d, 18H, $\text{C}(\text{CH}_3)_3$), 3.26 (d, $\text{CH}(\text{CH}_3)_3$), 3.44 (dd, 1H, $\text{CH}(\text{CH}_3)_3$), 6.62 (ddd, 1H, Ph), 7.22-7.05 (m, 7H, Ph), 7.29 (s, 5H, Ph), 7.37 (dd, 4H, Ph), 7.60-7.46 (m, 5H, Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 175.82 (s, $\text{N}\equiv\text{N}$), 150.01 (d, Ph), 136.14 (d, Ph), 134.14 (d, Ph), 133.77 (dd, Ph), 131.73 (d, Ph), 131.15 (d, Ph), 130.70 (s, Ph), 130.32 (s, Ph), 129.41 (d, Ph), 129.08 (s, Ph), 128.30 (d, Ph), 128.04 (s, Ph), 127.28 (d, Ph),

126.49 (s, Ph), 125.43 (d, Ph), 60.71 (d, $\underline{\text{CHCH}_3}_3$), 54.39 (s, $\underline{\text{C(CH}_3)_3}$), 53.80 (s, $\underline{\text{C(CH}_3)_3}$), 30.86 (s, $\text{C}(\underline{\text{CH}_3})_3$), 30.49 (s, $\text{C}(\underline{\text{CH}_3})_3$), 28.32 (s, $\text{C}(\underline{\text{CH}_3})_3$); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.97 MHz, 298 K): δ -18.87 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.49 MHz, 298 K): δ 15.45 ppm.

2B.5.9. Synthesis of 2B.7: **2B.1** (304 mg, 0.5mmol) and AgBr (93.9 mg, 0.5 mmol) were taken

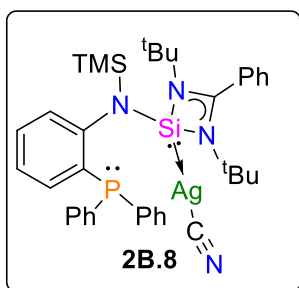


in a flask, and 40 mL of toluene was added to the reaction mixture.

After overnight stirring at room temperature, the reaction mixture was filtered off, and toluene was concentrated. The colourless crystals suitable for X-ray analysis were obtained from toluene after 1 day at room temperature. Yield: 70.5 % (280 mg). M.p. 215-220

$^{\circ}\text{C}$ ^1H NMR (401 MHz, CDCl_3) δ 0.08 (s, 9H, (SiCH_3) $_3$), 1.25 (d, 18H, ($\underline{\text{CH}_3}$) $_3\text{C}$), 7.07 (ddd, 3H, Ph), 7.23-7.18 (m, 2H, Ph), 7.30-7.23 (m, 6H, Ph), 7.41-7.30 (m, 5H, Ph), 7.45 (t, 2H, Ph), 7.53-7.48 (m, 1H, Ph) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 169.35 (s, NCN), 150.22 (s, Ph), 149.97 (s, Ph), 136.84 (d, Ph), 136.42 (s, Ph), 136.16 (d, Ph), 135.24 (d, Ph), 132.94 (t, Ph), 131.28 (d, Ph), 130.06 (s, Ph), 129.85 (s, Ph), 128.91 (s, Ph), 128.19-127.75 (m, Ph), 127.62-127.07 (m, Ph), 126.18 (s, Ph), 124.89 (s, Ph), 54.16 (s, $\underline{\text{C(CH}_3)_3}$), 53.80 (s, $\underline{\text{C(CH}_3)_3}$), 31.65 (d, $\text{C}(\underline{\text{CH}_3})_3$), 31.17 (s, $\text{C}(\underline{\text{CH}_3})_3$), 1.51 (s, $\text{Si}(\underline{\text{CH}_3})_3$) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.97 MHz, 298 K): δ -20.14 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.49 MHz, 298 K): δ 14.52 (b), 10.12 (s, $\underline{\text{SiMe}_3}$), 8.32 (b) ppm.

2B.5.10. Synthesis of 2B.8: **2B.1** (304 mg, 0.5mmol) and AgCN (66.9 mg, 0.5 mmol) were

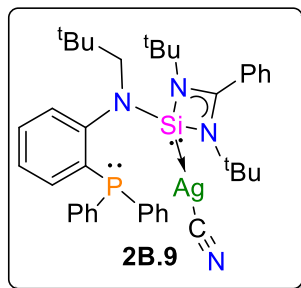


taken in a flask, and 40 mL of toluene was added to the reaction mixture. After overnight stirring at room temperature, the reaction mixture was filtered off, and toluene was concentrated. The colourless crystals suitable for X-ray analysis were obtained from toluene after 1 day at room temperature. Yield: 78.3 % (290 mg).

M.p. 225-235 $^{\circ}\text{C}$ ^1H NMR (400 MHz, CDCl_3) δ 0.12 (s, 9H, (SiCH_3) $_3$), 1.27 (d, 18H, ($\underline{\text{CH}_3}$) $_3\text{C}$), 7.12-7.04 (m, 2H, Ph), 7.18-7.12 (m, 1H, Ph), 7.22 (td, 2H, Ph), 7.29-7.24 (m, 3H, Ph), 7.32 (dt, 6H, Ph), 7.42-7.38 (m, 1H, Ph), 7.44 (d, 1H, Ph), 7.49 (dd, 2H, Ph), 7.58-7.53 (m, 1H, Ph) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 170.20 (s, NCN), 151.15 (s, Ph), 150.90 (s, Ph), 137.95 (d, Ph), 137.40 (s, Ph), 136.87 (d, Ph), 136.14 (d, Ph), 133.89 (dd, Ph), 132.31 (d, Ph), 131.10 (s, Ph), 130.89 (s, Ph), 129.92 (s, Ph), 129.32-128.71 (m, Ph), 128.71-128.03 (m, Ph), 127.15 (s, Ph), 125.88 (s, Ph), 55.07 (s, $\underline{\text{C(CH}_3)_3}$), 54.68 (s, $\underline{\text{C(CH}_3)_3}$), 32.68 (d, $\text{C}(\underline{\text{CH}_3})_3$), 32.19 (s, $\text{C}(\underline{\text{CH}_3})_3$), 2.48 (d, $\text{Si}(\underline{\text{CH}_3})_3$) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.97

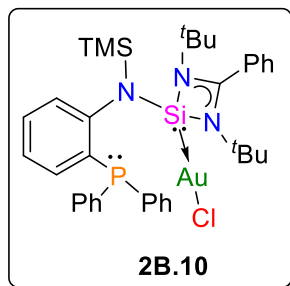
MHz, 298 K): δ -19.72 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.49 MHz, 298 K): δ 15.14 (b), 10.07 (s, SiMe_3), 8.32 (b) ppm.

2B.5.11. Synthesis of 2B.9: **2B.2** (303 mg, 0.5mmol) and AgCN (66.9 mg, 0.5 mmol) were

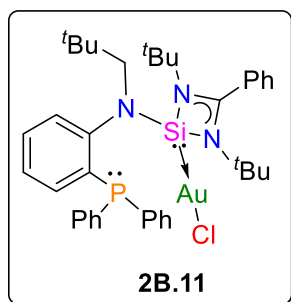


taken in a flask, and 40 mL of toluene was added to the reaction mixture. After overnight stirring at room temperature, the reaction mixture was filtered off, and toluene was evaporated. The colourless crystals suitable for X-ray analysis were obtained from a DCM and pentane mixture after 1 day at room temperature. Yield: 67.5 % (250 mg). M.p. 222-238 °C ^1H NMR (400 MHz, CDCl_3) δ 0.58 (s, 9H, $(\text{CHCH}_3)_3$), 1.17 (d, 18H, $(\text{CH}_3)_3\text{C}$), 3.22 (s, 2H, $(\text{CHCH}_3)_3$), 7.07-6.95 (m, 2H, Ph), 7.23 (dt, 12H, Ph), 7.33 (t, 2H, Ph), 7.52-7.39 (m, 3H, Ph) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 171.32 (s, NCN), 152.11 (s, Ph), 151.89 (s, Ph), 136.77-135.84 (m, Ph), 133.02 (d, Ph), 132.31 (d, Ph), 131.94 (d, Ph), 129.94 (d, Ph), 128.89 (s, Ph), 128.38 (s, Ph), 128.01 (d, Ph), 127.86-127.01 (m, Ph), 126.79 (d, Ph), 126.50 (s, Ph), 123.89 (s, Ph), 59.28 (s, CHCH_3), 53.37 (s, $\text{C}(\text{CH}_3)_3$), 53.11 (s, $\text{C}(\text{CH}_3)_3$), 52.44 (s, $\text{C}(\text{CH}_3)_3$), 32.92 (s, $\text{C}(\text{CH}_3)_3$), 31.29 (d, $\text{C}(\text{CH}_3)_3$), 30.59 (s, $\text{C}(\text{CH}_3)_3$), 28.09 (s, $\text{C}(\text{CH}_3)_3$) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.97 MHz, 298 K): δ -18.75 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.49 MHz, 298 K): δ 17.27 (b) ppm.

2B.5.12. Synthesis of 2B.10: **2B.1** (304 mg, 0.5mmol) and AuCl.SMe_2 (147 mg, 0.5 mmol)



were taken in a flask, and 40 mL of toluene was added to the reaction mixture. After overnight stirring at room temperature, the reaction mixture was filtered off, and toluene was evaporated. The colourless crystals suitable for X-ray analysis were obtained from a DCM and pentane mixture after 1 day at room temperature. Yield: 70.9 % (320 mg). M.p. 255-265 °C ^1H NMR (400 MHz, CDCl_3) δ 7.52 (ddd, 1H, Ph), 0.02 (s, 9H, $(\text{SiCH}_3)_3$), 1.29 (d, 18H, $(\text{CH}_3)_3\text{C}$), 7.09 (d, 2H, Ph), 7.05 (dd, 1H, Ph), 7.26-7.19 (m, 6H, Ph), 7.32-7.27 (m, 3H, Ph), 7.37-7.32 (m, 2H, Ph), 7.41 (ddd, 2H, Ph), 7.49-7.44 (m, 2H, Ph), 7.52 (ddd, 1H, Ph); ^{13}C NMR (101 MHz, CDCl_3) δ 174.00 (s, NCN), 150.94 (s, Ph), 150.68 (s, Ph), 138.14-137.29 (m, Ph), 136.88 (d, Ph), 134.50 (s, Ph), 134.30 (s, Ph), 133.77 (d, Ph), 132.02 (d, Ph), 131.06 (s, Ph), 130.59 (s, Ph), 129.74 (s, Ph), 128.68-128.11 (m, Ph), 127.93 (s, Ph), 127.35 (s, Ph), 125.90 (s, Ph), 55.44 (s, $\text{C}(\text{CH}_3)_3$), 55.02 (s, $\text{C}(\text{CH}_3)_3$), 53.44 (s, $\text{C}(\text{CH}_3)_3$), 32.52 (d, $\text{C}(\text{CH}_3)_3$), 32.01 (s, $\text{C}(\text{CH}_3)_3$), 2.50 (d, $\text{Si}(\text{CH}_3)_3$) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.97 MHz, 298 K): δ -19.63 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.49 MHz, 298 K): δ 11.95 (d, $J = 4.5$ Hz), 10.09 (s, SiMe_3) ppm.

2B.5.13. Synthesis of 2B.11: **2B.2** (303 mg, 0.5mmol) and AuCl.SMe₂ (147 mg, 0.5 mmol)

was taken in a flask, and 40 ml of toluene was added to the reaction mixture. After overnight stirring at room temperature, the reaction mixture was filtered off, and toluene was evaporated. The colourless crystals suitable for X-ray analysis were obtained from a DCM and pentane mixture after 1 day at room temperature. Yield: 66.6 % (300 mg). M.p. 260-272 °C ¹H NMR (401 MHz, CDCl₃) δ 0.58 (s, 9H, (CH₃)₃), 1.25 (d, 18H, (CH₃)₃C), 3.21 (d, 1H, CHCH₃), 3.51 (dd, 1H, CHCH₃), 7.09-7.01 (m, 2H, Ph), 7.22 (d, 3H, Ph), 7.30 (ddd, 11H, Ph), 7.55-7.42 (m, 3H, Ph) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 174.52 (s, N₂CN), 151.59 (s, Ph), 151.36 (s, Ph), 136.91 (d, Ph) 136.65 (d, Ph), 136.10 (d, Ph), 133.48 (s, Ph), 133.28 (s, Ph), 132.29 (d, Ph), 130.10 (s, Ph), 129.44 (s, Ph), 128.71-128.03 (m, Ph), 128.03-127.05 (m, Ph), 126.88 (s, Ph), 126.53 (s, Ph), 124.57 (s, Ph), 61.30 (d, CHCH₃), 53.67 (d, C(CH₃)₃), 52.43 (s, C(CH₃)₃), 32.92 (s, C(CH₃)₃), 31.04 (d, C(CH₃)₃), 30.59 (s, C(CH₃)₃), 27.97 (s, C(CH₃)₃) ppm; ³¹P {¹H} NMR (CDCl₃, 161.97 MHz, 298 K): δ -17.52 ppm (s); ²⁹Si {¹H} NMR (CDCl₃, 79.49 MHz, 298 K): δ 15.78 (d, J = 3.9 Hz) ppm.

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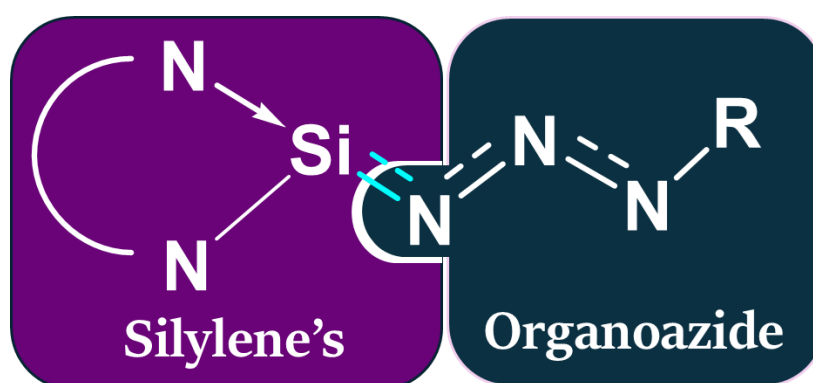
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Chapter 3: Multifaceted Reactivity of Organoazides with Silylenes and Disilenes



Adapted from: R. Akhtar, R. Panday, S. Khan* Multifaceted Reactivity of Organoazides with Silylenes and Disilenes (*Manuscript under preparation*)

3.1 Objective of the work

In this work, we systematically investigated the reactivity of recently reported Si(II) frameworks-including phosphine-based hybrid silylene's [Si{N(SiMe₃)C₆H₄(PPh₂)}{PhC(N^tBu)₂}] (**3.L1**) and [(PhC(N^tBu)₂SiN(PPh₂)(2,6-ⁱPr₂-C₆H₃))] (**3.L2**), a bis(trimethylsilyl)pyridine-2,6-diamide-based bis-silylene (**3.L3**), a carbazole-substituted silylene [PhC(N^tBu)₂Si(Cbz)] (**3.L4**), and a disilene [(TMS)₂N(η¹-Me₅C₅)Si=Si(η¹-Me₅C₅)-N(TMS)₂] (**3.L5**), toward organoazides such as trimethylsilyl and adamantyl azides (**3.1-3.8**). The results revealed strikingly different reactivity outcomes, ranging from stable silamine (**3.1, 3.2, 3.4-3.7**) to formation of azide-derived products (**3.3, 3.8**), depending on their ligand environment. These findings underscore the decisive role of ligand architecture in tuning Si(II) reactivity and provide new insights into the strategies for accessing stable silicon-nitrogen multiple bonds. Compounds **3.1-3.8** are stable under an inert atmosphere and were characterised by single-crystal X-ray diffraction studies, multinuclear magnetic resonance spectroscopy (¹H, ¹³C, ³¹P and ²⁹Si) and high-resolution mass spectrometry techniques.

3.2 Introduction

The pursuit of stable silicon compounds featuring multiple bonds has remained a central and intriguing theme in silicon chemistry for several decades. A major breakthrough in this field was the development of isolable silylenes, which opened up direct synthetic access to a variety of silicon-heteroatom multiple bonds (Si=X; X = O, P, S, Se, Te, N).¹⁻¹⁶ Among these, *silaimines* (R₂Si=NR', where R and R' are typically alkyl or aryl substituents) represent a particularly important subclass in which the pronounced polarity of the Si^{δ+}-N^{δ-} bond (due to the poor 3p-2p π-overlap) leads to challenges in synthesis and reactivity studies.¹⁷⁻²² Interest in this area was sparked in 1985 when Wiberg and Klingebiel independently reported the first stable silamine by thermal salt elimination, which laid the foundation for subsequent advances in the field.²³⁻²⁴ The silicon(II) species with organic azides represents a straightforward synthetic strategy for the development of silamine, azide-derived products and heterocycles.²⁵ The representative reactivity patterns of Si(II) compounds with azides are illustrated as follows (Figure 3.1).

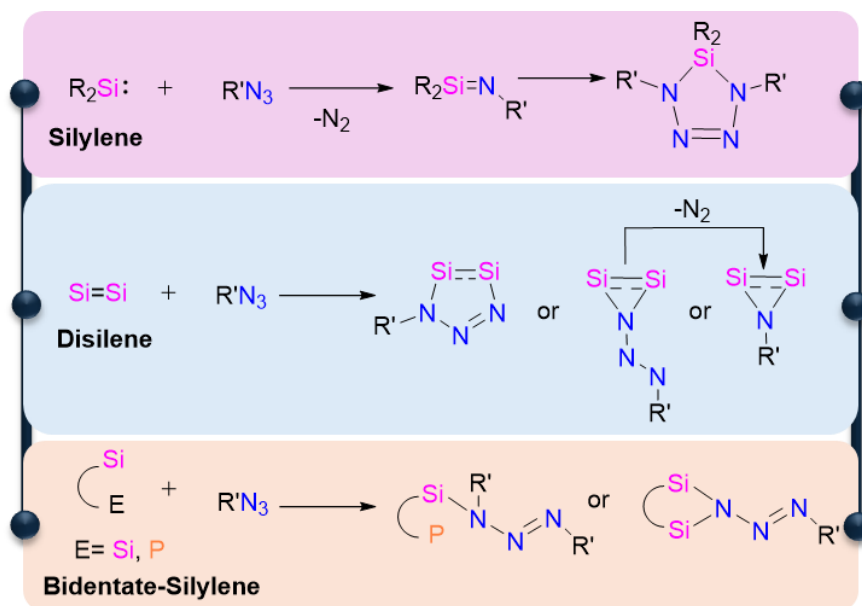


Figure 3.1. Representative reactivities of Si(II) compounds with organoazides

Since then, a wide variety of stable silaimines have been synthesised, featuring either three- or four-coordinate silicon centres and diverse substituents on silicon or nitrogen, including guanidines, amidines, halides, amides, silyls, siloxides, and deprotonated β -diketiminates.^{16, 19, 25-50} Chart 3.1 summarises the reported Si(II) species (silylene, bissilylene, and disilene) that have been explored with trimethylsilyl and adamantyl azides.^{16, 19, 25-50} To place our study in context, we highlight this literature as a basis for examining the reactivity of Si(II) toward these respective organic azides. The formation and isolation of silaimines are strongly governed by steric factors. Bulky substituents at silicon or nitrogen provide sufficient kinetic protection to stabilise the Si=N functionality, whereas in their absence, the initially generated silaimine tends to be highly transient and undergoes further reaction with organoazides, yielding azidosilanes or silatetrazolines.²⁵

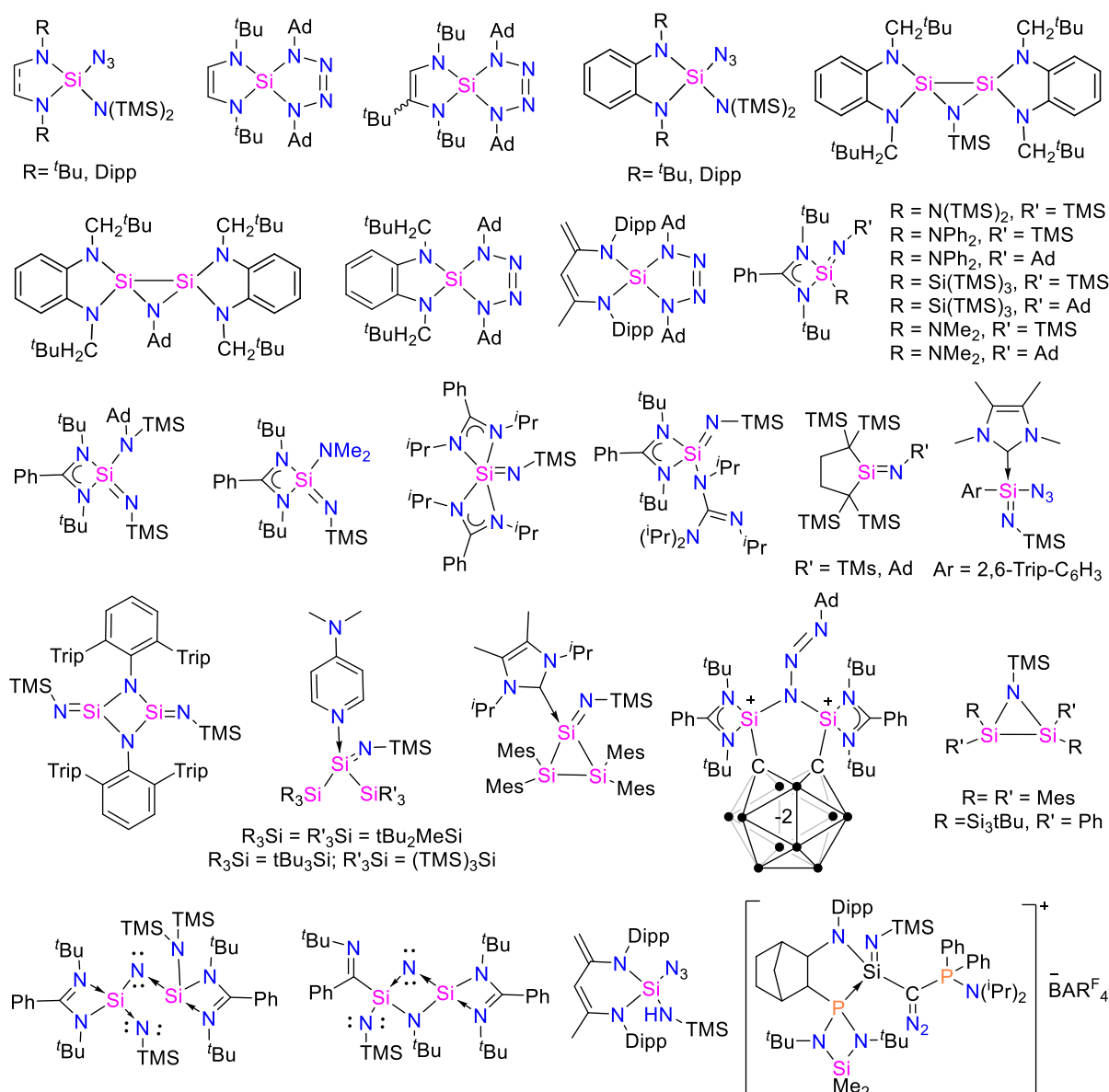
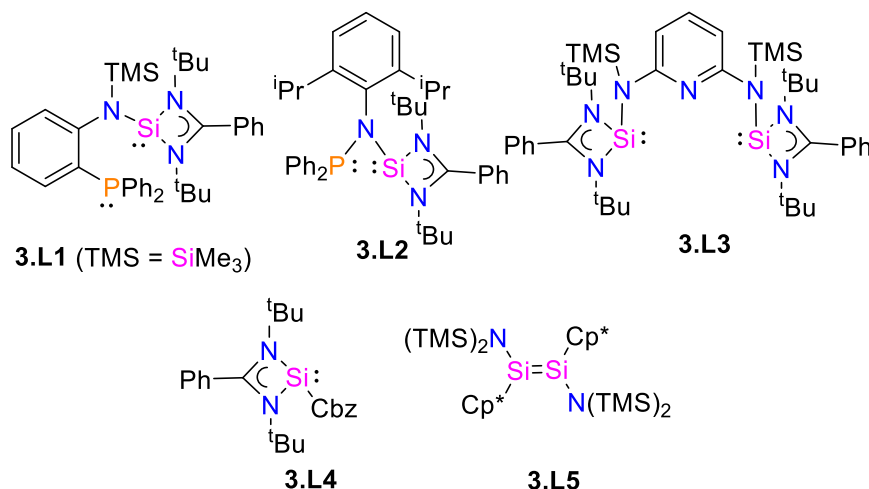


Chart 3.1. Reported examples of silylene reactivity with trimethylsilyl and adamantyl azide.

In this work, we have examined the reactivity of a range of previously reported silylene systems by our group, including a phosphine-based hybrid silylene $\text{Si}\{\text{N}(\text{SiMe}_3)\text{C}_6\text{H}_4(\text{PPh}_2)\}_2\{\text{PhC}(\text{N}^t\text{Bu})_2\}$ (**3.L1**) and $(\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN}(\text{PPh}_2)(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3))$ (**3.L2**), a bis(trimethylsilyl)pyridine-2,6-diamide-based bis-silylene (**3.L3**), a carbazole-substituted silylene $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(\text{Cbz})$ (**3.L4**), and a disilylene $[(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si}=\text{Si}(\eta^1\text{-Me}_5\text{C}_5)\text{-N}(\text{TMS})_2]$ (**3.L5**) toward trimethylsilyl and adamantyl azides (Scheme 1).⁵¹⁻⁵⁶ The outcomes reveal strikingly diverse reactivity patterns, wherein the nature of the ligand framework plays a decisive role in directing the reaction pathway. While certain ligand environments favoured the stabilisation and isolation of silaimines, others predominantly led to the formation of azidosilane derivatives. These findings highlight the crucial influence of

steric and electronic effects in governing the accessibility and stability of silaimines. Our results are reported here.

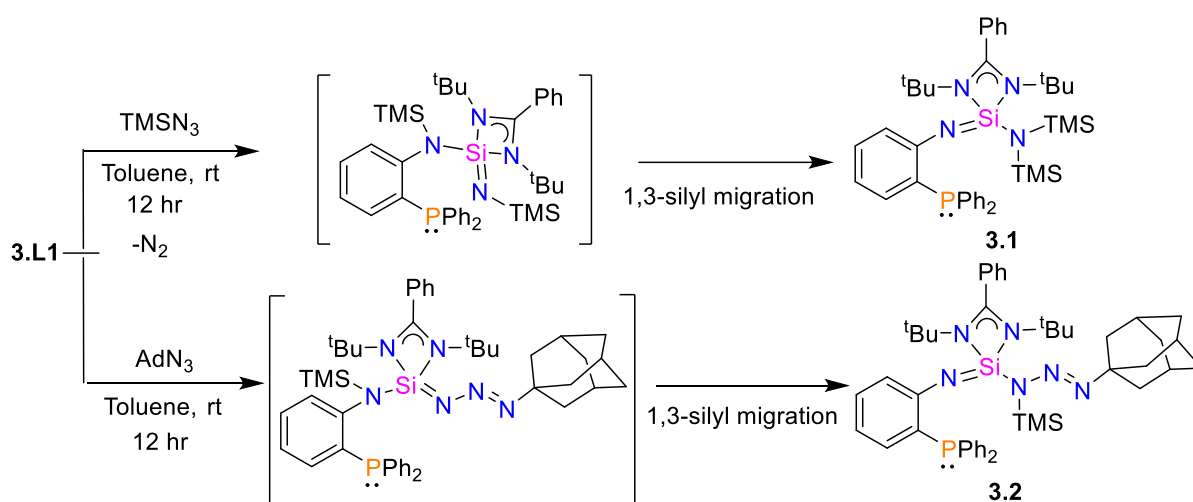


Scheme 3.1. Ligands utilised in this work toward trimethylsilyl and adamantyl azide

3.3 Results and Discussion.

The reaction of $\text{Si}\{\text{N}(\text{SiMe}_3)\text{C}_6\text{H}_4(\text{PPh}_2)\}\{\text{PhC}(\text{N}^t\text{Bu})_2\}$ (**3.L1**) with trimethylsilyl azide (Me_3SiN_3) and adamantly azide (AdN_3) in toluene at room temperature yielded the four-coordinated silaimines **3.1** and **3.2** in 86 % and 76 % yield as a pale yellow crystalline solid, respectively (Scheme 3.2). An intriguing observation was the unexpected migration of the SiMe_3 unit. The molecular structure discloses the migration. However, we propose that an unstable silaimine intermediate with a terminal SiMe_3 group initially forms through dinitrogen elimination in complex **3.1**. This intermediate then undergoes a 1,3-migration of one SiMe_3 group from one nitrogen atom to the other. In complex **3.2**, an unstable silaimine intermediate with a terminal adamantly group initially forms without the elimination of dinitrogen, which is further followed by the 1,3-migration of one SiMe_3 group. This type of nitrogen chain is only observed in the ortho carborane-based bis(silylene).⁵⁰ The proposed mechanism was illustrated in Scheme 3.2. Roesky and coworkers also observed a similar 1,3 silyl-migration when $\text{N}(\text{TMS})_2$ substituted amidante silylene was treated with AdN_3 .⁴³ The crystals of **3.1** and **3.2** suitable for single-crystal X-ray analysis were obtained after storing their concentrated solutions for 12 h. The $^{31}\text{P}\{\text{^1H}\}$ NMR spectra of **3.1** and **3.2** display a single peak at δ -14.33 and -13.26 ppm, respectively, which is downfield shifted compared to **3.L1** (δ -22.75).⁵¹ The $^{29}\text{Si}\{\text{^1H}\}$ NMR spectra of **1** display two sharp singlets for the $-\text{SiMe}_3$ group at δ 6.70 ppm (SiMe_3), 0.42 ppm (SiMe_3), and a upfield shifted sharp singlet for silaimine ($\text{Si}=\text{N}$) at -66.61 ppm was observed. The $^{29}\text{Si}\{\text{^1H}\}$ NMR spectra of **3.2** appeared at δ 4.99 ppm for $-\text{SiMe}_3$ group

and -73.43 ppm for silaimine ($\text{Si}=\text{N}$). The molecular structures of **3.1** and **3.2** were established by single-crystal X-ray diffraction studies. **3.1** and **3.2** crystallise in the triclinic *P*-1 space group and show that the Si(II) atom is connected to the four N atoms, whereas phosphorus remains uncoordinated (Figure 3.2). Due to the poor-quality crystal data, we refrain from discussing the bonding parameter of **3.2**. The Si1-N4 bond distance and N3-Si1-N2 bite angle of **3.1** is 1.625(5) Å and 71.5(3)°, respectively. The silaimine bond distance is slightly elongated, and the bite angle is consistent with the $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NSiMe}_3)\text{Si}(\text{SiMe}_3)_3$ [1.609(8) Å, N-Si-N 70.1(3)°] and $[\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NSiMe}_3)\text{N}(\text{SiMe}_3)_2]$ [1.5936(14) Å, N2-Si1-N 71.25(6)°].^{29, 43}



Scheme 3.2: Synthesis of complexes **3.1** and **3.2**

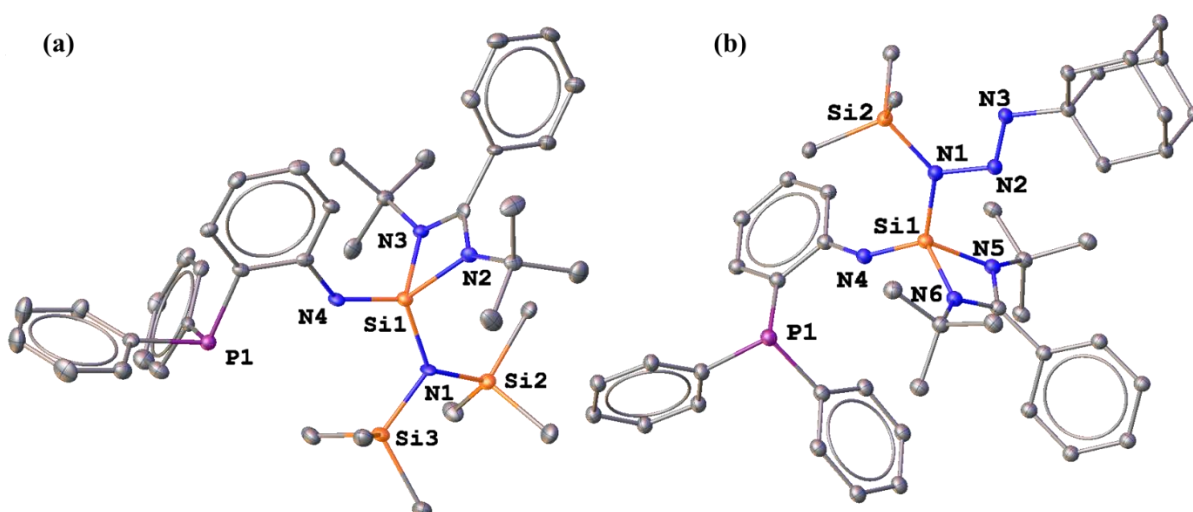
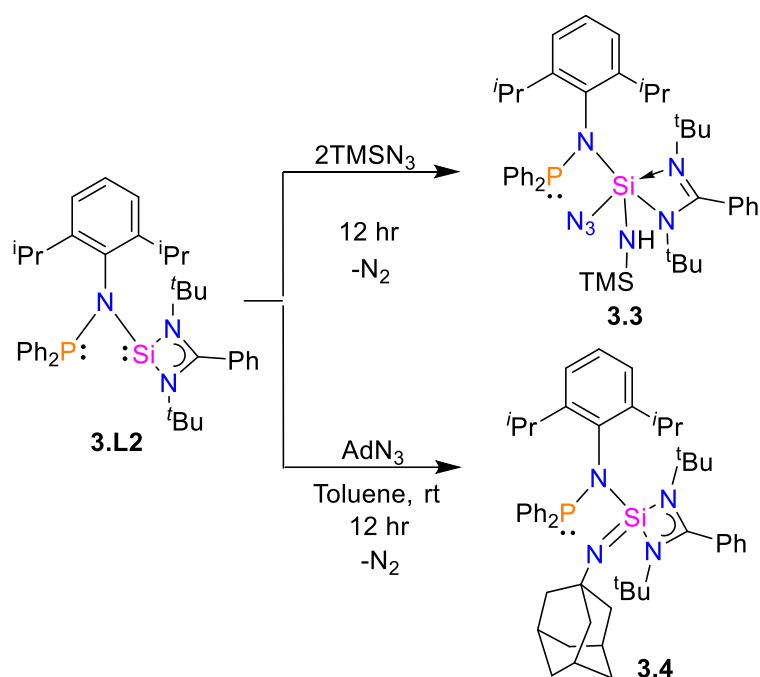


Figure 3.2. (a) Molecular structure of **3.1**. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): N4-Si1 1.625(5), Si1-N1 1.720(7), N1-Si2 1.756(5), N1-Si3 1.795(7), N2-Si1

1.851(6), N3-Si1 1.842(8); N4-Si1-N1 114.1(3), Si3-N1-Si2 118.2(3), N3-Si1-N2 71.5(3). (b) Molecular structure of **3.2**. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms are omitted for clarity.

Further, to avoid the 1,3-silyl migration, we used a dipp-substituted hybrid phosphine silylene (**3.L2**). The phosphine-based hybrid silylene ($\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN}(\text{PPh}_2)(2,6\text{-}i\text{Pr}_2\text{-C}_6\text{H}_3)$) (**3.L2**) was treated with trimethylsilyl azide (Me_3SiN_3) and adamantly azide (AdN_3) in toluene at room temperature, which yielded the complexes **3.3** and **3.4** in 66 % and 88 % yield as colourless crystalline solids, respectively (Scheme 3.3).⁵² The reactivity of **3.L2** with trimethylsilyl azide (**3.3**) leads to an azide bond and NH(TMS) on the silicon centre. The origin of the proton attached to nitrogen remains ambiguous, and the absence of any isolable side products suggests that it most likely originates from the solvent (toluene). Compound **3.3** displays silicon is five-coordinated and crystallises in the monoclinic $P21/n$ space group. The ^{29}Si NMR spectrum of this complex displays two resonances, one at δ -68.51 ppm (d, $J = 41.3$ Hz) for silylene-Si and the other at δ 2.27 ppm (s) for the SiMe_3 group. The ^{31}P NMR spectrum exhibits a signal at δ 51.82 ppm, which closely matches that of **3.L2** (δ 54.04 ppm), indicating the uncoordinated phosphine. The ^1H NMR shows the peaks at δ 1.11 (d) and 1.44 (s) for ^tBu 18 H, whereas NH appears at δ 1.23(s). The NH proton of compound **3.3** is downfield shifted compared to $\text{CH}(\text{C}=\text{CH}_2)\text{CMe}(\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2)\text{Si}=\text{NHTMS}$ (δ 0.22 ppm), which contains a similar NH(TMS) adjacent to the silicon centre.³⁸ There is hydrogen bonding noticed between the ^tBu hydrogen of the amidinate ring and the azide nitrogen on the silicon centre. The average and $\text{H}\cdots\text{N}$ and $\text{C}(\text{H})\cdots\text{N}$ distances are 2.217 and 2.985(6) Å, respectively, with an average CHN angle of 134.3° , which leads to the splitting in the ^1H NMR. The range of $\text{C}(\text{H})\cdots\text{N}$ bond length suited well with the reported $\text{H}\cdots\text{N}$ and $\text{C}(\text{H})\cdots\text{N}$ bond 2.21-2.15 and 3.23-3.31 Å, with an average CHN angle of $167\text{-}180^\circ$ (Figure 3.3).⁵⁷⁻⁵⁸ Compound **3.4** features a silaimine moiety with an uncoordinated phosphorus atom. The ^{29}Si NMR spectrum shows a resonance at δ -57.06 ppm (d, $J = 10.5$ Hz) attributable to the $\text{Si}=\text{N}$ unit, while the ^{31}P NMR spectrum exhibits a signal at δ 51.82 ppm. In the ^1H NMR spectrum, the *tert*-butyl protons (18H) resonate at δ 1.46 ppm, and the adamantyl protons (15H) appear within the range δ 1.12-2.21 ppm. The bond distance for Si1-N1 is 1.587(2) Å, and the bite angle for amidinate is $70.86(8)^\circ$ for N3-Si1-N4 (Figure 3.3). The bond length of $\text{Si}=\text{N}$ (1.594(5) Å) is similar to the previously reported $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NAd})\text{Si}(\text{SiMe}_3)_3$.²⁹



Scheme 3.3: Synthesis of complexes **3.3** and **3.4**

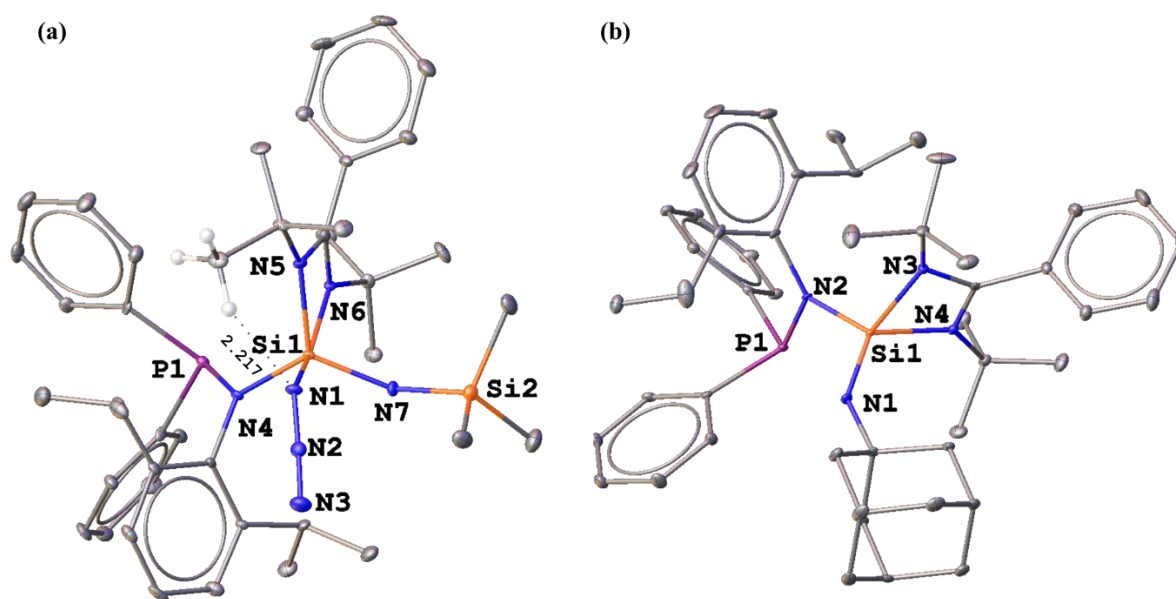
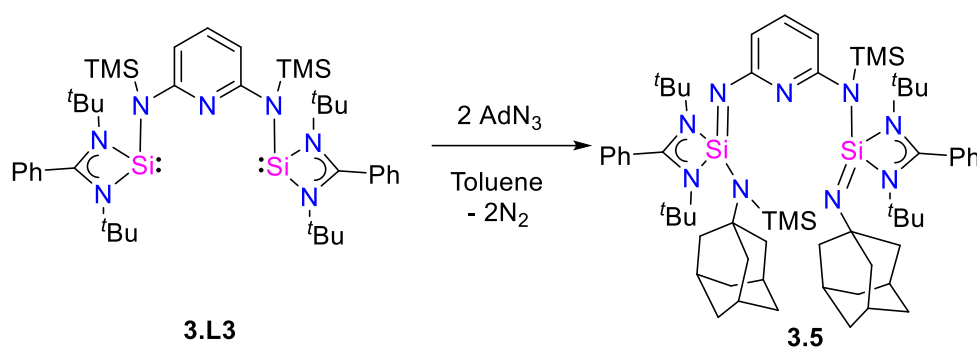


Figure 3.3. Molecular structure of **3.3** and **3.4**. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): (a) For **3.3**, H11B-N1 2.217, N1-N2 1.208(6), N2-N3 1.141(6), N5-Si1 1.835(4), N6-Si1 2.051(4), N7-Si1 1.735(5), N1-Si1 1.816(5), N4-Si1 1.773(4); N1-N2-N3 174.9(6), N4-Si1-N7 120.1(2), N1-Si1-N5 93.9(2). (b) For **3.4**, Si1-N1 1.587(2), N1-C16 1.445(3), N3-Si1 1.856(2), N4-Si1 1.868(2), N2-Si1 1.750(2); Si1-N1-C16 140.7(2), N2-Si1-N1 113.3(1), N3-Si1-N4 70.86(8).

After investigating phosphine-hybrid silylenes, we explored bis-silylenes, where a handful of examples on the reactivity of bis-silylene with azides are reported.⁵³ The previously synthesised bis(trimethylsilyl)pyridine-2,6-diamide-based bis-silylene by our group was treated with adamantyl azide (1:2) in toluene at room temperature, which yielded the complexes **3.5** in 74 % yield as colourless crystalline solids (Scheme 3.4). Here, one silicon centre underwent the 1,3-silyl migration, whereas the other remained unaltered. The ²⁹Si NMR spectrum of **3.5** appears at δ 5.38 (s, SiMe₃), 2.21 (s, SiMe₃), -73.63 (s, Si=N), -87.76 (s, Si=N) ppm. The bond length between Si1-N2 is 1.567(3) Å, and for N6-Si2 it is 1.603(3) Å (Figure 3.4). The reactivity of the *ortho*-carborane-based bis(silylene) with azides differs, as both silylene centres participate in stabilising the adamantyl azide, without elimination of nitrogen, and further stabilise the nitrene.⁵⁰



Scheme 3.4: Synthesis of complexes **3.5**

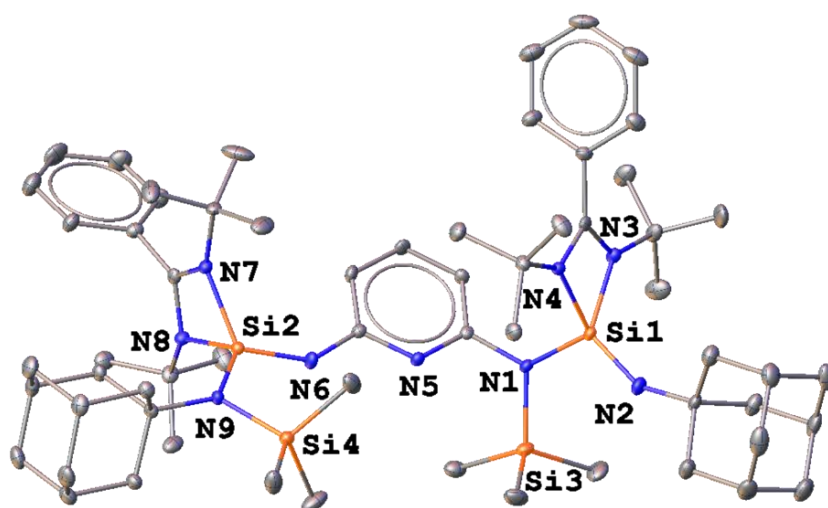
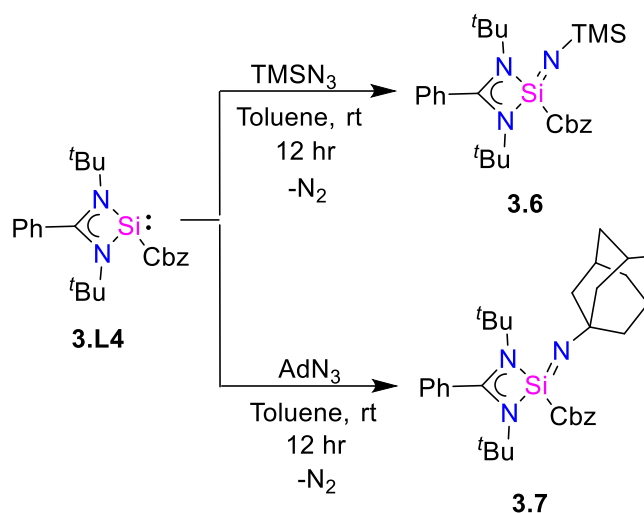


Figure 3.4. Molecular structure of **3.5**. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms and solvent are omitted for clarity. Selected bond distances (Å) and angles (deg): N6-Si2 1.603(3), Si2-N9 1.704(2), N9-Si4 1.799(3), N1-Si3 1.761(3), N1-Si1 1.724(3), Si1-N2 1.567(3), Si1-N3 1.848(2), Si1-N4 1.838(3), N8-Si2 1.827(3), N7-

Si2 1.828(3); N6-Si2-N9 108.6(1), N2-Si1-N1 111.8(1), N1-C29-N5 115.8(3), N5-C33-N6 116.8(3), C4-N2-Si1 148.5(3), Si2-N9-C37 126.6(2).

After examining chelating ligands, we next turned our attention to the monodentate carbazole-substituted silylene, whose reactivity pattern resembles that of the previously reported substituted amidinate silylene.⁵⁴ Compound $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NSiMe}_3)\text{Cbz}$ (**3.6**) and $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NAd})\text{Cbz}$ (**3.7**) were prepared by treating **3.L4** with trimethylsilyl and adamantly azide, respectively (Scheme 3.5). All the reactions take place with the release of nitrogen gas. Compounds **3.6** and **3.7** exhibit remarkable stability, remaining intact in both the solid state and in solution for extended periods under an inert atmosphere. The ^{29}Si NMR spectrum of **3.6** exhibits two resonances, at δ -74.39 (LSi) and -18.85 ($\text{Si}=\text{NSiMe}_3$) ppm. The ^{29}Si NMR spectrum of **3.6** matches well with previously reported complexes $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NSiMe}_3)\text{NPPh}_2$ (δ -71.65 (LSi) and -20.80 ($\text{Si}=\text{NSiMe}_3$) ppm), $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NSiMe}_3)\text{NMe}_2$ (δ -59.15 (LSi), -21.18 ($\text{Si}=\text{NSiMe}_3$) ppm).²⁸ The ^tBu protons for compound **3.6** in its ^1H NMR spectrum appear as a singlet (δ 0.92 ppm), whereas the SiMe_3 protons resonate at δ 0.73 (doublet) ppm. Like **3.6**, compound **3.7** displays silamine peak in ^{29}Si NMR spectrum at δ -67.48 ppm, whereas the ^tBu group resonates at δ 1.00 ppm in its ^1H NMR spectrum. The ^{29}Si NMR spectrum of reported compounds $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NAd})\text{NPPh}_2$ and $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NAd})\text{NMe}_2$ resonate at δ -66.60 and -67.19 ppm.²⁸ Compound **3.6** crystallised in the monoclinic space group $P2_1/n$, and compound **7** crystallises in the triclinic $P-1$ space group. The central silicon atom in compounds **3.6** and **3.7** is tetracoordinate and adopts a tetrahedral geometry (Figure 3.5). Its coordination sphere consists of four nitrogen donors: two from the amidinato ligand, one from the former azide unit, and one from the amide group. The bond length between the silicon and nitrogen atom of the amide group in compound **3.6** is 1.824(2) Å. The Si1-N3 bond length for **3.6** is 1.579(1) Å, which is comparable to the $\text{Si}=\text{N}$ value reported in the literature [$\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NSiMe}_3)\text{NPPh}_2$ 1.5828(15) Å]. The bite angle (N4-Si1-N3) at the silicon atom with the backbone ligand is $71.70(6)^\circ$, similar to $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NSiMe}_3)\text{NPPh}_2$ ($71.88(5)^\circ$).²⁸ The bond length between the silicon and nitrogen atom of the amide group in compound **3.7** is 1.824(2) Å. The Si1-N3 bond length for **3.7** is 1.572(2) Å, which is comparable to the $\text{Si}=\text{N}$ value reported in the literature [$\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NAd})\text{NPPh}_2$ and $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NAd})\text{NMe}_2$, 1.5728(12) and 1.584(5) Å]. The bite angle (N4-Si1-N3) at the silicon atom with the backbone ligand is $71.56(7)^\circ$, similar to $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NAd})\text{NPPh}_2$ ($71.10(5)^\circ$) and $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(=\text{NAd})\text{NMe}_2$ ($70.3(2)^\circ$).²⁸



Scheme 3.5: Synthesis of complexes **3.6** and **3.7**

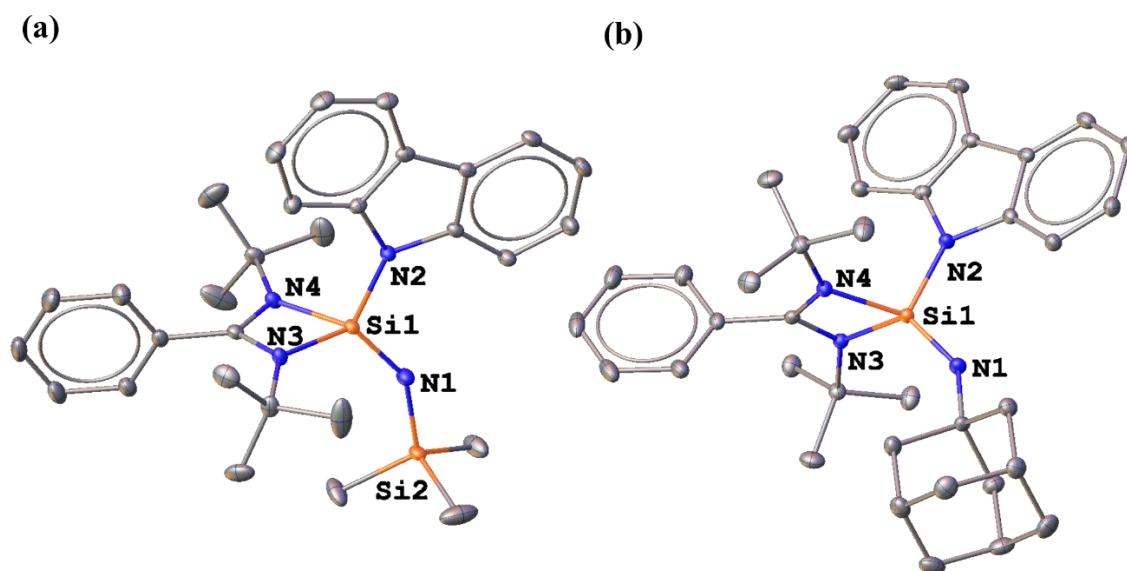
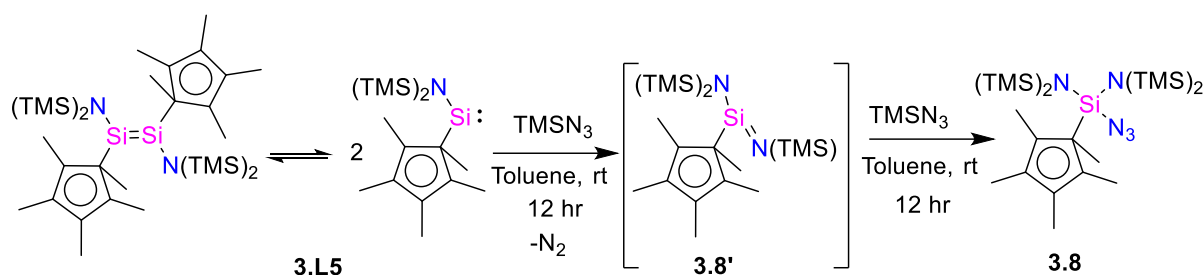


Figure 3.5. Molecular structure of **3.6** and **3.7**. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms and solvent are omitted for clarity. Selected bond distances (Å) and angles (deg): (a) For **3.6**, Si1-N1 1.579(1), N1-Si2 1.669(2), N3-Si1 1.824(2), N4-Si1 1.824(1), N2-Si1 1.759(1); Si1-N1-Si2 145.9(1), N1-Si1-N2 114.39(8), N1-Si1-N3 122.98(8), N4-Si1-N3 71.70(6). (b) For **3.7**, Si1-N1 1.572(2), N1-C16 1.438(3), Si1-N2 1.765(2), Si1-N3 1.833(2), Si1-N4 1.829(1); Si1-N1-C16 143.5(1), N1-Si1-N2 112.76(8), N1-Si1-N3 124.45(8), N4-Si1-N3 71.56(7).

The reactivity of disilenes with azides remains less explored. To gain further insights, Jutzi's disilene was employed to investigate reactivity toward azides.⁵⁵ Reactions of $[(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si}=\text{Si}(\eta^1\text{-Me}_5\text{C}_5)\text{-N}(\text{TMS})_2]$ (**3.L5**) were attempted with both trimethylsilyl and adamantyl azide; however, only the trimethylsilyl azide product could be isolated (Scheme 3.6).

Treatment with trimethylsilyl azide furnished the azidosilane **3.8**. The formation of **3.8** can be rationalised through the initial formation of a silanimine intermediate, which subsequently undergoes addition of $\text{Me}_3\text{Si-N}_3$.



Scheme 3.6: Synthesis of complexes **3.8**

The exclusive isolation of azidosilane rather than the expected cycloaddition product suggests that this disilene exhibits silylene-like behaviour in solution. Use of the less hindered trimethylsilyl azide and silylene did not result in the formation of the analogous silaimine **3.8'**. Instead, the silaimine is trapped by the addition of a second equivalent of azide, resulting in the formation of **3.8**. No formation of **3.8'** could be detected by NMR (^1H , ^{13}C , ^{29}Si) of the crude reaction mixture. The ^1H NMR spectrum of **3.8** displays a sharp singlet at δ 0.36 ppm, which corresponds to 36 TMS protons, while singlets at δ 2.02, 1.69, and 1.29 ppm correspond to 15 Cp^* methyl protons. The silicon NMR show two peaks, one at -30.04 for $\text{SiN}_3(\text{N}(\text{SiMe}_3)_2)_2\text{Cp}^*$ and the other at 3.64 for SiMe_3 . Single crystals of **3.8** suitable for the X-ray diffraction studies were obtained in toluene at room temperature. **3.8** crystallises in the triclinic space group $P-1$. The molecular structure of **3.8** reveals that the central silicon atom is four-coordinated, surrounded by three nitrogen and one carbon atom, resulting in a distorted tetrahedral geometry. The bond distance between the silicon and adjacent nitrogen is 1.766(1) Å for Si1-N1, 1.738(1) Å for Si1-N4, and 1.741(1) Å for Si1-N5. The bond length of silicon and adjacent nitrogen of molecule **3.8** matches well with the reported $(^t\text{BuNCH=CHN}^t\text{Bu})\text{Si}(\text{N}_3)\text{N}(\text{SiMe}_3)_2$ and $(^t\text{BuNCH}_2\text{CH}_2\text{N}^t\text{Bu})\text{Si}(\text{N}_3)\text{N}(\text{SiMe}_3)_2$ where the azide (N_3) and silicon bond length is 1.760(3) and 1.773(2) Å and for adjacent $\text{N}(\text{SiMe}_3)_2$ group it is 1.704(3) and 1.720(3) Å (shorter than **3.8**), respectively.^{16, 26} The Cp^* ring is bonded in η^1 fashion to the silicon atom, and the bond length between Si1-C1 is 1.931(2) Å (Figure 3.6).^{16, 26} The bond distance between the azide nitrogen is 1.210(2) Å for N1-N2 and 1.141(2) Å for N2-N3 similar to $(^t\text{BuNCH=CHN}^t\text{Bu})\text{Si}(\text{N}_3)\text{N}(\text{SiMe}_3)_2$ {1.219(5) and 1.128(5) Å} and $(^t\text{BuNCH}_2\text{CH}_2\text{N}^t\text{Bu})\text{Si}(\text{N}_3)\text{N}(\text{SiMe}_3)_2$ {1.215(4) and 1.128(4) Å}.^{16, 26}

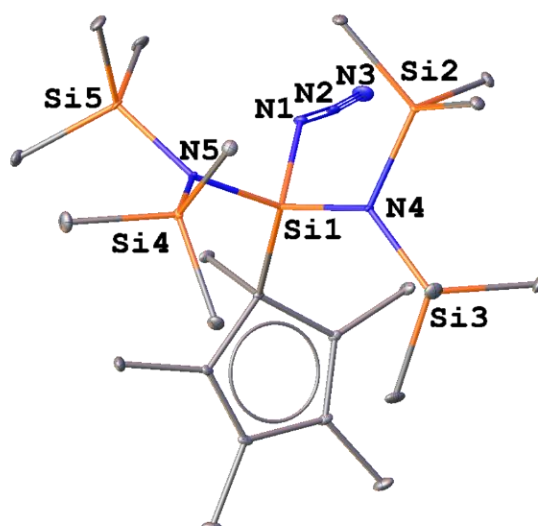
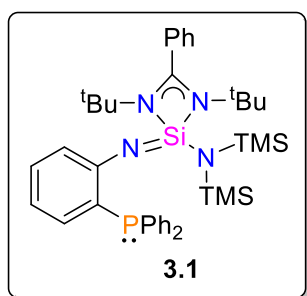


Figure 3.6. Molecular structure of **3.8**. Anisotropic displacement parameters are depicted at the 50 % probability level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si1-C1 1.931(2), N1-N2 1.210(2), N2-N3 1.141(2), Si1-N1 1.766(1), Si1-N5 1.738(1), N5-Si5 1.776(1), N5-Si4 1.777(1), Si1-N4 1.741(1), N4-Si3 1.774(1), N4-Si2 1.795(2); C1-Si1-N1 103.58(7), N5-Si1-C1 112.58(6), N1-Si1-N5 102.77(6), N4-Si1-N5 112.21(6), N4-Si1-C1 120.96(6), N4-Si1-N1 101.90(6).

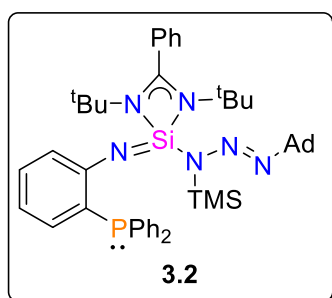
3.4 Conclusion.

We have demonstrated a systematic study of AdN_3 and TMSN_3 reaction with valuable Si(II) compounds. The unusual silaimine compounds formation from $\text{Si}\{\text{N}(\text{SiMe}_3)\text{C}_6\text{H}_4(\text{PPh}_2)\}\{\text{PhC}(\text{N}^t\text{Bu})_2\}$ (**3.L1**) and bis(trimethylsilyl)pyridine-2,6-diamide-based bis-silylene (**3.L3**) was observed while treating them with AdN_3 and TMSN_3 , which undergo the 1,3-migration of one SiMe_3 group. However, stable silaimine was synthesised by treating the $(\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN}(\text{PPh}_2)(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3))$ (**3.L2**) with adamantly azide, $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(\text{Cbz})$ (**3.L4**) with both adamantly and TMS azide, where silicon is three-coordinate silicon. The azidosilane was synthesised while treating the $(\text{PhC}(\text{N}^t\text{Bu})_2\text{SiN}(\text{PPh}_2)(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3))$ (**3.L2**) and $[(\text{TMS})_2\text{N}(\eta^1\text{-Me}_5\text{C}_5)\text{Si}=\text{Si}(\eta^1\text{-Me}_5\text{C}_5)\text{-N}(\text{TMS})_2]$ (**3.L5**), with TMS azide. Notably, compounds **3.1-3.4** represent the first examples of hybrid phosphine-silylene reactivity with organoazides. Herein reported silaimines can be further functionalised and pave the way for the isolation of various important silanes.

3.5 Synthesis of 1-8.

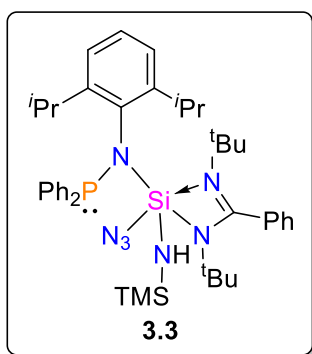
3.5.1 Synthesis of 3.1. 30 mL of toluene was added to the mixture of **3.L1** (304 mg, 0.5 mmol)

and trimethylsilyl azide (66 μ L, 1 mmol) in a 100 mL Schlenk flask, and the solution was stirred overnight at room temperature. The yellow solution was filtered and reduced under vacuum to 5 mL. Storage of the concentrated solution at room temperature afforded pale yellow block-shaped crystals of **3.1**. Yield: 86 % (300 mg). M.p. 180-190 $^{\circ}$ C. ^1H NMR (C_6D_6 , 400 MHz, 298 K, TMS): δ 0.41 (s, 9H, (SiCH_3)₃), 0.64 (s, 9H, (SiCH_3)₃), 1.12 (s, 18H, (CH_3)₃C), 6.64-6.68 (m, 1H, Ph), 6.84-6.92 (m, 4H, Ph), 7.02-7.15 (m, 6H, Ph), 7.18-7.22 (m, 3H, Ph), 7.32-7.36 (m, 1H, Ph), 7.40-7.45 (m, 1H, Ph), 7.72-7.65 (m, 4H, Ph) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100.613 MHz, C_6D_6 , 298 K) δ 174.67 (s, NCN), 159.72 (s, Ph), 159.47 (s, Ph), 141.09 (d, Ph), 134.80 (s, Ph), 133.49 (d, Ph), 129.34 (s, Ph), 128.19 (s, Ph), 126.26 (s, Ph), 125.74 (s, Ph), 122.95 (s, Ph), 113.08 (s, Ph), 53.47 (s, $\text{C}(\text{CH}_3)_3$), 31.10 (s, $\text{C}(\text{CH}_3)_3$), 29.84 (d, $\text{C}(\text{CH}_3)_3$), 4.90 (d, $\text{Si}(\text{CH}_3)_3$), 4.32 (s, $\text{Si}(\text{CH}_3)_3$) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 161.97 MHz, 298 K): δ -14.33 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 79.49 MHz, 298 K): δ 6.70 ppm (s, SiMe_3), 0.42 ppm (s, SiMe_3), -66.61 ppm (s, $\text{Si}=\text{N}$).

3.5.2 Synthesis of 3.2. 30 mL of toluene was added to the mixture of **3.L1** (304 mg, 0.5 mmol)

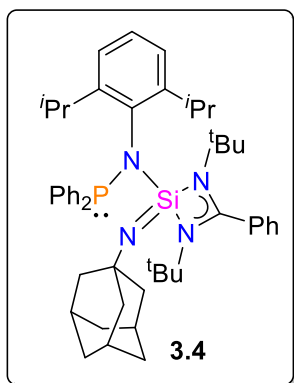
and adamantyl azide (88 mg, 0.5 mmol) in a 100 mL Schlenk flask, and the solution was stirred overnight at room temperature. The yellow solution was filtered and reduced under vacuum. The residue was treated with toluene and pentane for the crystallisation and kept at -30 $^{\circ}$ C to afford the yellow block-shaped crystals of **3.2**. Yield: 76 % (300 mg). M.p. 190-200 $^{\circ}$ C. ^1H NMR (C_6D_6 , 400 MHz, 298 K, TMS): δ 0.62 (s, 9H, (SiCH_3)₃), 1.09 (s, 18H, (CH_3)₃C), 1.22 (s, 2, Ad), 1.43 (s, 1, Ad), 1.63 (q, 8H, Ad), 1.91 (s, 5H, Ad), 2.11 (s, 2H, toluene), 6.72 (t, $J = 7.2$ Hz, 1H, Ph), 6.86-6.92 (m, 3H, Ph), 6.95-7.07 (m, 5H, Ph), 7.08-7.13 (m, 5H, Ph), 7.28-7.32 (m, 1H, Ph), 7.38-7.44 (m, 2H, Ph), 7.67 (dd, 4H, Ph) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K) δ 173.84 (s, NCN), 139.75 (s, Ph), 132.63 (d, Ph), 132.13 (s, Ph), 128.47 (s, Ph), 128.07 (s, Ph), 127.50 (s, Ph), 127.03 (s, Ph), 126.27 (s, Ph), 123.40 (s, Ph), 112.84 (d, Ph), 60.70 (s, Ad), 51.84 (s, $\text{C}(\text{CH}_3)_3$), 40.02 (s, Ad), 34.67 (d, $\text{C}(\text{CH}_3)_3$), 28.86 (d, $\text{C}(\text{CH}_3)_3$), 27.58 (d, $\text{C}(\text{CH}_3)_3$), 0.21 (d, $\text{Si}(\text{CH}_3)_3$) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 161.97 MHz, 298 K): δ -13.26 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 79.49 MHz, 298 K): δ 4.99 ppm (s, SiMe_3), -73.43 ppm (s, $\text{Si}=\text{N}$).

3.5.3 Synthesis of 3.3.



and trimethylsilyl azide (66 μL , 1 mmol) in a 100 mL Schlenk flask, and the solution was stirred overnight at room temperature. The colourless solution was filtered and reduced under vacuum to 5 mL. Storage of the concentrated solution at room temperature afforded colourless block-shaped crystals of **3.3**. Yield: 66 % (250 mg). M.p. 195-210 $^{\circ}\text{C}$. ^1H NMR (401 MHz, C_6D_6 , 298 K) δ 0.30 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.34 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.11 (d, 3H, $\text{C}(\text{CH}_3)_3$), 1.23 (s, 1H, NH), 1.44 (s, 15H, $\text{C}(\text{CH}_3)_3$), 1.47 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 2.11 (s, 2H, toluene), 3.41 (dt, 2H, $\text{CH}(\text{CH}_3)_2$), 6.78 (dd, 1H, Ph), 6.93 (dt, 3H, Ph), 7.03 (d, 8H, Ph), 7.11 (dd, 4H, Ph), 7.25-7.18 (m, 2H, Ph), 7.52-7.43 (m, 5H, Ph) ppm; ^{13}C NMR (101 MHz, C_6D_6 , 298 K) δ 178.28 (s, NCN), 147.04 (s, Ph), 139.86 (s, Ph), 138.11 (d, Ph), 134.84 (s, Ph), 134.60 (s, Ph), 131.37 (s, Ph), 130.58 (d, Ph), 129.01 (s, Ph), 128.15 (d, Ph), 125.03 (s, Ph), 124.49 (s, Ph), 123.52 (s, Ph), 54.71 (s, $\text{C}(\text{CH}_3)_3$), 31.02 (d, $\text{C}(\text{CH}_3)_3$), 28.26 (s, $\text{C}(\text{CH}_3)_3$), 27.09 (s, $\text{CH}(\text{CH}_3)_2$), 22.95 (s, $\text{CH}(\text{CH}_3)_2$), 21.34 (s, $\text{CH}(\text{CH}_3)_2$), 20.24 (s, $\text{CH}(\text{CH}_3)_2$), 4.45 (s, $\text{Si}(\text{CH}_3)_3$), 0.21 (s, $\text{Si}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 161.97 MHz, 298 K): δ 52.11 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 79.49 MHz, 298 K): δ 2.27 ppm (s, SiMe_3), -68.51 ppm (d, $J = 41.3$ Hz, $\text{Si}=\text{N}$).

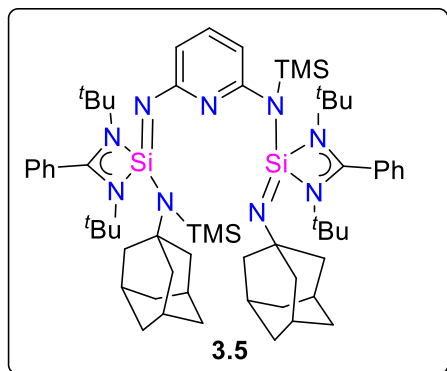
3.5.4 Synthesis of 3.4.



and adamantyl azide (88 mg, 0.5 mmol) in a 100 mL Schlenk flask, and the solution was stirred overnight at room temperature. The colourless solution was filtered and reduced under vacuum to 5 mL. Storage of the concentrated solution at room temperature afforded colourless block-shaped crystals of **3.4**. Yield: 88 % (340 mg). M.p. 195-210 $^{\circ}\text{C}$. ^1H NMR (401 MHz, C_6D_6) δ 0.38 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.12 (s, 1H, Ad), 1.23 (s, 1H, Ad), 1.46 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.55 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.65 (s, 1H, Ad), 1.74 (d, 3H, Ad), 1.84 (d, 3H, Ad), 2.03 (s, 5H, ad), 2.11 (s, 1H, toluene), 2.21 (s, 3H, Ad), 3.60 (s, 2H, $\text{CH}(\text{CH}_3)_2$), 6.83-6.77 (m, 1H, Ph), 6.93 (dd, 2H, Ph), 7.09-7.00 (m, 7H, Ph), 7.13 (d, 2H, Ph), 7.25-7.19 (m, 2H, Ph), 7.52 (d, 1H, Ph), 7.66 (s, 3H, Ph) ppm; ^{13}C NMR (101 MHz, C_6D_6) δ 175.99 (s, NCN), 147.26 (s, Ph), 141.22 (d, Ph), 135.30 (s, Ph), 134.90 (d, Ph), 131.73 (s, Ph), 128.77 (s, Ph), 128.13 (s, Ph), 127.91 (s, Ph), 124.72 (s, Ph), 123.42 (s, Ph), 54.23 (s, $\text{C}(\text{CH}_3)_3$), 50.28 (s, Ad), 49.38 (s, Ad), 36.66 (s, Ad), 31.39 (s, Ad), 30.42 (s, $\text{C}(\text{CH}_3)_3$), 28.16 (s, $\text{C}(\text{CH}_3)_3$), 27.18 (s, $\text{CH}(\text{CH}_3)_2$),

22.01 (s, $\text{CH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 161.97 MHz, 298 K): δ 51.82 ppm (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 79.49 MHz, 298 K): δ -57.06 ppm (d, $J = 10.5$ Hz, $\text{Si}=\text{N}$).

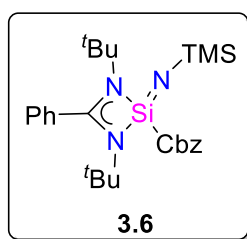
3.5.5 Synthesis of 5.



and adamantyl azide (88mg, 0.5 mmol) in a 100 mL Schlenk flask, and the solution was stirred overnight at room temperature. The colourless solution was filtered and reduced under vacuum. The residue was treated with 5 mL of pentane and kept at room temperature overnight to afford the colourless block-shaped crystals of **3.5**. Yield: 56 % (300 mg). M.p. 180-200 °C. ^1H NMR (401

MHz, C_6D_6); $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, C_6D_6 , 298 K) δ 5.38 (s, SiMe_3), 2.21 (s, SiMe_3), -73.63 (s, $\text{Si}=\text{N}$), -87.76 (s, $\text{Si}=\text{N}$) ppm. HRMS: $\text{C}_{61}\text{H}_{97}\text{N}_9\text{Si}_4$ Calculated m/z 1067.6944; Observed m/z $[\text{M}]^+$

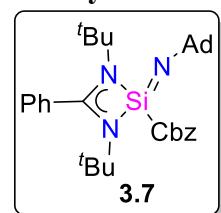
3.5.6 Synthesis of 3.6.



and trimethylsilyl azide (66 μL , 1 mmol) in a 100 mL Schlenk flask, and the solution was stirred overnight at room temperature. The colourless solution was filtered and reduced under vacuum. The residue was treated with 5 mL of pentane and kept at room temperature overnight to afford the colourless block-shaped crystals of **3.6**. Yield: 78 % (200 mg). M.p.

185-200 °C. ^1H NMR (401 MHz, C_6D_6) δ 0.73 (d, 9H, $\text{Si}(\text{CH}_3)_3$), 0.92 (s, 18H, $\text{C}(\text{CH}_3)_3$), 7.04-6.87 (m, 3H, Ph), 7.20 (d, 1H, Ph), 7.30 (dd, 2H, Ph), 7.47 (ddd, 2H, Ph), 7.62 (dt, 1H, Ph), 7.96 (d, 1H, Ph), 8.07 (ddd, 2H, Ph), 10.08 (t, 1H, Ph) ppm; ^{13}C NMR (101 MHz, C_6D_6) δ 177.19-176.47 (NCN), 146.22 (s, Ph), 142.34 (s, Ph), 130.62 (d, Ph), 126.67 (s, Ph), 126.34 (s, Ph), 126.01 (d, Ph), 124.66 (d, Ph), 121.06 (s, Ph), 120.39 (d, Ph), 118.99 (s, Ph), 118.64 (s, Ph), 113.49 (s, Ph), 54.44 (s, $\text{C}(\text{CH}_3)_3$), 30.43 (s, $\text{C}(\text{CH}_3)_3$), 5.73 (d, $\text{Si}(\text{CH}_3)_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 79.49 MHz, 298 K): δ 3.16 ppm (s, SiMe_3), -74.39 ppm (s, $\text{Si}=\text{N}$). HRMS: $\text{C}_{30}\text{H}_{40}\text{N}_4\text{Si}_2$ Calculated m/z 512.2792; Observed m/z $[\text{M}]^+$

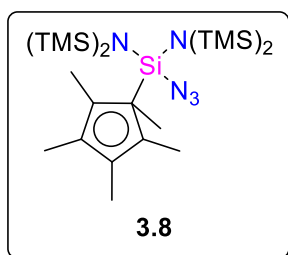
3.5.7 Synthesis of 3.7.



and trimethylsilyl azide (88mg, 0.5 mmol) in a 100 mL Schlenk flask, and the solution was stirred overnight at room temperature. The colourless solution was filtered and reduced under vacuum. The residue was treated with 5 mL of pentane and kept at room temperature overnight to afford the

colourless block-shaped crystals of **7**. Yield: 74 % (210 mg). M.p. 190-200 °C. ^1H NMR (401 MHz, C_6D_6) δ 1.00 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.22 (d, 2H, Ad), 1.43 (s, 1H, Ad), 1.92-1.82 (m, 5H, Ad), 1.99 (d, $J = 12.2$ Hz, 4H), 2.11 (s, 2H, toluene), 2.38 (s, 3H), 2.43 (s, 6H, Ad), 6.97-6.90 (m, 1H, Ph), 7.07-6.98 (m, 4H, Ph), 7.12 (d, 1H, Ph), 7.20 (d, 1H, Ph), 7.33 (dd, 2H, Ph), 7.54-7.47 (m, 2H, Ph), 7.68 (t, 1H, Ph), 8.01 (d, 1H, Ph), 8.09 (d, 1H, Ph), 8.14 (d, 1H, Ph), 10.62 (d, 1H, Ph) ppm; ^{13}C NMR (101 MHz, C_6D_6) δ 175.48 (s, NCN), 146.70 (s, Ph), 142.52 (s, Ph), 139.28 (s, Ph), 137.52 (s, Ph), 130.32 (d, Ph), 128.96 (s, Ph), 128.19 (s, Ph), 126.95 (s, Ph), 126.23 (d, Ph), 125.55 (s, Ph), 125.33 (s, Ph), 124.23 (s, Ph), 120.71 (s, Ph), 120.33 (s, Ph), 119.87 (d, Ph), 118.67 (s, Ph), 113.82 (s, Ph), 54.19 (s, $\text{C}(\text{CH}_3)_3$), 52.42 (s, Ad), 50.95 (s, Ad), 45.93 (s, ad), 44.65 (s, Ad), 37.50 (s, Ad), 36.25 (s, Ad), 32.64 (s, Ad), 31.37 (s, Ad), 30.89 (d, Ad), 30.68-30.55 (m, $\text{C}(\text{CH}_3)_3$), 30.31 (s, $\text{C}(\text{CH}_3)_3$), 30.09 (s, $\text{C}(\text{CH}_3)_3$), 28.84 (s, Ad), 21.07 (s, Ad) ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 79.49 MHz, 298 K): δ -67.48 ppm (d, $J = 18.3$ Hz, $\text{Si}=\text{N}$). HRMS: $\text{C}_{37}\text{H}_{46}\text{N}_4\text{Si}$ Calculated m/z 574.3492; Observed m/z $[\text{M}]^+$

3.5.8 Synthesis of 3.8. 30 mL of toluene was added to the mixture of disilene **3.L5** (323 mg, 0.5 mmol) and trimethylsilyl azide (66 μL , 1 mmol) in a 100 mL Schlenk flask, and the solution was stirred overnight at room temperature. The colourless solution was filtered and reduced under vacuum to 5 mL. Storage of the concentrated solution at room temperature afforded colorless block shape crystals of **3.8**. Yield: 91.6 %



(240 mg). M.p. 180-190 °C. ^1H NMR (C_6D_6 , 400 MHz, 298 K, TMS): δ 0.36 (s, 36H, ($\text{Si}(\text{Me}_3)$)), 1.29 (s, 3H, ($\text{C}(\text{Me}_3)$)), 1.69 (s, 6H, ($\text{C}(\text{Me}_3)$)), 2.02 (s, 6H, ($\text{C}(\text{CH}_3)$)) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100.613 MHz, C_6D_6 , 298 K): δ 5.82 (SiMe_3), 10.27 (Me_5C_5), 12.34 (Me_5C_5), 21.95 (Me_5C_5), 56.94 (Me_5C_5), 136.15 (Me_5C_5), 139.17 (Me_5C_5) ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 79.49 MHz, 298 K): δ 3.65 (s, SiMe_3), -30.04 (s, $\text{SiN}_3(\text{N}(\text{SiMe}_3)_2)_2\text{Cp}^*$) ppm. HRMS: $\text{C}_{22}\text{H}_{51}\text{N}_5\text{Si}_5$ Calculated m/z 525.2991; Observed m/z $[\text{M}]^+$

3.6 Bibliography

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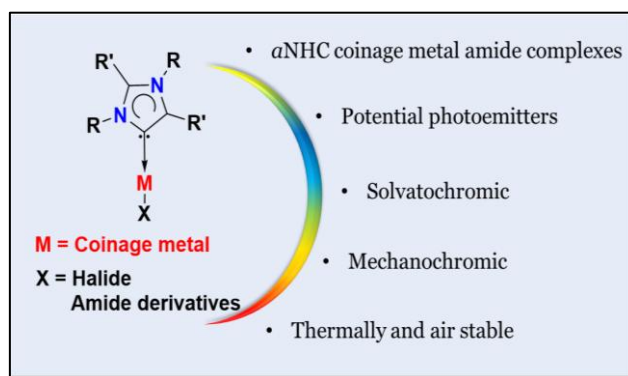
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Chapter 4: Expanding the Photophysical and Reactivity Landscape of Abnormal NHC Complexes.

Chapter 4A. Air-Stable “Abnormal” Carbene-Metal Amide TADF Emitters: An Approach towards Near-Unity Quantum Yield



Adapted from: **R. Akhtar**, A. Chatterjee, H. Sharma, A. Kudlu, R. Panday, G. Venugopal, R. Verma, K. Vanka, and S. Khan* Air-Stable “Abnormal” Carbene-Metal Amide TADF Emitters: An Approach towards Near-Unity Quantum Yield (*Manuscript under preparation*)

4A.1 Objective of the work

Carbene-metal-amide (CMA) complexes have emerged as an efficient class of thermally activated delayed fluorescence (TADF) emitters for optoelectronic applications. Although N-heterocyclic carbene (NHC)-based CMAs are widely researched, abnormal NHC (*a*NHC) counterparts are underexplored despite providing unique electronic structures and enhanced σ -donor properties. In this work, we present a series of air-stable *a*NHC coinage metal amide complexes (**4A.5-4A.10**) (Cu, Ag, Au) with imidazolylidene-derived ligands, representing the first systematic investigation of their photophysical behaviour. These complexes exhibit dual locally excited (LE) and charge-transfer (CT) emissions, where the latter is highly oxygen sensitive and contains long-lived microsecond components, establishing TADF as the emission channel. The emission maxima are also heavily influenced by both donor substituents (carbazole versus *tert*-butyl carbazole) and metal identity, falling between 575 and 618 nm in solution and preserved in solid-state and PMMA matrices. Quantum yields for photoluminescence as high as 0.97 in deaerated toluene, 0.91 in PMMA, and delayed lifetimes on the order of tens of microseconds highlight effective triplet harvesting. Temperature-dependent photoluminescence (PL) and time-resolved PL studies demonstrate low singlet-triplet energy splitting ($\Delta E_{ST} \approx 0.14$ eV) and high radiative decay rate constants [$k_r(S_1) \approx 1.8 \times 10^7$ s⁻¹], which make these complexes efficient emitters. Moreover, donor-substituted (**4A.5-4A.10**) complexes exhibit excellent mechanochromic luminescence (MCL) properties, and their incorporation in UV-excited converted LED prototypes proves their stability and usability in device applications. These results make imidazolylidene *a*NHC-metal amides a new family of earth-abundant, high-efficiency TADF emitters with strong applications toward next-generation OLEDs.

4A.2 Introduction

Two-coordinate carbene-metal-amide (CMA) complexes have emerged as a versatile class of photoemissive materials owing to their remarkable optical and electronic properties.¹⁻⁴ Their unique photophysics enable applications from photocatalysis and sensing to dye-sensitised solar cells and organic electronics.⁵⁻¹⁰ In particular, their strong emissive characteristics make them promising dopants for organic light-emitting diodes (OLEDs), where efficient microsecond-scale phosphorescence is essential for high electroluminescence efficiency.¹¹⁻¹² Thermally activated delayed fluorescence (TADF) has emerged as a powerful strategy to achieve near-unity quantum efficiency in organic light-emitting diodes (OLEDs) by harvesting

both singlet and triplet excitons. Unlike traditional fluorescent emitters, which are limited to 25% efficiency, and phosphorescent emitters, which rely on scarce heavy metals (Ir, Pt), TADF materials offer a sustainable and cost-effective route to 100% exciton utilisation. Their molecular tunability further enables colour control, short emission lifetimes, and reduced efficiency roll-off, positioning TADF emitters as key candidates for high-performance, next-generation optoelectronic devices. In CMA complexes, the π -donating amide transfers electron density to the π -accepting carbene, activating thermally activated delayed fluorescence (TADF). This mechanism enables near-unity quantum yields by upconverting non-emissive triplet excitons into emissive singlets, thereby achieving full 100% exciton utilisation. TADF not only maximises device efficiency but also reduces reliance on scarce noble-metal phosphors, offering a sustainable and cost-effective strategy for OLED development.¹³ Moreover, the inherently short emission lifetimes of CMA-based TADF emitters help mitigate efficiency roll-off at high brightness, an ongoing challenge in display and lighting technologies. Recent advances in two-coordinate coinage metal (Cu, Ag, Au) complexes have delivered tunable colours, short lifetimes, high quantum yields, and exceptional device performance. CMA-type emitters typically exhibit a small singlet-triplet energy gap ($\Delta E(S_1-T_1)$) due to the spatial separation of electrons and holes across the donor (amide) and acceptor (carbene) units, respectively.¹⁴ A broad range of carbenes, including CAACs, mono- and di-amino carbenes (MACs and DACs), and various substituted NHCs, have been employed to enhance performance (Selected examples are mentioned in Figure 4A.1).^{3, 15-16} Likewise, carbazole-functionalized amides and their derivatives have been extensively investigated for modulating photophysical properties. Parameters such as molecular planarity, amide angle distortion, and carbene chirality have also been systematically explored to optimise TADF efficiency.¹⁷

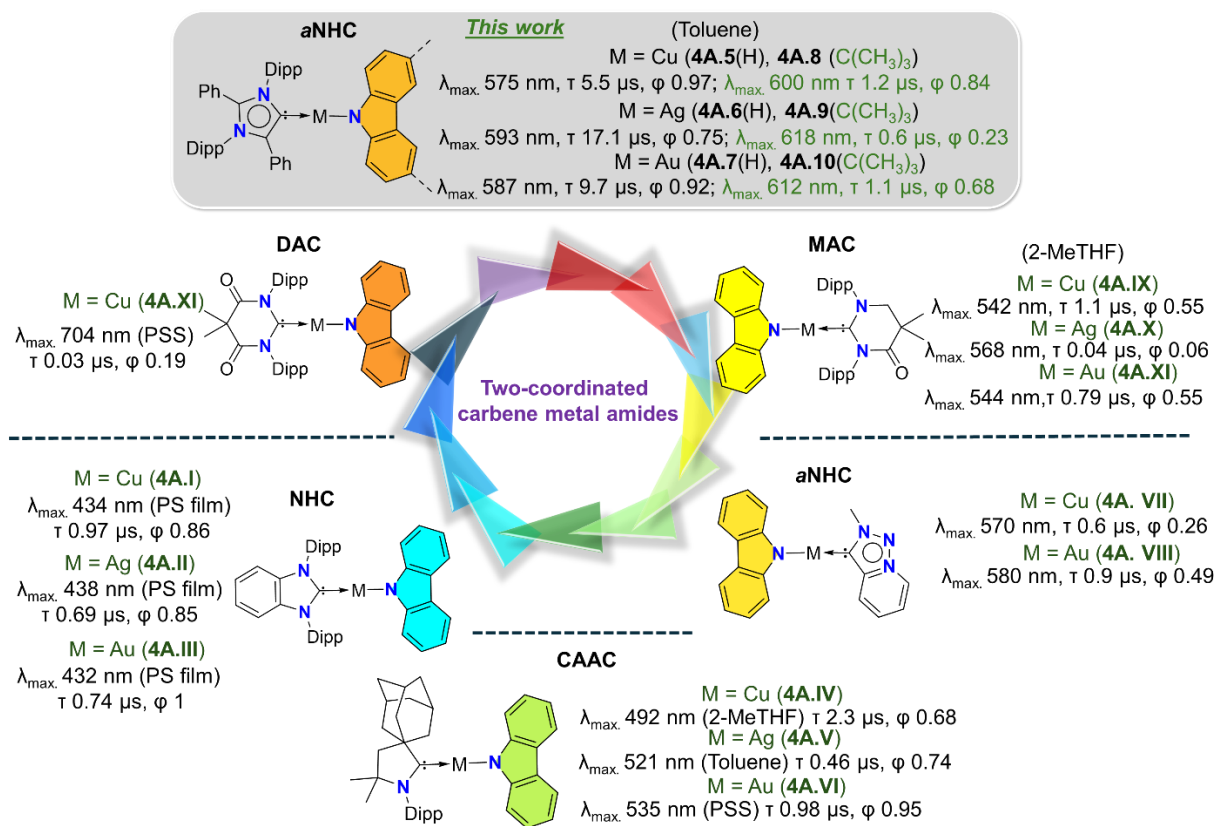


Figure 4A.1: Reported selected examples of carbene metal carbazolid (amide) complexes for exploration of luminescent properties.

Beyond classical carbenes, other low-valent main-group species such as functionalized disilenes, N-heterocyclic silylenes (NHSi), heavier tetrylenes, and diboryne-ligated coinage metal complexes have also displayed intriguing emission.¹⁸⁻²⁶ While luminescence in two-coordinate carbene-metal complexes has been well documented, analogous systems based on abnormal N-heterocyclic carbenes (*a*NHCs) remain virtually unexplored.²⁷⁻²⁹ There are only two reports where the photophysical behaviour of the two coordinated abnormal carbene (triazolylidene derivatives) metal (Cu, Au) amides (*a*CMAs) was studied (Figure 4A.1).³⁰⁻³¹ The reported triazolylidene-based CMA complexes exhibit moderate photoluminescence quantum yields (0.20–0.35) and display dual emission along with TADF. The high ϕ_{PL} of the complexes in solid and fluid media can be achieved if the ligand provides sufficient steric hindrance to prevent structural distortion in the excited state.³ However, imidazolylidene *a*NHCs constitute a distinctive subclass of carbenes that diverge from classical NHCs in their electronic and structural features.³² *a*NHCs and their derivatives have been utilised in many applications, including stabilising reactive intermediates, facilitating small molecule activation, mediating metal-catalysed transformations, modulating polymerisation processes,

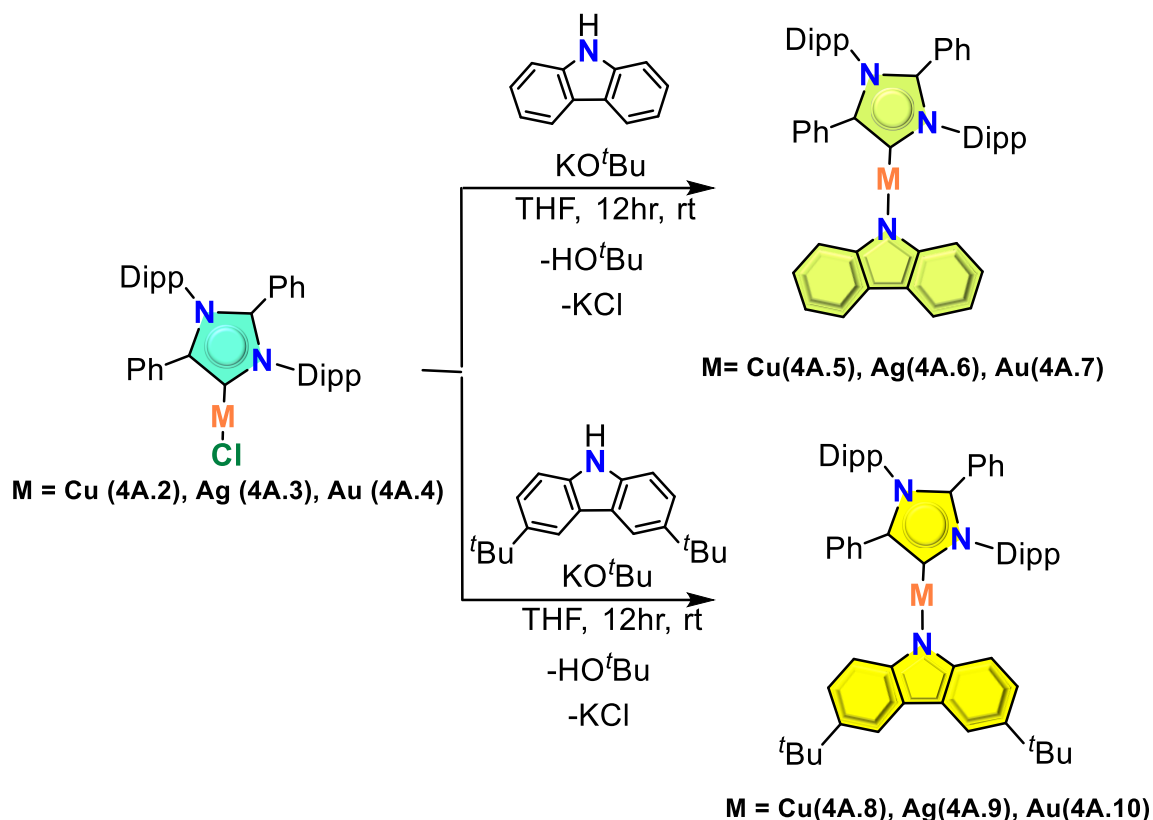
and influencing photophysical behaviour, as well as extending to medicinal chemistry.³³⁻³⁶ Our work focuses on the photophysical properties of two-coordinate metal amides bearing imidazolylidene-based abnormal N-heterocyclic carbenes (*a*NHCs) as the ligand. This imidazolylidene class of ligands garnered significant attention after the isolation of a stable mesoionic imidazolylidene by Bertrand and co-workers in 2009.³⁷ Despite this progress, the potential of abnormal N-heterocyclic carbenes (*a*NHCs) in CMA architectures remains largely untapped. Their stronger σ -donation and altered π -acceptor properties offer an unexplored opportunity to modulate excited-state dynamics and emission colour. Our work addresses this gap by systematically investigating the photophysical behaviour of two-coordinate metal amides supported by imidazolylidene *a*NHC ligands (**4A.5-4A.10**), establishing them as efficient, robust, and earth-abundant TADF emitters for next-generation OLEDs.³⁸⁻³⁹ Notably, the *a*NHC-Cl complexes (**4A.2-4A.4**) exhibited emissive behaviour in both solution and solid state, representing, to the best of our knowledge, the first report of luminescent *a*NHC-halide complexes. All complexes were structurally authenticated by single-crystal X-ray diffraction (XRD), multinuclear NMR spectroscopy, powder XRD (PXRD), and high-resolution mass spectrometry (HRMS). Our results are discussed below. These findings establish the first class of *a*NHC-metal amide (*a*CMA) emitters, opening new avenues in the development of TADF-active materials. Our results are discussed below.

4A.3 Result and Discussion

4A.3.1 Structural elucidation

The imidazolylidene coinage-metal complexes *a*NHC-M-Cl (M = Cu, Ag, Au) (**4A.2-4A.4**) were synthesised according to the procedure described in the literature.³⁸⁻³⁹ In situ deprotonation of imidazolium salt with KHMDS (HMDS = hexamethyldisilazane) at -78 °C in the presence of MCl (M = Cu, Ag, Au) led to the formation of linear two-coordinated [(MCl(*a*NHC))] (**4A.2-4A.4**), of which we obtained colourless single crystals in 85-90 % yield by utilising DCM (dichloromethane) and pentane. Complex **4A.2-4A.4** serves as a synthon, providing access to a series of *a*NHC-M-carbazolide complexes (**4A.5-4A.10**) by treatment of **4A.2-4A.4** with carbazole (HCz) and tert-butyl substituted carbazole (H^tBuCz) in the presence of KO^tBu in excellent isolated yields of 80-90 % from THF (tetrahydrofuran) and pentane (Scheme 4A.1). The complexes possess good solubility in aromatic and polar non-protic solvents like DCM, THF, and moderate solubility in acetonitrile. All complexes have been characterised by ¹H, ¹³C, and high-resolution mass spectroscopy. Complexes **4A.2-4A.10** were

isolated as white to yellow powders and display no degrees of sensitivity to O₂ and moisture in the solid-state and molecular levels.



Scheme 4A.1. *a*NHC coordinated coinage amide complexes (4A.2–4A.10) discussed in this work.

The ¹³C{¹H} carbene-C resonance follows the Ag < Cu < Au trend that reflects increasing metal→carbene back-donation and the relativistic enhancement of Au-C bonding, which shifts the ¹³C carbene carbon resonance progressively upfield (see the appendix figure 4A.A.1–4A.A.12).⁴⁰ X-ray crystallography (Figure 4A.2) confirmed the linear two-coordinate monomeric structures and the lack of close intermolecular contacts (Table 4A.1). Complexes 4A.5–4A.7 crystallise in the triclinic *P*–1 space group, while 4A.8–4A.10 adopt the orthorhombic *P*2₁2₁2₁ space group. Due to the poor-quality crystal data, we refrain from discussing the bonding parameter of 10. However, the structure of 4A.10 was established unambiguously (see the appendix figure 4A.A.13 for the molecular structure of 4A.10). The donor-acceptor distances C_{carbene}⋯N_{amide} for carbazole donor reflect the increase in covalent radii in the order Cu (~3.74 Å) < Au (~4.01 Å) < Ag (~4.12 Å) which is similar to the previously reported NHC carbene amide complexes (4A.I–4A.III) (Cu (~3.73 Å) < Au (~4.00 Å) < Ag (~4.11 Å)).¹⁵ The distortion by angle β while taking the angle between the M–N–Cg

(Cg centroid of the amide moieties), which shows that the deviation from planarity is more prominent in *tert*-butyl substituted carbazole (**4A.8-4A.10**) [for **4A.8** (170.08°), **4A.9** (171.90°)]. However, **4A.5-4A.7** do not deviate significantly [for **4A.5** (174.27°), **4A.6** (173.43°), and **4A.7** (175.39°)] and are in line with CAAC-coordinated copper amide complexes (see the appendix figure 4A.A.14). The torsion angles (α) also disclose the deviation of coplanarity. The thermal stability of all the complexes and weight loss were checked by thermogravimetric analysis (TGA) (see the appendix figure 4A.A.15). All complexes exhibited stability up to 260-290 °C, indicating their robust thermal resistance.

Table 4A.1. $^{13}\text{C}\{^1\text{H}\}$ chemical shift for the carbene atom, Selected distances [Å], Angles [°] and bond parameters of *a*NHC coordinated M-amide complexes **4A.5-4A.10**.

Complex No.	$^{13}\text{C}\{^1\text{H}\}$ chemical shift ppm	Carbenic C→M(I) (Å)	M-N (Å)	C...N (Å)	C-M-N (°)	α^a (°)	β^b (°)
4A.5	160.01	1.882(3)	1.864(3)	3.741(4)	174.1(4)	17.4(4)	174.27
4A.6	162.75 and 160.62	2.065(3)	2.063(2)	4.123(3)	174.14(9)	19.7(3)	173.43
4A.7	156.50	2.01(1)	2.039(9)	4.04(1)	176.1(4)	15(1)	175.39
4A.8	160.36	1.92(1)	1.86(1)	3.78(2)	178.8(5)	8(1)	170.08
4A.9	162.99 and 160.89	2.11(2)	2.10(1)	4.21(2)	177.6(7)	4(2)	171.90
4A.10	158.12	-	-			-	-

Note: ^atorsion angle (α) N2-C1-N1-C51 for **4A.5**, N3-C1-N1-C40 for **4A.6**, N2-C1-N3-C38 for **4A.7**, N1-C1-N3-C51 for **4A.8**, N2-C1-N3-C40 for **4A.9** ^b β is the tilt angle between the Cu, amide nitrogen group and Cg (centroid for the carbazolate five-membered ring). Cg centroid for the carbazolate five-membered ring N1,C40,C45,C46,C51 for **4A.5**; N1,C40,C45,C46,C51 for **4A.6**; N3,C51,C46,C46,C38 for **4A.7**; N3,C40,C45,C46,C51 for complex **4A.8**; N3,C40,C45,C46,C51 for complex **4A.9**.

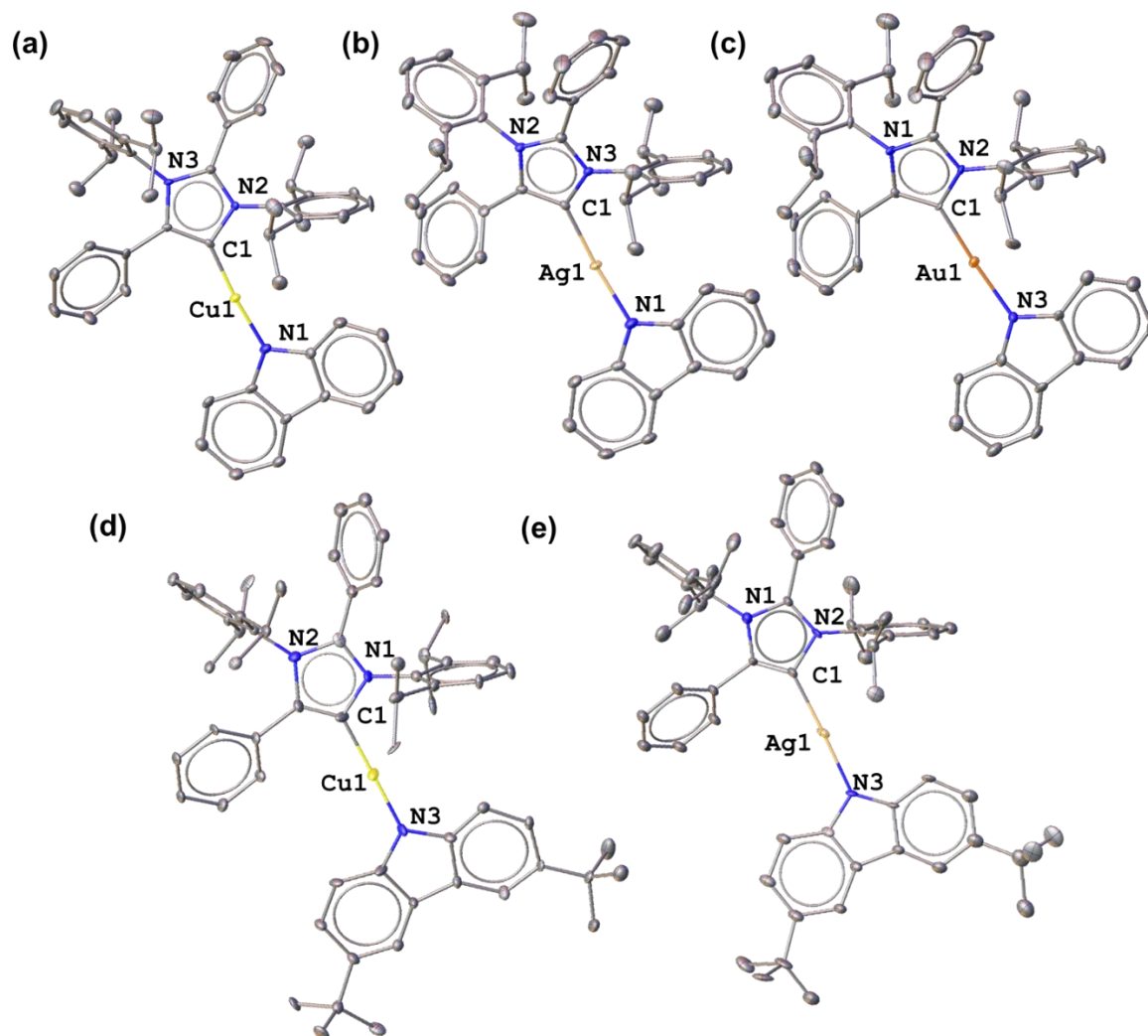


Figure 4A.2. Molecular structures of **4A.5-4A.9**. Anisotropic displacement parameters are depicted at the 50 % probability level. Solvent moiety, disordered atoms, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): for **4A.5** (a) C1–Cu1 1.882(3), 1.864(3), C1–Cu1–N1 174.1(1); for **4A.6** C1–Ag1 2.065(3), Ag1–N1 2.063(2) Å, C1–Ag1–N1 174.14(9); for **7** (c) C1–Au1 2.01(1) Å, Au1–N3 2.039(1) Å; C1–Au1–N3 176.1(4); for **4A.8** C1–Cu1 1.921(1) Å, Cu1–N3 1.86(1), Å C1–Cu1–N3 178.8(5); for **4A.9** C1–Ag1 2.11 (2) Å, Ag1–N3 2.10(1), C1–Ag1–N3 177.67(7).

4A.3.2 Photophysical properties

The photophysical properties of the complexes (**4A.2-4A.10**) were initially investigated in the solution phase. The absorption spectra of complexes (**4A.2-4A.10**) were recorded in toluene (Figure 4A.3). For the chloride-based complexes (**4A.2-4A.4**), a distinct low-energy absorption band was observed in the UV-vis spectra centred at 332 nm for **4A.2**, 317 nm for **4A.3** and 324

nm for **4A.4**. This band is absent in the spectra of the abnormal carbene salt (**4A.1**) and its molecular fragments, indicating that it originates upon metal coordination (see the appendix figure 4A.A.16). Solvent-dependent absorption studies revealed that this band exhibits pronounced negative solvatochromism, gradually shifting to higher energy from non-polar toluene to highly polar acetonitrile (see the appendix figure 4A.A.17). This suggests that the associated electronic transition involves a more polar ground state and a less polar excited state, consistent with a metal-to-ligand charge transfer (MLCT) process in which electron density is delocalized away from the metal centre or chloride ligand; the resulting excited state is therefore more ligand-centred and less polar, which explains the stronger stabilization of the ground state in polar solvents and the observed blue shift. The most red-shifted absorption in the Cu(I) complex implies stronger donor-acceptor interactions and enhanced covalency between the Cu centre (**2**) and the π -accepting ligand framework compared to Ag (**4A.3**) and Au (**4A.4**).

Further, the UV-vis absorption spectra for **4A.5-4A.10** were recorded in toluene and in solvents of varying polarity to understand the effect of donor substitution and solvent polarity on electronic transitions. In toluene, all complexes exhibit structured, broad absorption bands in the 300-500 nm region, arising from π - π^* ligand-centred (LC) transitions (evident from the absorption spectra of the free ligands or the molecular fragments) and overlapping CT bands (Figure 4A.3). The copper complexes (**4A.5** and **4A.8**) display the most intense and red-shifted features, indicating stronger metal-donor orbital interactions and enhanced charge transfer (CT) contributions in the ground state. In contrast, silver complexes (**4A.6** and **4A.9**) show blue-shifted and weaker absorption, consistent with reduced metal-ligand orbital overlap due to the larger ionic radius and lower relativistic stabilisation. The gold complexes (**4A.7** and **4A.10**) show intermediate behaviour with moderately intense and structured bands. A distinct absorption tail above 400 nm is observed for all complexes (**4A.2-4A.10**), more prominent in Cu and Au species and significantly diminished in Ag analogues (see the appendix figure 4A.A.17). This tail gains intensity particularly in coordinating solvents such as THF, implying enhanced stabilisation of low-energy CT states through solvent-metal interactions (see the appendix figure 4A.A.17). Notably, the Ag complexes (**4A.3**, **4A.6**, and **4A.9**) show consistently weak or absent >400 nm absorption across all solvents, underscoring their reduced CT character in the ground state. Solvent-dependent studies further reveal a general blue shift of the >400 nm absorption band with increasing solvent polarity, from toluene to acetonitrile, mirroring trends observed for the chloride analogues (**4A.2-4A.4**). This inverse

solvatochromism suggests that the transition involves a state with reduced dipolar character in polar solvents, possibly due to solvent-induced stabilisation of the ground state.

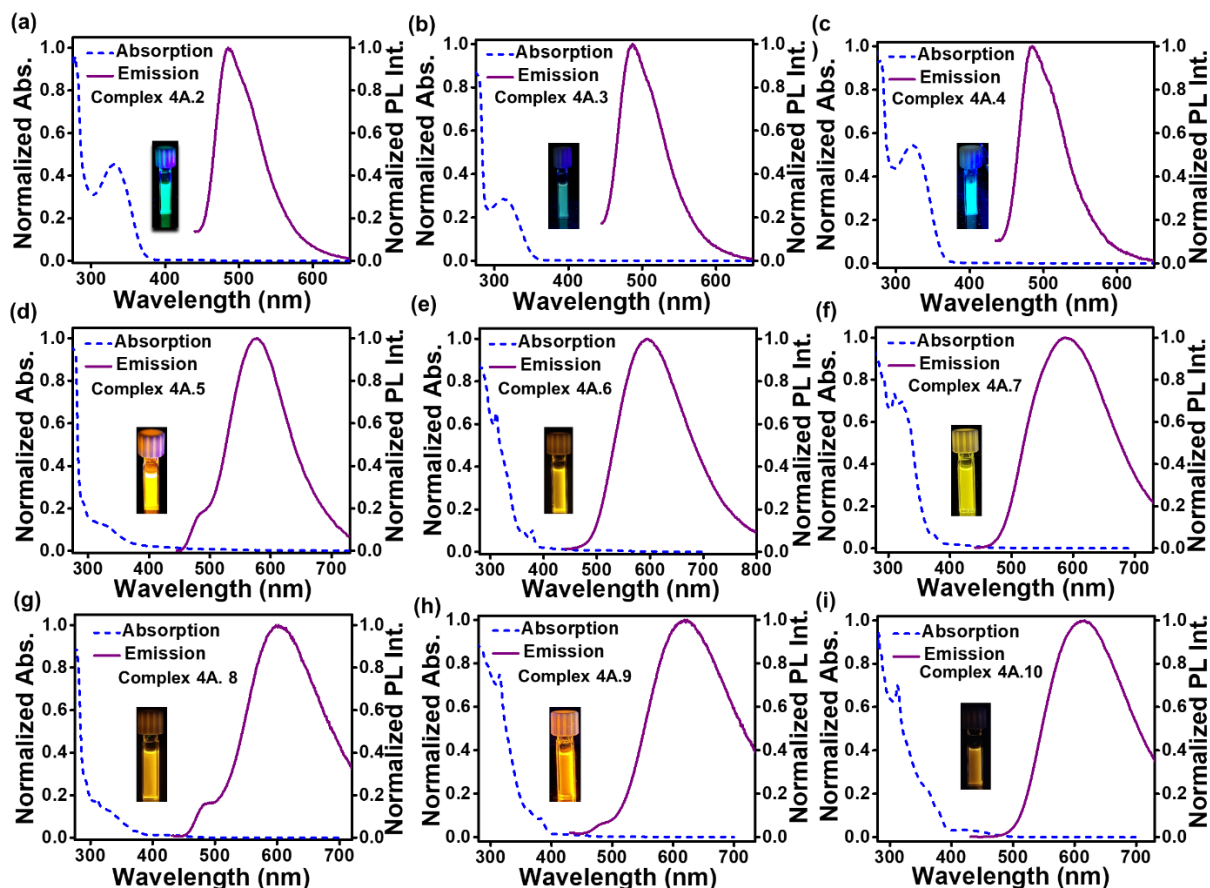


Figure 4A.3: The emission spectra of complex 4A.2-4A.10 in toluene at 375 nm excitation wavelengths. (a) complex 4A.2, (b) complex 4A.3, (c) complex 4A.4, (d) complex 4A.5, (e) complex 4A.6, (f) complex 4A.7, (g) complex 4A.8, (h) complex 4A.9, (i) complex 4A.10.

Photoluminescence studies were then carried out in deaerated toluene. Upon excitation at 300 nm, the chloride-bound complexes (4A.2-4A.4) display two well-resolved emission bands (see the appendix figure 4A.A.19). The first, centred at approximately 375 nm, closely matches the emission profile of the abnormal carbene salt precursor (4A.1) in both peak position and FWHM (~62 nm) (Full-width half maxima), confirming its origin from the *a*NHC-centred singlet LE state (see the appendix figure 4A.A.19 and 4A.A.20). Upon changing the solvent polarity, this emission band was found to be unaltered, further assuring its locally excited (LE) nature. The second band, appearing around 485 nm, is also consistently observed across the coinage metal series and remains unshifted across different solvents, implying its assignment as a second LE emission from the carbene-metal-chloride chromophore. The donor-substituted analogues (Cbz and ^tBu-Cbz) (4A.5-4A.10) preserve the two LE bands but introduce key spectral changes (see the appendix figure 4A.A.21 and 4A.A.22). The high-energy LE band

undergoes a distinct blue shift to ~360 nm and becomes vibronically structured. This emission closely resembles the photoluminescence spectra of the isolated donor fragments, carbazole and *tert*-butyl carbazole, in DCM solvent, with identical emission maxima and FWHM, suggesting that the highest-energy emission now originates from the donor unit itself (see the appendix figure 4A.A.20). Interestingly, the 485 nm LE band persists in these derivatives as well, remaining unchanged in position, intensity, and shape. This emission likely arises from a ligand-centred locally excited state that is activated (or stabilised) only upon metal coordination, i.e., a metal-assisted π - π^* transition on the ligand framework. This does not involve metal *d*-orbitals directly (hence the metal-insensitivity), but rather, metal coordination perturbs the electronic structure of the ligand (e.g., conjugation or electron density redistribution), enabling a new emissive state at ~480 nm. In addition to the two LE (locally excited) features, the donor-substituted complexes exhibit a third emission band at longer wavelengths. This band becomes more prominent upon excitation at 375 nm and displays pronounced solvent-dependent red shifts, particularly in polar solvents (see the appendix figure 4A.A.21 and 4A.A.22).

The red-edge broadening (4A.5-4A.10) (see the appendix figure 4A.A.21 and 4A.A.22), its absence in the corresponding chloride derivatives (see the appendix figure 4A.A.19), and its sensitivity to solvent polarity collectively suggest that this emission originates from an intramolecular charge transfer (CT) state between the donor moiety (Cbz and *t*Bu-Cbz) and the *a*NHC-metal acceptor unit. Furthermore, a systematic red shift in the emission maxima is observed with an increase in donor strength, from carbazole to *tert*-butyl carbazole. For instance, in toluene, the photoluminescence maxima shift from 575 nm (4A.5) to 600 nm (4A.8) for Cu-based emitters, from 593 nm (4A.6) to 618 nm (4A.9) for Ag-based emitters, and from 587 nm (4A.7) to 612 nm (4A.10) for the Au-based emitter (Figure 4A.3). Additionally, a clear dependence on the metal centre is observed: for a given donor, the PL maxima shift progressively from shorter to longer wavelengths in the order Cu < Au < Ag. This trend suggests that the identity of the metal significantly modulates the acceptor strength of the *a*NHC-metal unit and the degree of stabilisation of the CT excited state.

The increasing red shift from Cu to Ag can be attributed to enhanced stabilisation of the LUMO due to increased metal polarizability and relativistic effects, particularly in Au and Ag complexes. Moreover, the participation of metal *d*-orbitals in the acceptor orbital manifold may further tune the CT character and emission energy. Noticeably, the CT emission was found to be highly sensitive to oxygen quenching, a hallmark of a spin-flip process in the emission

mechanism (Figure 4A.4). Comparative PLQY measurements under deaerated and oxygenated conditions illustrate a stark drop in quantum efficiency upon exposure to air. For example, the PLQY of complex **4A.5** decreases from 0.97 to 0.11, while that of complex **4A.6** drops from 0.75 to 0.03. Similarly, complex **4A.7** drops from 0.92 to 0.04. (Table 4A.2). This behaviour is absent in the LE bands, which remain largely unaffected, indicating that only the CT emission is mediated through a spin-flip process, likely *via* thermally activated delayed fluorescence (TADF).⁴¹⁻⁴²

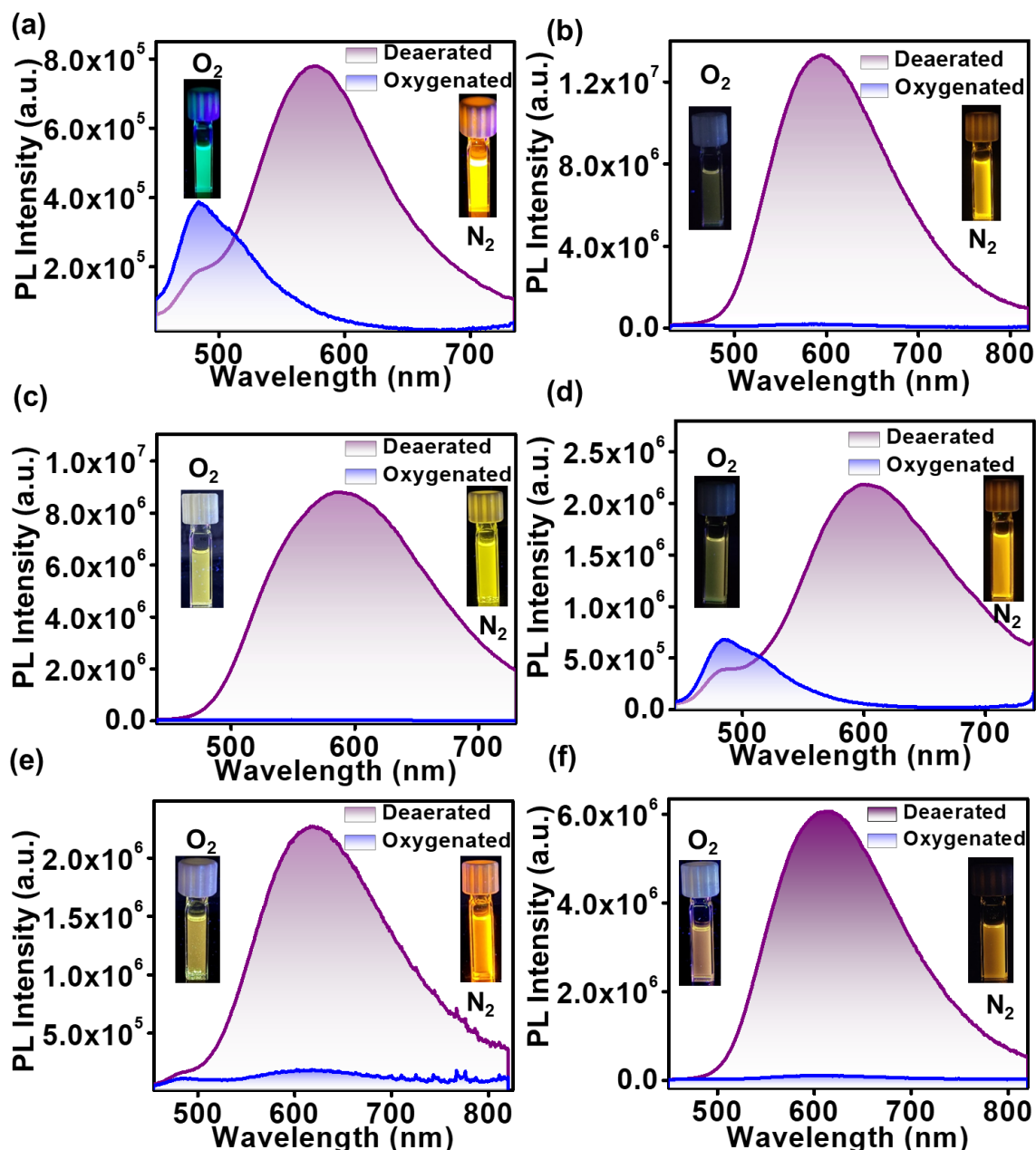


Figure 4A.4. Emission spectra of complexes **4A.5-4A.10** in toluene solution under deaerated and oxygenated conditions at 375 nm excitation. (a) Complex **4A.5**. (b) Complex **4A.6**. (c) Complex **4A.7**. (d) Complex **4A.8**. (e) Complex **4A.9**. (f) Complex **4A.10**.

Similarly, for the *tert*-butyl carbazole derivatives, complex **4A.8** shows a high PLQY of 0.84 in deaerated toluene, which drops sharply to 0.08 upon oxygen exposure. Likewise, complexes **4A.9** and **4A.10** display PLQYs of 0.23 and 0.68, respectively, in deaerated toluene, but these values collapse to <5% and 0.07 under oxygen. Next, to assess the origin of these distinguished emission bands, time-resolved photoluminescence (TRPL) experiments were carried out. Notably, the high-energy LE emission at 485 nm displays lifetimes exclusively in the nanosecond regime across all nine complexes, with no evidence of long-lived decay components in the microsecond-millisecond domain, consistent with the prompt fluorescence mechanism (see the appendix figure 4A.A.23). Earlier, it was shown that, this particular emission band remains unaffected by donor substitution; the photoluminescence maxima are identical for the chloride and donor-substituted derivatives. It was also noted that this emission band is insensitive towards oxygen or moisture, a typical feature observed in most of the fluorescent emitters. In contrast, the low-energy CT emission band observed in the donor-substituted complexes is characterised by significantly longer lifetimes in the microsecond time-scale, indicative of a probable thermally activated spin-flip process, typically observed in two-coordinated linear CMA complexes with strong CT nature. Herein complexes, **4A.5**, **4A.6**, and **4A.7** display average delayed lifetimes of 5.5 μ s, 17.1 μ s, and 9.7 μ s, respectively, while the *tert*-butyl-substituted analogues **4A.8**, **4A.9**, and **4A.10** exhibit shorter lifetimes of 1.2 μ s, 0.6 μ s, and 1.1 μ s, respectively (Table 4A.2). These long-lived components are significantly quenched under oxygenated conditions, further supporting the involvement of triplet states and a spin-mixing mechanism in the CT emission process (see the appendix figure 4A.A.24).

Table 4A.2: Photophysical data of **4A.5–4A.10** (carbene metal amide complexes) in toluene solution, including both LE (485 nm) and CT emissions.

Complex	λ_{em} (LE) [nm]	τ_{avg} (LE)	λ_{em} (CT) [nm]	τ_{avg} (CT)	PLQY (Deaerated)	PLQY (Air)
4A.2	485	4.1 ns	-	-	0.70	-
4A.3	485	4.2 ns	-	-	0.23	-
4A.4	485	4.1 ns	-	-	0.18	-
4A.5	485	4.1 ns	575	5.5 μ s	0.97	0.11
4A.6	485	4.3 ns	593	17.1 μ s	0.75	0.03
4A.7	485	3.2 ns	587	9.7 μ s	0.92	0.04
4A.8	485	4.1 ns	600	1.2 μ s	0.84	0.08
4A.9	485	3.9 ns	618	0.6 μ s	0.23	<0.05
4A.10	485	4.2 ns	612	1.1 μ s	0.68	0.07

Note: λ_{em} = Emission maximum; τ_{avg} = Average lifetime. LE = Locally excited state (centred around 485 nm); CT = Charge-transfer emission; PLQY = Photoluminescence quantum yield. PLQY measured under deaerated and air-equilibrated conditions. LE emission is constant across complexes and donor-insensitive. CT emission appears only in donor-substituted complexes.

Having established the presence of a long-lived intramolecular CT state in solution, we extended our investigation to the solid state. This is particularly relevant for device-oriented applications, where the material must perform efficiently in a host matrix or as a crystalline film. Importantly, while imidazolylidene-based abnormal N-heterocyclic carbene (*a*NHC)-metal complexes have been extensively studied for their coordination chemistry, their triplet-harvesting behaviour through TADF in the solid state remains unexplored. Our findings present the first such observation in this class of materials. However, there are only two reports where the photophysical behaviour of the two coordinated abnormal carbene (triazolylidene derivatives) metal (Cu, Au) amides (*a*CMA) was studied (Figure 4A.1).³⁰⁻³¹ The reported triazolylidene-based CMA complexes exhibit moderate photoluminescence quantum yields (0.20-0.35) and display dual emission along with TADF. The high ϕ_{PL} of the complexes in solid and fluid media can be achieved if the ligand provides sufficient steric hindrance to prevent structural distortion in the excited state.³

The complexes (**4A.2-4A.10**) were embedded in a PMMA matrix (1 wt%) to mimic host-guest conditions relevant for OLED applications (see the appendix figure 4A.A.25-27). This approach ensures spatial isolation of emissive sites, suppressing intermolecular quenching while enabling rigid conformational environments. Remarkably, the donor-substituted complexes retained the low-energy CT emission observed in solution. Complexes **4A.5**, **4A.6**, and **4A.7** exhibit broad CT emission centred at 502, 531, and 515 nm, respectively, while **4A.8**, **4A.9**, and **4A.10** show red-shifted emission at 541, 537, and 541 nm (Table 4A.3, appendix figure 4A.A.26 and 4A.A.27). Noticeably, the systematic red shift with increasing donor strength from carbazole to *tert*-butyl carbazole echoes solution-state behaviour, indicating that the CT state is preserved and emissive in PMMA (Table 4A.3). Photoluminescence quantum yields (PLQYs) of the emitters in PMMA are found to exhibit moderate to high values, with complex **4A.8** (0.75) and **4A.10** (0.91) showing particularly high values, assuring their efficiency for real OLED applications. Moreover, the presence of microsecond-scale delayed emission components further supports the operation of a triplet-involved emissive mechanism. Average lifetimes from time-resolved PL measurements are as follows: for carbazole-based emitters: 33.7 μ s (**4A.5**), 19.7 μ s (**4A.6**), and 44.5 μ s (**4A.7**); for the *t*Bu-substituted analogues: 15.6 μ s (**4A.8**), 47.1 μ s (**4A.9**), and 22.2 μ s (**4A.10**) (see the appendix figure 4A.A.28).

However, not all complexes exhibit long-lived components, as also observed in the solution state studies. The chloride-bound complexes-**4A.2**, **4A.3**, and **4A.4** show only nanosecond-range lifetimes (**4A.2**: mono-exponential, avg. 3.8 ns; **4A.3**: bi-exponential, avg. 3.2 ns, and **4A.4**: bi-exponential, avg. 3.6 ns), indicating that their emission arises from ligand-centred singlet LE states without any triplet participation (see the appendix figure 4A.A.29).

Crystalline samples of all complexes were next studied to probe the role of lattice packing and rigidity (Table 4A.3). Like in PMMA host doped films, the CT emission is preserved in the crystalline phase as well, with the emission maxima observed at: 485 nm (**4A.5**), 529 nm (**4A.6**), 551 nm (**4A.7**), and for the *tert*-butyl carbazole series, 510 nm (**4A.8**), 530 nm (**4A.9**), and 541 nm (**4A.10**) (see the appendix figure 4A.A.30). Next for complex 5-10, time-gated emission spectra were collected with a 20 μ s detector-delay and 5 ms sample window to probe the possible emission mechanism. Noticeably, no shift in the emission maxima were found for all 6 complexes, which may possibly indicate the TADF-based triplet harvesting. (see the appendix figure 4A.A.31). Lifetimes in the crystalline state show a broad range, revealing the sensitivity of excited-state dynamics to both donor strength and metal identity. Complexes **4A.5**, **4A.6**, and **4A.7** exhibit delayed lifetimes of 12.4 μ s, 1.6 ms, and 93.3 μ s, respectively, while **4A.8**, **4A.9**, and **4A.10** show values of 17.9 μ s, 0.7 ms, and 9.7 μ s, respectively (see the appendix figure 4A.A.32).

Table 4A.3: Photophysical data of **4A.2-4A.10** carbene metal amide complexes in PMMA film and solid state.

Complex	λ_{em} (nm)	τ_{avg}	PLQY	λ_{em} (nm)	τ_{avg}	PLQY
PMMA film				Crystalline state		
4A.2	467	3.8 ns	0.81	478	2.7 ns	0.70
4A.3	473	3.2 ns	0.21	468	2.3 ns	0.17
4A.4	466	3.6 ns	0.15	478	2.9 ns	0.30
4A.5	502	33.7 μ s	0.48	490	12.4 μ s	0.15
4A.6	531	19.7 μ s	0.41	529	32.7 μ s	0.12
4A.7	515	44.5 μ s	0.27	551	93.3 μ s	0.17
4A.8	541	15.6 μ s	0.75	510	17.9 μ s	0.12
4A.9	537	47.1 μ s	0.37	530	30.1 μ s	0.16
4A.10	541	22.2 μ s	0.91	541	9.7 μ s	0.14

Note: λ_{em} = Emission maximum; τ_{avg} = Average lifetime. LE = Locally excited state (centred around 485 nm); PLQY = Photoluminescence quantum yield.

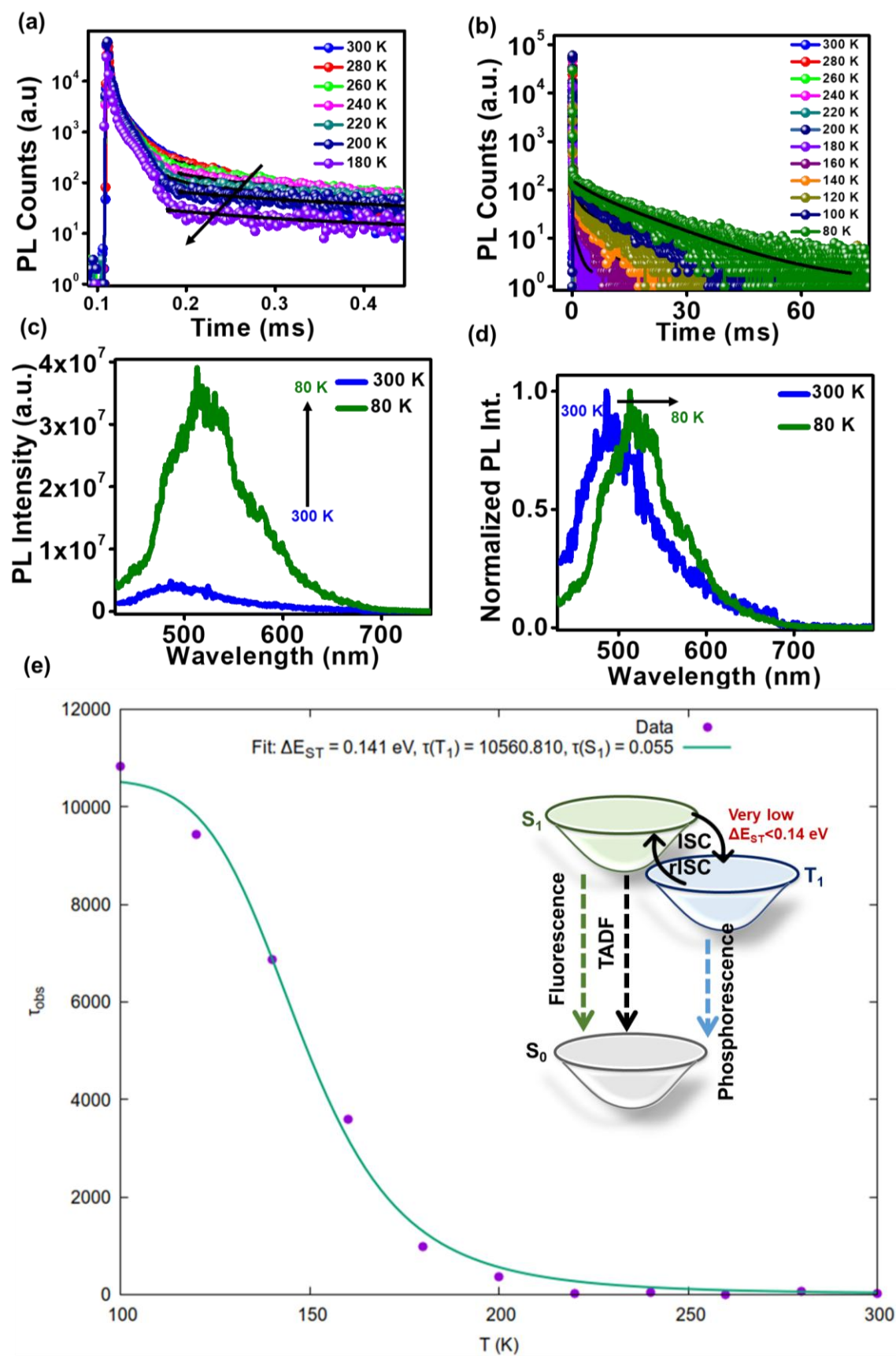


Figure 4A.5. (a) Selected temperature-dependent (300-180 K) PL decay profile of complex 4A.5 collected at 490 nm, (b) Full range temperature-dependent PL decay profile of complex

4A.5 collected at 490 nm, (c) Temperature-dependent emission spectra of **4A.5**, (d) Normalized emission spectra of **4A.5** at 300 K and 5 K, which is red-shifted at low temperature, (e) τ_{obs} vs. temperature plot of **4A.5** (Schematic representation of TADF mechanism).

To conclusively establish the nature of the long-lived CT emission in the solid state-whether originating from thermally activated delayed fluorescence (TADF) or direct phosphorescence, we performed temperature-dependent photophysical studies on a representative complex **4A.5** (Figure 4A.5). The electronic structure thus facilitates spatially separated HOMO-LUMO character, enabling potential singlet-triplet interconversion *via* reverse intersystem crossing (rISC).

The temperature-resolved emission lifetime measurements reveal three distinct regimes when plotted against temperature, as supported by Boltzmann distribution modelling: In the high temperature regime (300 K-180 K), a careful examination of the zoomed-in lifetime axis shows that a decrease in the delayed emission lifetime is observed with decreasing temperature (Figure 4A.5a). This behaviour is a definitive hallmark of TADF, as thermal energy enables rISC from the triplet (T_1) to the singlet (S_1) manifold, thereby shortening the emission lifetime at lower temperatures. Below ~ 180 K, a sharp increase in lifetime is observed, marking a transition from TADF-dominated emission to a regime where both TADF and phosphorescence contribute (Figure 4A.5b). At temperatures below ~ 120 K, the emission becomes predominantly phosphorescent, with long-lived decay components indicating that rISC is effectively quenched. To support this interpretation, temperature-dependent steady-state emission spectra were also recorded from 300 K to 80 K (Figure 4A.5c). A clear red shift of approximately 0.13 eV (from peak maxima) is observed between the high-temperature (TADF-dominated) and low-temperature (phosphorescence-dominated) spectra. (Figure 4A.5d) This spectral shift is consistent with the energy gap between the S_1 and T_1 states. The singlet-triplet energy splitting (ΔE_{ST}) estimated from the Boltzmann distribution fit to the lifetime data yields a value of 0.14 eV, in excellent agreement with the spectral shift observed from the emission maxima (Figure 4A.5e). This convergence of lifetime-based and spectroscopic ΔE_{ST} estimates provides strong evidence that the delayed emission arises from a TADF process with efficient triplet harvesting. Furthermore, rate constants derived from photophysical modelling support this assignment. For **4A.5**, the radiative rate constants are determined as $k_r(S_1) \approx 1.8 \times 10^7 \text{ s}^{-1}$ and $k_r(T_1) \approx 0.9 \times 10^2 \text{ s}^{-1}$, values consistent with both prompt fluorescence and delayed TADF. The long-lived triplet lifetime (~ 10.6 ms) at low temperature, combined with a singlet lifetime of 55 ns, underscores the efficient thermal upconversion pathway available in this emitter.

4A.3.3. Oxygen Sensitivity

After the establishment of TADF, another particularly remarkable feature of these emitters is their outstanding solid-state stability. Even when stored in the crystalline state under ambient conditions, the complexes (**4A.2-4A.10**) retain nearly identical emission intensity and spectral features after 30 days (Figure 4A.6). This level of robustness is exceptionally rare among carbene-metal amide systems, which often suffer from degradation, and is especially noteworthy here as this represents the first demonstration of abnormal carbene-metal emitters. The persistence of their luminescence highlights not only their inherent molecular stability but also their promise for durable device applications.

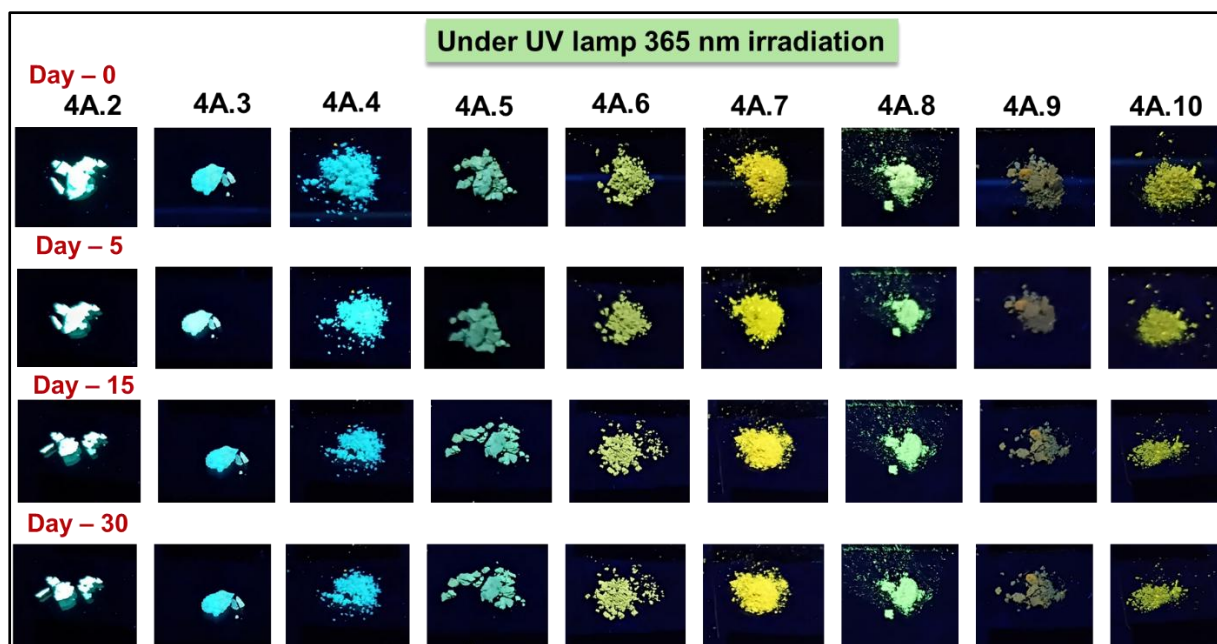


Figure 4A.6. Stability of complex **4A.2-4A.10** in ambient conditions for 30 days.

4A.3.4. Mechanochromic luminescent (MCL) properties

Stimuli-responsive luminescent materials, particularly those exhibiting mechanochromic luminescence (MCL), have attracted wide attention owing to their potential utility in optoelectronic devices, sensing, anti-counterfeiting, and information storage. MCL generally arises from mechanically induced perturbations in molecular packing or conformation, leading to distinct and reversible shifts in solid-state emission. While a variety of organic and organometallic luminogens have been documented to display such behaviour, reports on carbene-metal amide (CMA) systems remain extremely scarce, and no example has been described in the case of *a*NHC-metal amides until now.⁴³⁻⁴⁶

In this context, complexes **4A.5-4A.10** represent the first demonstration of mechanochromic luminescence in an *a*NHC-metal amide framework, and only the third example within the

entire CMA family.⁴³⁻⁴⁶ In the reported literature, Bochmann and co-workers described a CMA-based gold emitter that displays a pronounced bathochromic shift of 65 nm upon mechanical stimulation. In contrast, Tang and co-workers reported a CMA-based bimetallic gold system in which the Au-Cz complex undergoes a substantial hypsochromic shift of 60 nm, while the other derivatives (Au-CzCN, Au-Cz^tBu, and Au-CzOMe) exhibit bathochromic shifts of approximately 50 nm.⁴³⁻⁴⁵ In this case, the chloride precursors (**4A.2-4A.4**) remain mechano-inactive, highlighting the crucial role of donor-functionalization at the amide fragment in activating MCL behaviour (see the appendix figure 4A.A.34).⁴⁷ Upon application of external mechanical force (grinding), complexes **4A.5-4A.10** exhibit pronounced solid-state emission changes, whereas complexes **4A.2-4A.4** retain unchanged photophysical properties. The difference can be traced to their underlying excited-state character: chloride-based complexes (**4A.2-4A.4**) predominantly display metal-to-ligand charge transfer (MLCT) features, whereas donor-substituted derivatives (**4A.5-4A.10**) engage in significant donor-acceptor (ligand-to-ligand) charge transfer, rendering their emission more sensitive to variations in molecular conformation and packing (Figure 4A.7a-f). Crystal symmetry exerts a decisive influence on the extent of mechanochromic response. Complexes **4A.5-4A.7**, crystallising in centrosymmetric lattices, undergo only minor spectral shifts upon grinding (~15-20 nm), consistent with the resistance of densely packed centrosymmetric structures to conformational reorganisation. By contrast, the tert-butyl carbazole-based analogues **4A.8-4A.10**, which crystallise in non-centrosymmetric arrangements with looser packing, display striking red-shifts of ca. 50 nm (e.g., 510→561 nm for **4A.8**; 530→585 nm for **4A.9**; 541→592 nm for **4A.10**) (Figure 4A.7a-f). These large shifts are indicative of packing disruption, enhanced conformational flexibility, and modified intermolecular interactions under mechanical stress.⁴⁸⁻

⁴⁹ Powder X-ray diffraction (PXRD) measurements further substantiate this distinction (see the appendix figure 4A.A.35-40). For centrosymmetric complexes (**4A.5-4A.7**), the diffraction patterns remain sharp and essentially unchanged upon grinding, consistent with their small mechanochromic shifts and the structural rigidity of densely packed lattices. In contrast, the non-centrosymmetric complexes (**4A.8-4A.10**) exhibit pronounced peak broadening and intensity reduction after grinding, indicating partial amorphisation and packing rearrangements under mechanical stress. This dichotomy is well rationalised by Wallach's rule, which associates higher density and thermodynamic stability with centrosymmetric crystals, making them less susceptible to mechano-induced transformations.⁴⁸⁻⁴⁹ Taken together, these results clearly establish that (i) donor-acceptor charge transfer character is indispensable for triggering mechanochromic activity in aCMA frameworks, and (ii) crystal packing symmetry plays a

decisive role in dictating the magnitude of mechano-responsiveness. The discovery of MCL in this unprecedented class of abnormal carbene-metal amides not only broadens the functional scope of aNHC coordination chemistry but also provides a guiding principle for the development of stimuli-responsive, TADF-active luminophores with promising applications in sensing, security technologies, and optoelectronic devices.

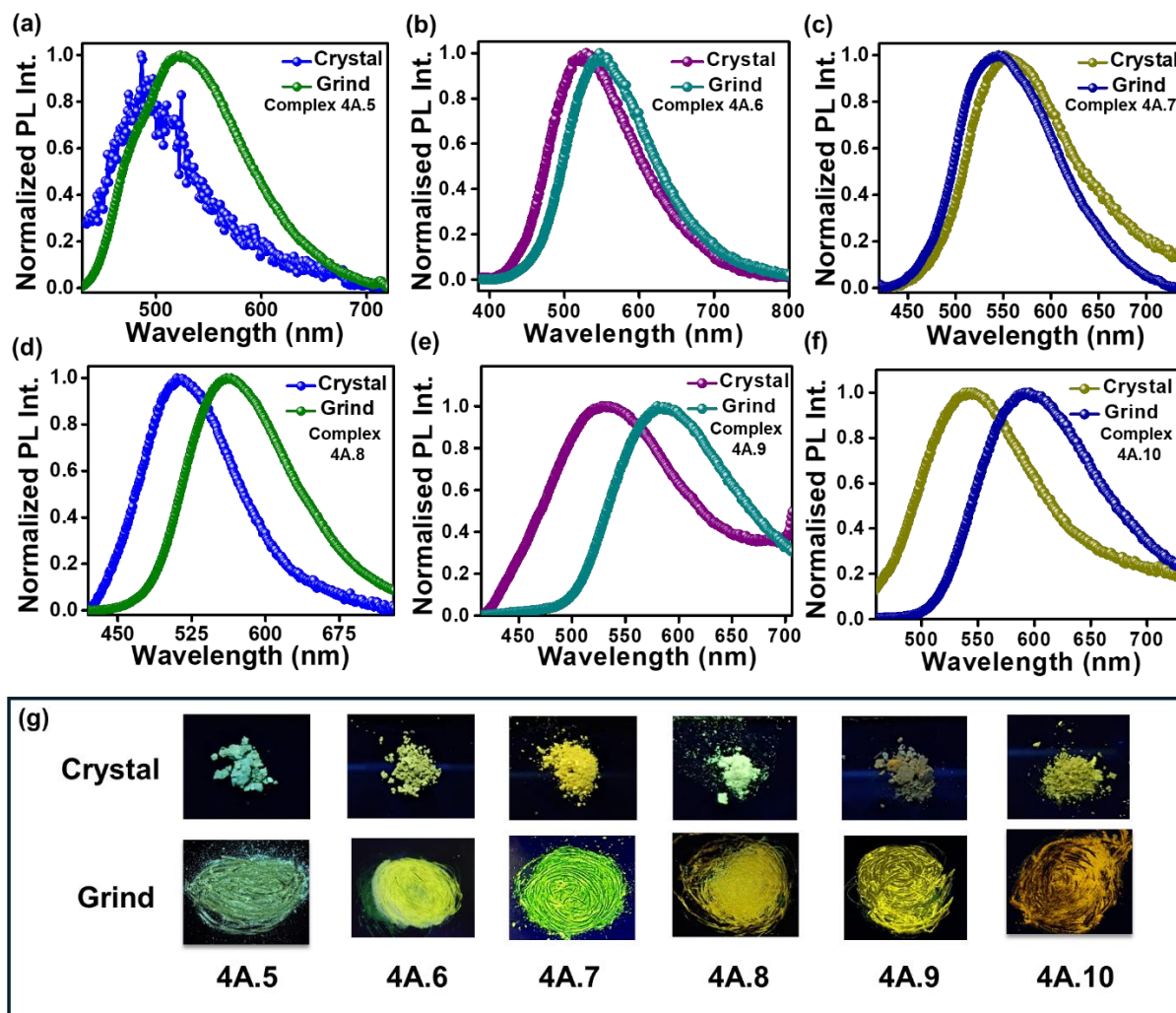


Figure 4A.7. Mechanical grinding of crystals, emission of crystal and grind recorded at ex. 375 nm (a) Complex 4A.5, (b) Complex 4A.6, (c) Complex 4A.7, (d) Complex 4A.8, (e) Complex 4A.9, (f) Complex 4A.10, and (g) Complexes 4A.5-4A.10 crystal and grind under external stimuli (photos collected using a 365 nm UV lamp).

4A.3.5 Fabrication of phosphor-converted LED (pc-LED)

To evaluate the practical potential of these abnormal carbene-metal amide emitters, we fabricated phosphor-converted LEDs (pc-LEDs) using complexes 4A.5-4A.10 as emissive layers (see the appendix figure 4A.A.41). This approach, although simplified in construction,

provides an efficient means of testing the performance and stability of new luminophores under device-relevant conditions before advancing to full OLED architectures. Inorganic InGaN UV-LED chips ($\lambda_{\text{em}} = 390\text{--}395\text{ nm}$) were coated with dichloromethane solutions of the complexes in the presence of PMMA host, yielding bright greenish-yellow to yellow emissions upon electrical excitation at 3 V (Figure 4A.8a-c).²⁶ The emitted colours directly correspond to the characteristic charge-transfer states of the complexes, confirming effective energy conversion from the inorganic UV source. Such pc-LED demonstrations serve as a practical first validation of electroluminescent viability for NHC-based CMA. The fact that the essential photophysical features—high photoluminescence quantum yields in PMMA host, thermally activated delayed fluorescence (TADF) with efficient triplet harvesting preserved under operating device conditions—underscores the strong translation of their fundamental properties into functional light-emitting platforms.

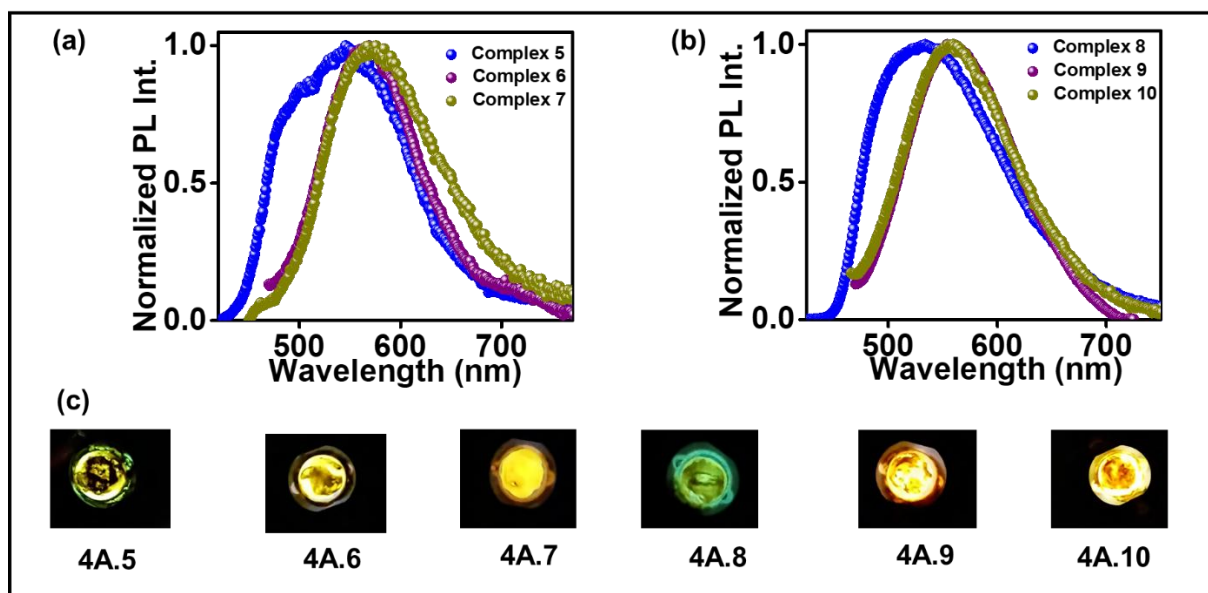


Figure 4A.8. (a) Emission spectra of fabricated c-LEDs of complex 4A.5-4A.7, (b) Emission spectra of fabricated c-LEDs of complex 4A.8-4A.10, (c) Emission glow of InGaN UV-LED chip, complex 4A.5-4A.10 under 3 V bias.

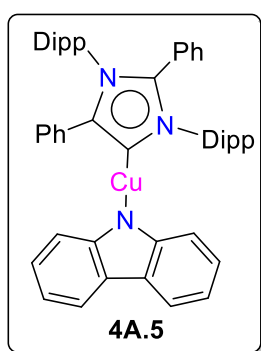
4A.4 Conclusion

In conclusion, herein, abnormal carbene-metal amides are defined as a novel family of efficient and air-stable TADF emitters. Solution-state complexes exhibit dual LE/CT emissions with long-lived delayed components, exceptionally small singlet-triplet gaps ($\Delta E_{\text{ST}} \approx 0.14\text{ eV}$), highly high radiative decay rates [$k_{\text{r}}(\text{S}_1) \approx 1.8 \times 10^7\text{ s}^{-1}$], and near-unity quantum yields (up to 0.97 in toluene, 0.91 in PMMA), attesting efficient triplet harvesting. In the solid state, they are donor-acceptor tunable, mechanochromic luminescent, and possess exceptional crystalline

stability, retaining intact emission for more than 30 days under ambient conditions, a scarce quality in carbene-metal chemistry. Initial phosphor-converted LED prototypes also support their utility. This work is the first to report emission and mechanochromic luminescence for abnormal carbene-metal amides and demonstrates unequivocal design rules for stimuli-induced TADF luminophores. By combining exceptional intrinsic efficiency with long-term stability, these air-stable complexes present a more sustainable route toward next-generation OLEDs, sensing, and solid-state lighting.

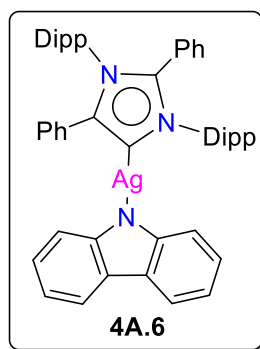
4A.5 Synthesis of 4A.5-4A.10.

4A.5.1. Synthesis of complex 4A.5.



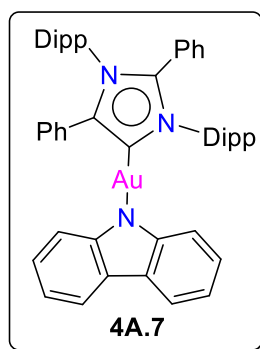
in THF (15 mL), a solution of carbazole (1 equiv., 0.50 mmol, 83.60 mg) and KO^tBu (1.1 equiv., 0.55 mmol, 61.71 mg) in THF (15 mL) was added. The solution was stirred for 12 h and was removed under vacuum to yield a pale-yellow solid. Then, 30 ml of DCM was added, and the resulting solution was filtered through a sintered glass frit under an argon atmosphere. Colourless single crystals suitable for X-ray analysis were grown in a THF and pentane mixture at room temperature.

Yield: 85 %. M.P. 230-245 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 7.6 Hz, 2H, aromatic C-H), 7.76 – 7.66 (m, 3H, aromatic C-H), 7.54 (t, *J* = 7.8 Hz, 1H, aromatic C-H), 7.41 (d, *J* = 7.8 Hz, 2H, aromatic C-H), 7.39 – 7.34 (m, 3H, aromatic C-H), 7.27 (s, 1H, aromatic C-H), 7.26 (s, 2H, aromatic C-H), 7.13 (dd, *J* = 14.4, 7.3 Hz, 4H, aromatic C-H), 7.04 – 6.93 (m, 4H, aromatic C-H), 6.86 (d, *J* = 8.1 Hz, 2H, aromatic C-H), 2.82 (dt, *J* = 13.5, 6.7 Hz, 2H, CH(CH₃)₂), 2.71 (dt, *J* = 13.4, 6.7 Hz, 2H, CH(CH₃)₂), 1.40 (d, *J* = 6.7 Hz, 6H, CH(CH₃)₂), 1.05 (d, *J* = 6.9 Hz, 6H, CH(CH₃)₂), 0.89 (dd, *J* = 9.4, 6.9 Hz, 12H, CH(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃) δ 160.01 (s, Cu-C, C≡N), 149.37 (s, aromatic C), 144.04 (s, aromatic C), 143.54 (s, aromatic C), 140.39 (s, aromatic C), 135.42 (s, aromatic C), 130.60–129.80 (m, aromatic C), 129.44 (d, *J* = 7.0 Hz, aromatic C), 128.40 (s, aromatic C), 128.10 (s, aromatic C), 127.36 (d, *J* = 13.3 Hz), 127.09 (s, aromatic C), 124.34 (s, aromatic C), 123.86 (s, aromatic C), 123.00 (s, aromatic C), 122.63 (s, aromatic C), 121.84 (s, aromatic C), 118.19 (s, aromatic C), 113.86 (s, aromatic C), 113.57 (s, aromatic C), 28.06 (s, CH(CH₃)₂), 27.68 (s, CH(CH₃)₂), 24.70 (s, CH(CH₃)₂), 22.76 (s, CH(CH₃)₂), 22.45 (s, CH(CH₃)₂), 21.67 (s, CH(CH₃)₂). HRMS C₅₁H₅₂CuN₃: Calculated *m/z* 769.3457; Observed *m/z* 770.7689 [M+1]⁺.

4A.5.2. Synthesis of complex 4A.6. Over a stirred solution of **4A.3** (0.50 mmol, 342.05 mg)

in THF (15 mL), a solution of carbazole (1 equiv., 0.50 mmol, 83.60 mg) and KO^tBu (1.1 equiv., 0.55 mmol, 61.71 mg) in THF (15 mL) was added. The solution was stirred for 12 h, and the solvent was removed under vacuum to yield a pale-yellow solid. Then, 30 ml of DCM was added, and the resulting solution was filtered through a sintered glass frit under an argon atmosphere. Colourless single crystals suitable for X-ray analysis were grown in THF and pentane mixture at room

temperature. Yield: 75 %. M.P. 250-270 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.7 Hz, 2H, aromatic C-H), 7.63 (dd, *J* = 9.1, 6.2 Hz, 3H, aromatic C-H), 7.53 (t, *J* = 7.8 Hz, 1H, aromatic C-H), 7.44 – 7.30 (m, 6H, aromatic C-H), 7.24 (s, 2H, aromatic C-H), 7.14 (dd, *J* = 18.1, 7.9 Hz, 4H, aromatic C-H), 7.06 – 6.93 (m, 6H, aromatic C-H), 2.79 (dt, *J* = 13.6, 6.8 Hz, 2H CH(CH₃)₂), 2.68 (dq, *J* = 13.5, 6.7 Hz, 2H, CH(CH₃)₂), 1.43 (d, *J* = 6.7 Hz, 6H, CH(CH₃)₂), 1.02 (d, *J* = 6.9 Hz, 6H, CH(CH₃)₂), 0.88 (t, *J* = 6.9 Hz, 12H, CH(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃) δ 162.75 (d, *J* = 15.5 Hz, Ag-C, C≡N), 160.62 (d, *J* = 15.5 Hz, Ag-C, C≡N), 149.76 (d, *J* = 4.3 Hz, aromatic C), 144.06 (dd, *J* = 24.1, 10.0 Hz, aromatic C), 140.39 (d, *J* = 16.4 Hz, aromatic C), 135.71 (s, aromatic C), 130.24 (s, aromatic C), 130.06–129.44 (m, aromatic C), 128.43 (s, aromatic C), 128.07 (s, aromatic C), 127.36 (d, *J* = 5.7 Hz, aromatic C), 124.70 (s, aromatic C), 124.37 (s, aromatic C), 123.90 (s, aromatic C), 122.99 (d, *J* = 4.6 Hz, aromatic C), 122.66 (s, aromatic C), 121.90 (s, aromatic C), 119.19 (s, aromatic C), 118.33 (s, aromatic C), 113.65 (s, aromatic C), 113.36 (s, aromatic C), 109.54 (s, aromatic C), 27.97 (s, CH(CH₃)₂), 27.69 (s, CH(CH₃)₂), 24.75 (s, CH(CH₃)₂), 22.78 (s, CH(CH₃)₂), 22.49 (s, CH(CH₃)₂), 21.76 (s, CH(CH₃)₂). HRMS C₅₁H₅₂AgN₃: Calculated *m/z* 813.3212; Observed *m/z* 813.3198[M]⁺.

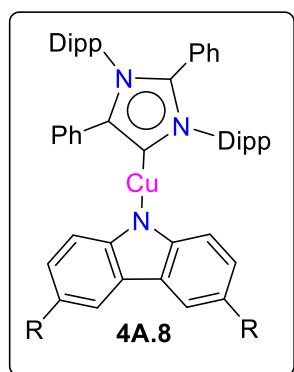
4A.5.3. Synthesis of complex 4A.7. Over a stirred solution of **4A.4** (0.50 mmol, 386.60 mg)

in THF (15 mL), a solution of carbazole (1 equiv., 0.50 mmol, 83.60 mg) and KO^tBu (1.1 equiv., 0.55 mmol, 61.71 mg) in THF (15 mL) was added. The solution was stirred for 12 h, and the solvent was removed under vacuum to yield a pale-yellow solid. Then, 30 ml of DCM was added, and the resulting solution was filtered through a sintered glass frit under an argon atmosphere. Colourless single crystals suitable for X-ray analysis were grown in THF and pentane mixture at room

temperature. Yield: 80 %. M.P. 250-270 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.80 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J*

= 7.8 Hz, 2H), 7.34 (s, 3H), 7.24 (d, $J = 7.8$ Hz, 3H), 7.18 – 7.09 (m, 6H), 7.00 (d, $J = 7.5$ Hz, 2H), 6.95 (ddd, $J = 7.8, 6.4, 1.6$ Hz, 2H), 2.79 (dt, $J = 13.6, 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.70 (dt, $J = 13.5, 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.48 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.00 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.86 (dd, $J = 6.7, 4.0$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (101 MHz, CDCl_3) δ 156.50 (s, Au-C, $\text{C}\equiv\text{N}$), 148.85 (s, aromatic C), 144.08 (d, $J = 13.4$ Hz, aromatic C), 143.03 (s, aromatic C), 138.47 (s, aromatic C), 134.95 (s, aromatic C), 130.35 (s, aromatic C), 130.01 – 129.25 (m, aromatic C), 128.90 (s, aromatic C), 128.48 (d, $J = 10.8$ Hz, aromatic C), 127.22 (d, $J = 16.2$ Hz, aromatic C), 124.39 (s, aromatic C), 123.81 (s, aromatic C), 122.71 (s, aromatic C), 122.38 (s, aromatic C), 121.96 (s, aromatic C), 118.21 (s, aromatic C), 114.03 (s, aromatic C), 113.04 (s, aromatic C), 28.13 (s, $\text{CH}(\text{CH}_3)_2$), 27.70 (s, $\text{CH}(\text{CH}_3)_2$), 24.47 (s, $\text{CH}(\text{CH}_3)_2$), 22.76 (s, $\text{CH}(\text{CH}_3)_2$), 22.48 (s, $\text{CH}(\text{CH}_3)_2$), 21.83 (s, $\text{CH}(\text{CH}_3)_2$). HRMS $\text{C}_{51}\text{H}_{52}\text{AuN}_3$: Calculated m/z 903.3827; Observed m/z 904.3902 $[\text{M}+1]^+$.

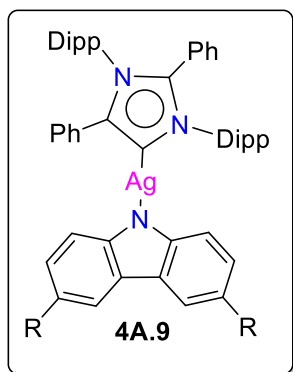
4A.5.4. Synthesis of complex 4A.8. Over a stirred solution of **4A.2** (0.50 mmol, 319.89 mg)



in THF (15 mL), a solution of tertiary butyl carbazole (1 equiv., 0.50 mmol, 139.71 mg) and KO^tBu (1.1 equiv., 0.55 mmol, 61.71 mg) in THF (15 mL). The solution was stirred for 12 h, and the solvent was removed under vacuum to yield a pale-yellow solid. Then, 30 ml of toluene was added, and the resulting solution was filtered through a sintered glass frit under an argon atmosphere. Colourless single crystals suitable for X-ray analysis were grown in toluene at room temperature. Yield: 85 %. M.P. 295-310 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (s, 2H, aromatic C-H), 7.68 (dd, $J = 13.1, 5.5$ Hz, 3H, aromatic C-H), 7.52 (t, $J = 7.7$ Hz, 1H, aromatic C-H), 7.41 (d, $J = 7.8$ Hz, 2H, aromatic C-H), 7.35 (s, 3H, aromatic C-H), 7.24 (s, 3H, aromatic C-H), 7.12 (t, $J = 8.9$ Hz, 4H, aromatic C-H), 6.99 (d, $J = 7.7$ Hz, 2H, aromatic C-H), 6.78 (d, $J = 8.5$ Hz, 1H, aromatic C-H), 2.80 (dt, $J = 13.0, 6.5$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.70 (dt, $J = 13.2, 6.5$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.48 – 1.38 (m, 24H, $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$), 1.04 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.87 (dd, $J = 9.4, 7.1$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (101 MHz, CDCl_3) δ 160.36 (s, Cu-C, $\text{C}\equiv\text{N}$), 147.96 (s, aromatic), 144.04 (d, $J = 11.3$ Hz, aromatic), 143.35 (s, aromatic), 140.34 (s, aromatic), 135.80 (s, aromatic), 135.40 (s, aromatic), 130.09 (d, $J = 10.2$ Hz, aromatic), 129.35 (s, aromatic), 128.44 (s, aromatic), 128.12 (s, aromatic), 127.33 (d, $J = 17.0$ Hz, aromatic), 127.02 (s, aromatic), 124.30 (s, aromatic), 123.83 (s, aromatic), 122.64 (s, aromatic), 122.42 (s, aromatic), 119.54 (s, aromatic), 113.90 (s, aromatic), 113.00 (s, aromatic), 109.00 (s, aromatic), 33.39 (s, $\text{C}(\text{CH}_3)_3$), 31.32 (s, $\text{C}(\text{CH}_3)_3$),

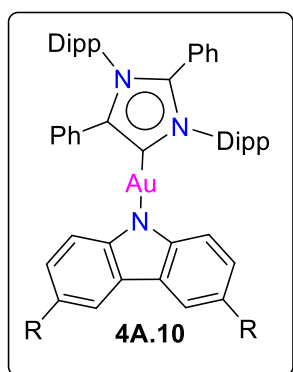
31.01 (s, C(CH₃)₃), 28.08 (s, CH(CH₃)₂), 27.66 (s, CH(CH₃)₂), 24.74 (s, CH(CH₃)₂), 22.77 (s, CH(CH₃)₂), 22.46 (s, CH(CH₃)₂), 21.66 (s, CH(CH₃)₂). HRMS C₅₉H₆₈CuN₃: Calculated m/z 881.4709; Observed m/z 881.4612 [M]⁺.

4A.5.5. Synthesis of complex 4A.9 Over a stirred solution of **4A.3** (1 equiv., 0.50 mmol,



342.05 mg) in THF (15 mL), a solution of tertiary butyl carbazole (1 equiv., 0.50 mmol, 139.71 mg) and KO^tBu (1.1 equiv., 0.55 mmol, 61.71 mg) in THF (15 mL) was added. The solution was stirred for 12 h and removed under vacuum to yield a greyish-white solid. Then, 30 ml of toluene was added, and the resulting solution was filtered through a sintered glass frit under an argon atmosphere. Colourless single crystals suitable for X-ray analysis were grown in toluene at room temperature. Yield: 75 %. M.P. 260-270 °C. ¹H NMR (400 MHz,

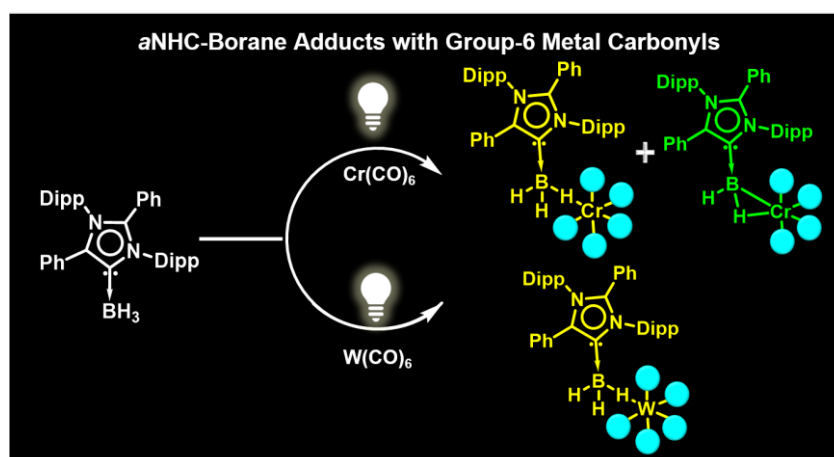
CDCl₃) δ 8.02 (d, J = 1.8 Hz, 2H, aromatic C-H), 7.60 (dd, J = 10.2, 5.3 Hz, 3H, aromatic C-H), 7.51 (t, J = 7.8 Hz, 1H, aromatic C-H), 7.35 (d, J = 7.8 Hz, 2H, aromatic C-H), 7.32 – 7.28 (m, 3H, aromatic C-H), 7.23 (d, J = 7.8 Hz, 3H, aromatic C-H), 7.20 (d, J = 2.0 Hz, 1H, aromatic C-H), 7.18 (d, J = 2.0 Hz, 1H, aromatic C-H), 7.11 (t, J = 7.9 Hz, 2H, aromatic C-H), 6.97 (t, J = 8.3 Hz, 4H, aromatic C-H), 2.76 (dt, J = 13.6, 6.8 Hz, 2H, CH(CH₃)₂), 2.68 (dt, J = 13.5, 6.7 Hz, 2H, CH(CH₃)₂), 1.47 – 1.39 (m, 24H, CH(CH₃)₂, C(CH₃)₃), 1.00 (d, J = 6.9 Hz, 6H, CH(CH₃)₂), 0.86 (dd, J = 8.5, 6.9 Hz, 12H, CH(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃) δ 162.99 (d, J = 15.1 Hz, Ag-C, C≡N), 160.89 (d, J = 15.1 Hz, Ag-C, C≡N), 148.40 (d, J = 4.5 Hz, aromatic C), 144.00 (s, aromatic C), 143.77 (s, aromatic C), 135.87–135.44 (m, aromatic C), 130.10 (d, J = 16.4 Hz, aromatic C), 129.71 (s, aromatic C), 129.49 (d, J = 3.4 Hz, aromatic C), 128.42 (s, aromatic C), 128.08 (s, aromatic C), 127.27 (dd, J = 9.8, 6.1 Hz, aromatic C), 124.30 (d, J = 6.2 Hz, aromatic C), 123.81 (d, J = 9.2 Hz, aromatic C), 122.91–122.51 (m, aromatic C), 122.40 (s, aromatic C), 119.59 (s, aromatic C), 114.02 (s, aromatic C), 112.74 (s, aromatic C), 33.41 (s, C(CH₃)₃), 31.35 (s, C(CH₃)₃), 31.01 (s, C(CH₃)₃), 27.96 (s, CH(CH₃)₂), 27.66 (s, CH(CH₃)₂), 24.80 (s, CH(CH₃)₂), 22.79 (s, CH(CH₃)₂), 22.49 (s, CH(CH₃)₂), 21.76 (s, CH(CH₃)₂). HRMS C₅₉H₆₈AgN₃: Calculated m/z 925.4464; Observed m/z 925.4514 [M]⁺.

4A.5.6. Synthesis of complex 4A.10. Over a stirred solution of **4A.4** (0.50 mmol, 386.60 mg)

in THF (15 mL), a solution of tertiary butyl carbazole (1 equiv., 0.50 mmol, 139.71 mg) and KO^tBu (1.1 equiv., 0.55 mmol, 61.71 mg) in THF (15 mL) was added. The solution was stirred for 12 h. The solvent was removed under vacuum to yield a pale-yellow solid. Then, 30 ml of toluene was added, and the resulting solution was filtered through a sintered glass frit under an argon atmosphere. Colourless single crystals suitable for X-ray analysis were grown in toluene at room temperature. Yield: 80 %. M.P. 320-337 °C. ¹H NMR (401 MHz,

CDCl₃) δ 8.02 (s, 2H, aromatic C-H), 7.83 – 7.77 (m, 2H, aromatic C-H), 7.65 (t, *J* = 7.8 Hz, 1H, aromatic C-H), 7.51 (t, *J* = 7.8 Hz, 1H, aromatic C-H), 7.38 (d, *J* = 7.9 Hz, 2H, aromatic C-H), 7.33 (dd, *J* = 3.7, 2.4 Hz, 3H, aromatic C-H), 7.27 – 7.22 (m, 4H, aromatic C-H), 7.20 (ddd, *J* = 8.4, 3.5, 1.9 Hz, 2H, aromatic C-H), 7.11 (t, *J* = 7.8 Hz, 2H, aromatic C-H), 7.07 (dd, *J* = 6.9, 5.2 Hz, 2H, aromatic C-H), 7.00 (d, *J* = 8.3 Hz, 2H, aromatic C-H), 2.84 – 2.74 (m, 2H, CH(CH₃)₂), 2.70 (dt, *J* = 13.4, 6.7 Hz, 2H, CH(CH₃)₂), 1.50 (d, *J* = 6.7 Hz, 6H, CH(CH₃)₂), 1.45 – 1.41 (m, 18H, C(CH₃)₃), 1.01 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 0.86 (t, *J* = 5.8 Hz, 12H, CH(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃) δ 158.12 (s, Au-C, CCN), 148.48 (s, aromatic C), 145.12 (d, *J* = 2.3 Hz, aromatic C), 143.92 (s, aromatic C), 139.50 (s, aromatic C), 137.33 (s, aromatic C), 136.01 (s, aromatic C), 131.31 (s, aromatic C), 130.98 (s, aromatic C), 130.55 (s, aromatic C), 129.99 (s, aromatic C), 129.56 (d, *J* = 12.2 Hz, aromatic C), 128.23 (d, *J* = 13.1 Hz, aromatic C), 125.40 (s, aromatic C), 124.84 (s, aromatic C), 123.50 (d, *J* = 15.2 Hz, aromatic C), 120.71 (s, aromatic C), 115.01 (s, aromatic C), 113.22 (s, aromatic C), 34.46 (s, C(CH₃)₃), 32.35 (s, C(CH₃)₃), 29.19 (s, CH(CH₃)₂), 28.74 (s, CH(CH₃)₂), 25.57 (s, CH(CH₃)₂), 23.83 (s, CH(CH₃)₂), 23.54 (s, CH(CH₃)₂), 22.89 (s, CH(CH₃)₂). HRMS C₅₉H₆₈AuN₃: Calculated *m/z* 1015.5079; Observed *m/z* 1015.5053 [M]⁺.

Chapter 4B: Reactivity of *a*NHC-Borane Adducts with Group-6 Metal Carbonyls



Adapted from: **R. Akhtar**, R. Panday, S. Khan* Reactivity of *a*NHC-Borane Adducts with Group-6 Metal Carbonyls. (*Manuscript under preparation*)

4B.1 Objective and motivation

The reaction of an abnormal N-heterocyclic carbene (*a*NHC) with $\text{BH}_3\cdot\text{SMe}_2$ affords the borane adduct $\text{aNHC}\cdot\text{BH}_3$ (**1**), which serves as a precursor for coordination to group-6 metal carbonyls under photolytic conditions. Photoreaction of $\text{Cr}(\text{CO})_6$ with **4B.1** produces the B–H σ -bond-coordinated complex $[\text{Cr}(\text{CO})_5(\eta^1\text{-H}_3\text{B}\cdot\text{aNHC})]$ (**4B.2a**) as the major product, along with a minor hydride species, $[(\text{CO})_4\text{CrH}(\text{H}_3\text{B}\cdot\text{aNHC})]$ (**4B.2b**). Under analogous conditions, $\text{Mo}(\text{CO})_6$ undergoes decomposition, whereas $\text{W}(\text{CO})_6$ cleanly generates the tungsten analogue $[\text{W}(\text{CO})_5(\eta^1\text{-H}_3\text{B}\cdot\text{aNHC})]$ (**4B.3**). Single-crystal X-ray diffraction confirms that in all complexes, the $\text{aNHC}\cdot\text{BH}_3$ fragment binds through a B–H–M three-centre two-electron interaction with negligible direct B–M bonding. Minimal metal-to-borane π -backdonation is observed, highlighting the primarily σ -donor nature of the borane coordination. These results expand the understanding of *a*NHC-stabilised borane interactions with low-valent transition metals.

4B.2 Introduction

The synthesis and investigation of transition-metal complexes featuring boron-centred ligands have attracted significant attention over the past decades.⁵⁰⁻⁵³ Numerous structural motifs, including σ -borane/borate,⁵⁴⁻⁵⁶ boryl,^{50, 53} borylene,^{51, 57} and metallaborane frameworks,⁵⁸⁻⁶⁰ have been isolated and characterised. Since Hartwig's seminal report of the first σ -B–H complex of titanium,⁶¹ substantial efforts have focused on elucidating the interactions between three- and four-coordinate boranes/borates and transition metals.⁶²⁻⁶⁷ These σ -borane complexes, defined by a 3-centre-2-electron B–H–M interaction, are now considered as key intermediates in C–H borylation,⁶⁸ hydroboration,⁶⁹⁻⁷⁰ and amine-borane dehydrogenation.⁷¹⁻⁷² Braunschweig, Tobita, and Shimoji *et al.* have shown that Lewis base-stabilised boranes (BH_3 adducts) can also coordinate to transition metals, forming complexes such as $[\text{M}(\text{CO})_5(\eta^1\text{-H}_3\text{B-L})]$ ($\text{M} = \text{Mo}, \text{Cr}, \text{W}$; $\text{L} = \text{IME}_2, \text{IME}_4, \text{I}^t\text{Pr}_2\text{Me}_2, \text{NMe}_3, \text{PMe}_3, \text{PPh}_3$).⁶⁴⁻⁶⁷ The complementary interaction between the strong Lewis basicity of NHCs and the Lewis acidity of boranes supports the ease of adduct formation, analogous to classical borane complexes with ethers, amines, sulfides, or phosphines.⁷³

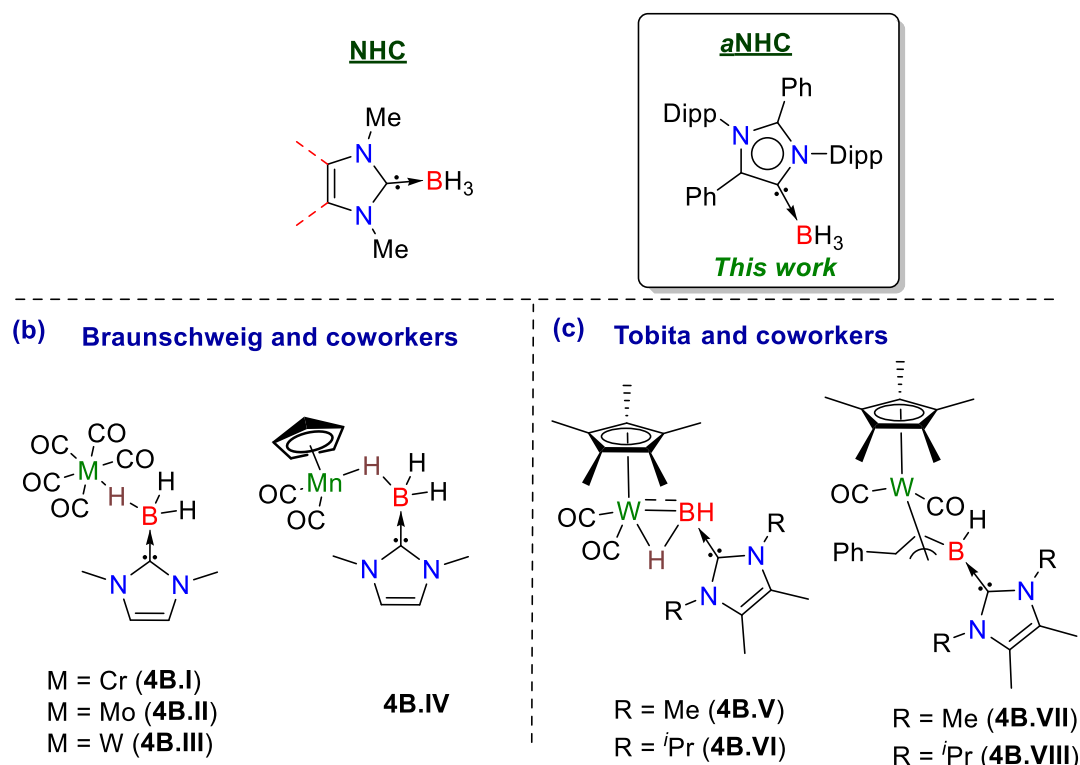
(a) Examples of carbene-BH₃ adducts reacted with group-6 metal carbonyls

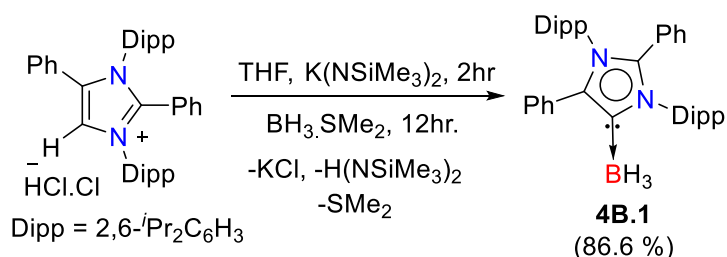
Chart 4B.1: (a) Selected examples of carbene-borane complexes; (b) Reported examples of NHC-borane reactivity with group-6 carbonyl complexes.

However, the exceptionally strong σ -donor ability of NHC ligands imparts far greater stability to NHC-borane adducts compared with those formed from conventional donors. Still, σ -borane complexes remain relatively underexplored, largely due to the limited availability of a straightforward and efficient synthetic route.⁷³⁻⁷⁶ Steric and electronics play a huge role while isolating the BH₃ adduct, as ^{Me}CAAC (cyclic alkyl amino carbene) and MAC (monosubstituted aminocarbene) undergo the side carbene insertion reaction into the B-H bond upon complex formation.⁷⁷ Hence, the reports on such complexes are limited.⁴³⁻⁴⁵ Only the N-heterocyclic carbene-stabilized BH₃ complexes are known to react with group 6 carbonyl complexes mentioned in Chart 1. Although there are several classes of carbenes that have been isolated and explored for various reactivity studies,⁷³⁻⁷⁴ the exploration of group-6 metal carbonyls to form B-H-M bonded compounds is only known for NHCs.⁶⁴⁻⁶⁷ Motivated by this observation, we sought to investigate how an abnormal carbene (*a*NHC), an unusual class of carbenes distinguished by their strong σ -donor ability, reacts with group 6 metal carbonyls. Our aim was to explore whether an *a*NHC could give rise to complexes featuring a three-centre, two-electron (3c-2e) B-H-M bonding interaction. Interestingly, *a*NHCs have not yet been

employed for the isolation of such complexes, and their enhanced σ -donor strength makes them particularly well-suited for stabilizing electron-deficient boron centers. This, in turn, can facilitate the formation and persistence of highly reactive σ -borane complexes. Thus, in this work, we have explored the reaction of group-6 metal carbonyls with $a\text{NHC}\cdot\text{BH}_3$ under photolysis, which resulted in the formation of σ -borane complexes of chromium (**4B.2**) and tungsten (**4B.3**). Our results are presented herein.

4B.3 Results and Discussion

To initiate the investigation, we first isolated the $a\text{NHC}\cdot\text{BH}_3$ adduct (**4B.1**) through the reaction of in-situ-generated $a\text{NHC}$ with $\text{BH}_3\cdot\text{SMe}_2$ (Scheme 4B.1).⁷⁸ Colourless crystals of **4B.1**, suitable for X-ray diffraction studies, were grown from a saturated solution of **4B.1** in toluene at room temperature (see SI for details).



Scheme 4B.1: Synthesis of **4B.1**.

The $^{11}\text{B}\{^1\text{H}\}$ spectrum of **4B.1** displays a quartet that resonates between δ -34.33 (q) ppm, which matches well with the previously reported $\text{NHC}\rightarrow\text{BH}_3$ ($\text{NHC} = \text{IMe}_4$) adduct (δ -37.2 (q) ppm).⁶⁷ The complex **4B.1** crystallises in the orthorhombic *Aea2* space group. The molecular structure of **4B.1** (Figure 4B.1) discloses that the B1-C1 bond distance is 1.62(1) Å, which is slightly elongated than the B-C bond distance of $\text{NHC}\rightarrow\text{BH}_3$ adduct (1.600(4) Å).²⁹

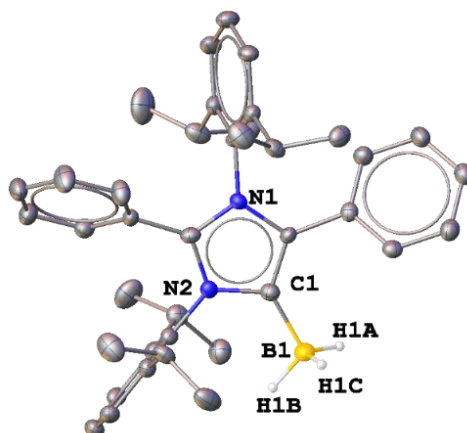
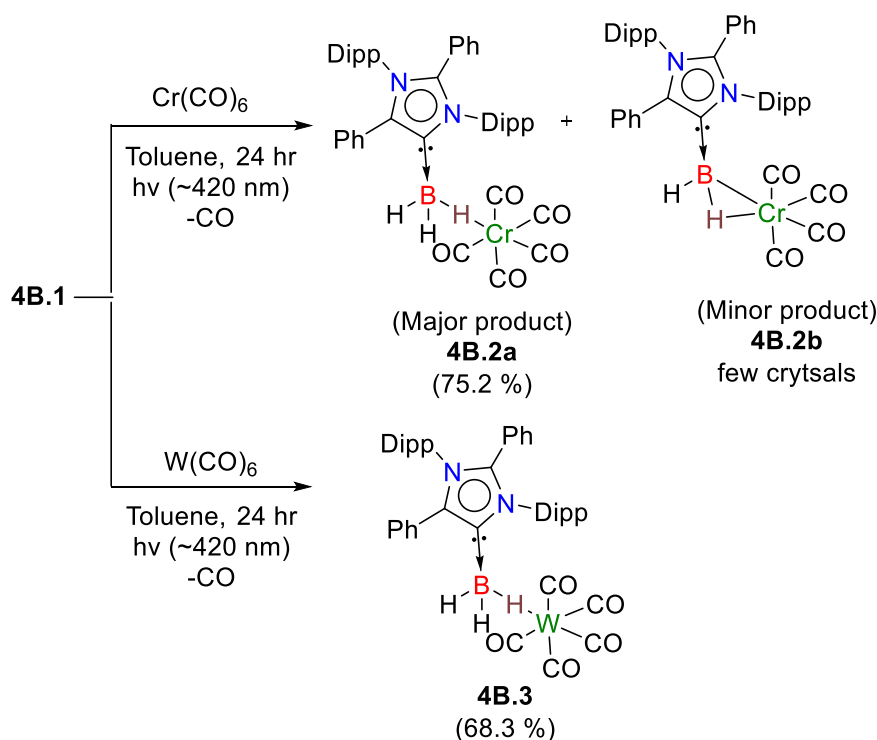


Figure 4B.1. Molecular structures of **4B.1**. Anisotropic displacement parameters are depicted at the 50 % probability level. Disordered atoms and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): C1-B1 1.62(1), C2-C1 1.395(9), N2-C1 1.410(8), B1-H1C 1.12(9), B1-H1A 1.16(7), B1-H1B 1.12(8); C2-C1-B1 132.9(6), N2-C1-B1 122.7(6).



Scheme 4B.2: Synthesis of **4B.2a**, **4B.2b**, and **4B.3**.

Furthermore, irradiation of **4B.1** with $[\text{Cr(CO)}_6]$ in toluene yielded two distinct complexes: $[\text{Cr(CO)}_5(\eta^1\text{-H}_3\text{B-}a\text{NHC})]$ (**4B.2a**) and $[(\text{CO})_4\text{CrH(HB-}a\text{NHC)}]$ (**4B.2b**), which were isolated as orange and red crystalline solids, respectively (**Scheme 4B.2**). The solid-state structures of **4B.2a** and **4B.2b** were validated by single-crystal X-ray diffraction analysis (**Figure 4B.2**). The ^1H NMR spectrum of **4B.2a** exhibits a significant signal broadening, making it difficult to deconvolute the resonances. However, a broad peak for BH_3 was observed in the ^1H NMR spectrum of **4B.2a** at δ -3.22 ppm, which is in good accordance with the reported complex **4B.I** (δ -3.16 ppm (br q)).⁶⁷ The ^{11}B NMR spectrum of **4B.2a** shows a peak at δ -38.16 ppm, slightly downfield shifted with respect to the complex **4B.I** (δ -42.5 ppm).⁶⁷

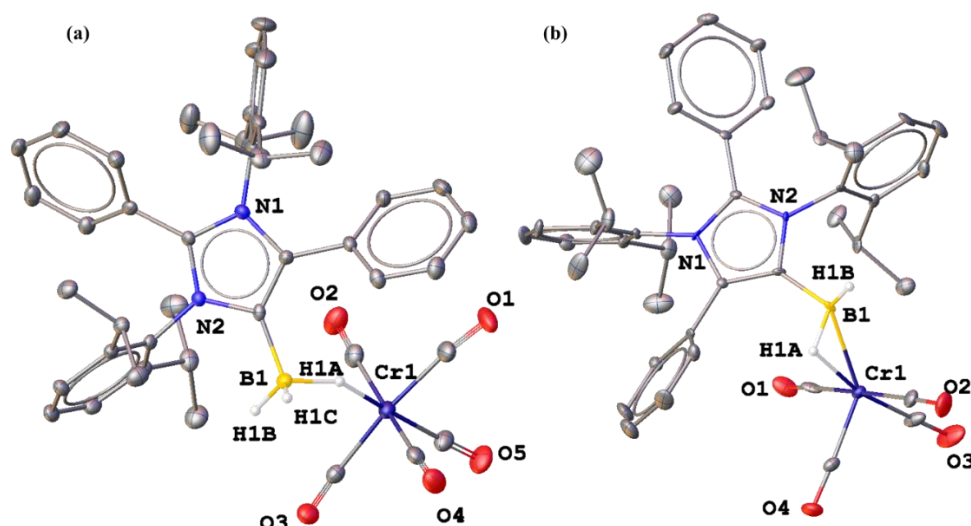


Figure 4B.2. Molecular structures of **4B.2a** (a) and **4B.2b** (b). Anisotropic displacement parameters are depicted at the 50 % probability level. Disordered atoms and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): For **4B.2a**, Cr1-H1A 1.65(4), B1-H1A 1.29(5), B1-Cr1 2.813(5), C6-B1 1.608(6); C6-B1-H1A 108(2), Cr1-H1A-B1 146(3). For **4B.2b**, C5-B1 1.618(9), B1-Cr1 2.273(7), Cr1-H1A 1.84(5), H1A-B1 1.20(5); C5-B1-H1A 110(2), Cr1-B1-C5 123.9(5), Cr1-H1A-B1 94(2).

Complex **4B.2a** crystallises in the $C2/c$ monoclinic space group and **2b** in the $P21/n$ monoclinic space group. In complex **4B.2a**, the $a\text{NHC} \rightarrow \text{BH}_3$ fragment is bound to the metal centre *via* a B-H-Cr three-centre two-electron interaction, with no significant direct B-M bonding, while metal-to-ligand π -backdonation to the borane fragment appears to be a minimum. In contrast, **4B.2b** displays direct coordination from B-Cr as observed in the molecular structure (**Figure 4B.2**). The chromium centre in **4B.2a** features a nearly ideal octahedral coordination environment with the B1-H1A-Cr1 angle of 140(2)°, which unambiguously confirms an end-on coordination mode of the borane NHC adducts. A difference in the bond lengths of the bridging and terminal B-H bonds of **4B.2a** is observed (bridging B-H bond distance is 1.24(3) Å, and both terminal B-H bond distances are 1.13(3) Å), which is due to the different coordination environment around them.²⁹ The B-C bond distance of **4B.2a** [C6-B1 = 1.608(6) Å] is similar to the B-C bond distance observed for complex **4B.I** (1.600(4) Å) and is only marginally shorter than **4B.1** (1.62(4) Å), indicating a slight contraction of the B-C bond upon coordination to the metal.⁶⁷ The B-Cr separation distance in **4B.2a** is 2.813(5) Å (B1-Cr1), which is also similar to that of **4B.I** (2.838 Å), indicating the absence of any coordination between the boron and the chromium centre. In contrast, the B1-Cr1 bond distance of **4B.2b** is 2.273(7) Å, which is significantly smaller than that of **4B.2a** and **4B.I**, supporting the

coordination between the boron and the chromium centre. Complex **4B.2b** contains one terminal and one bridged hydrogen at the boron centre, with a significant variation (bridged H1A-B1 bond distance 1.20(4) Å and terminal H1B-B1 bond distance is 1.09(5) Å).

After the successful isolation of chromium complexes, **4B.2a** and **4B.2b**, **4B.1** was treated with $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ under the same reaction conditions, respectively. In the case of molybdenum hexacarbonyl, decomposition was observed; a similar observation was also made for the previously reported analogous molybdenum complexes $[(\text{CO})_5\text{Mo}(\eta^1\text{-H}_3\text{B.L})]$ ($\text{L} = \text{IMe}_4, \text{PMe}_3, \text{PPh}_3, \text{NMe}_3$).^{64, 67} However, the irradiation of the **4B.1** and $[\text{W}(\text{CO})_6]$ in toluene afforded the desired complex $[\text{W}(\text{CO})_5(\eta^1\text{-H}_3\text{B-}a\text{NHC})]$ (**4B.3**) in 60 % yield as a yellow crystalline solid (Scheme 4B.2). The ^1H NMR of **4B.3** displays a broad peak for the BH_3 group at δ -0.82 ppm, which matches well with the reported analogous complex **4B.III** (δ -1.45 ppm (br q)).⁶⁷ The ^{11}B NMR spectrum of **4B.3** shows a peak at δ -40.48 ppm, comparable to that of complex **4B.III** (δ -47.1 ppm). Complex **4B.3** crystallises in the monoclinic $C2/c$ space group (Figure 4B.3). The tungsten centre in **4B.3** features nearly an ideal octahedral coordination environment with the W-H1A-B angle of 135.2, which unambiguously confirms an end-on coordination mode of the borane- $a\text{NHC}$ adduct. Similar to complex **4B.2a**, complex **4B.3** also exhibits a clear distinction between the bridging and terminal B-H bond lengths. The bridging B-H bond measures 1.19(4) Å, whereas the terminal B-H bonds are notably shorter, at 1.11(4) and 1.13(4) Å. The B-C1 bond distance (1.613(4) Å) remains nearly unaffected by the metal coordination and is similar to those observed in free $a\text{NHC.BH}_3$ (1.62(1) Å). The B1-W1 separation distance in **4B.5** is 2.923 (4) Å (**4B.5**), which matches well with the B-W bond distance of complex **4B.III** (2.898 Å).⁶⁴⁻⁶⁷

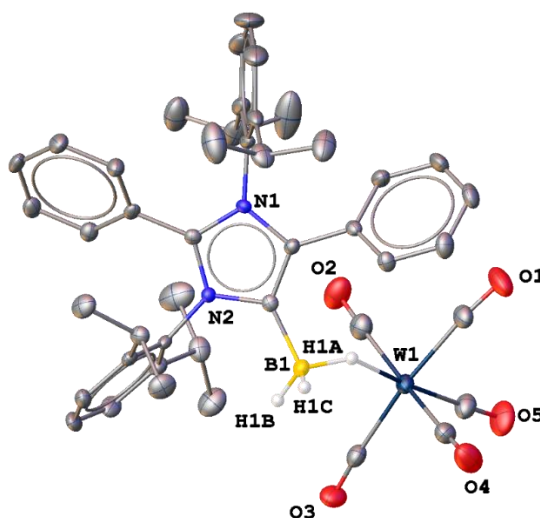


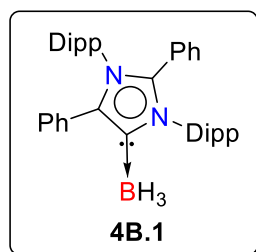
Figure 4B.3. Molecular structures of **4B.3**. Anisotropic displacement parameters are depicted at the 50 % probability level. Disordered atoms and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): For **4B.3** B1-H1A 1.19(4), H1A-W1 1.96(4), B1-C6 1.613(4), C6-N2 1.404(4), C6-C7 1.374(4), N2-C6 1.404(4); B1-H1A-W1 135(2), C6-B1-H1A 104(2).

4B.4 Conclusion

Herein, we have isolated the first series of abnormal carbene-supported several *a*NHC·BH₃ group-6 metal carbonyl complexes displaying a three-centre-two-electron B-H-M σ -bond (**4B.2a**, **4B.2b**, and **4B.3**). All the complexes are well-characterised using multinuclear NMR techniques and single-crystal X-ray diffraction studies. It is essential to note that the exploration of an *a*NHC is primarily limited to a small number of applications, especially in catalysis. This study further confirms that the strong σ -donation of an abnormal carbene can be useful in isolating such a unique bonding situation, paving the way for an *a*NHC to be utilised as a strong donor ligand.

4B.5. Synthesis of 4B.1-4B.3.

4B.5.1. Synthesis of 4B.1: Under an argon atmosphere, THF (30 mL) was added at -78 °C to

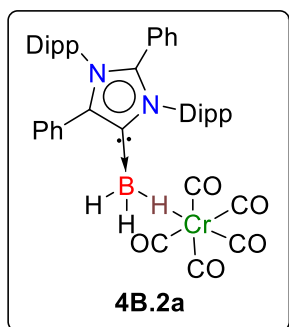


a mixture of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolium salt (308 mg, 0.50 mmol), potassium bis(trimethylsilyl)amide (200 mg, 1 mmol), and borane dimethyl sulfide (50 μ L, 0.5 mmol). After 30 min at ~ -78 °C, the mixture was warmed to room temperature and stirred for 12 h. Solvent was evaporated under reduced pressure, and the residue

was extracted with dichloromethane (3 $\times$ 20 mL). The pure colourless compound was obtained by recrystallisation from THF/pentane. Yield: 86.6 % (240 mg). M.P. 200-210 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (ddd, J = 7.4, 4.6, 2.9 Hz, 4H, aromatic C-H), 7.28 (d, J = 3.0 Hz, 2H, aromatic C-H), 7.24 – 7.15 (m, 6H, aromatic C-H), 7.02 (dd, J = 10.8, 5.2 Hz, 2H, aromatic C-H), 6.89 (dd, J = 8.6, 1.0 Hz, 4H, aromatic C-H), 2.76–2.61 (m, 8H, CH(CH₃)₂), 1.40 (d, J = 6.7 Hz, 6H, CH(CH₃)₂), 0.87 (d, J = 6.9 Hz, 6H, CH(CH₃)₂), 0.81 (dd, J = 6.7, 5.0 Hz, 12H, CH(CH₃)₂), 0.10 (s, 4H, BH₃), 0.03 (s, 1H, BH₃) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 145.10 (d, J = 1.0 Hz, aromatic C), 141.28 (s, aromatic C), 134.57 (s, aromatic C), 133.59 (s, aromatic C), 131.34 (s, aromatic C), 131.04 (d, J = 10.8 Hz, aromatic C), 130.08 (d, J = 15.9 Hz, aromatic C), 129.71 (s, aromatic C), 129.39 (s, aromatic C), 127.89 (s, aromatic C), 127.32 (d, J = 11.8 Hz, aromatic C), 125.23 (s, aromatic C), 124.38 (s, aromatic C), 123.62 (s, aromatic

C), 28.88 (s, $\underline{\text{CH}}(\text{CH}_3)_2$), 28.54 (s, $\underline{\text{CH}}(\text{CH}_3)_2$), 24.40 (s, $\text{CH}(\underline{\text{CH}_3})_2$), 23.79 (s, $\text{CH}(\underline{\text{CH}_3})_2$), 23.48 (s, $\text{CH}(\underline{\text{CH}_3})_2$), 23.00 (s, $\text{CH}(\underline{\text{CH}_3})_2$) ppm. ^{11}B NMR (128 MHz, CDCl_3) δ -32.55 – -35.62 (m, $\underline{\text{BH}_3}$) ppm. MALDI TOF: $\text{C}_{39}\text{H}_{47}\text{BN}_2$ Calculated m/z 553.3832 Observed m/z 553.9787 $[\text{M}]^+$

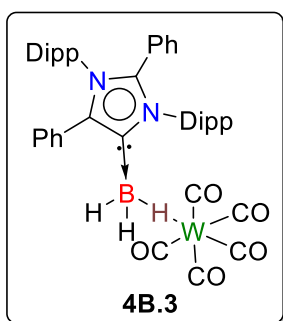
4B.5.2. Synthesis of 4B.2a and 4B.2b: A mixture of $[\text{Cr}(\text{CO})_6]$ (110 mg, 0.5 mmol) and 4B.1



(277 mg, 0.5 mmol) was irradiated for 20 h at room temperature in toluene (30 mL). The solution was stirred for 24 h, filtered through a sintered glass frit under an argon atmosphere, and the solvent was removed under vacuum. Concentrated dark orange solution kept at room temperature. Dark yellow (major product 4B.2a) and red (a few crystals 4B.2b) single crystals suitable for X-ray analysis were grown in toluene at room temperature. Yield: 75.2 % (270 mg). 2a: M.P. 260–

270 °C, 2b: 240–250 °C. ^1H NMR (400 MHz, C_6D_6) δ -3.22 (br, $\underline{\text{BH}_3}$) ppm, broad spectra, difficult to deconvolute. ^{11}B NMR (128 MHz, C_6D_6) δ -34.35 (dd, starting material), -38.22 (b, $\underline{\text{BH}_3}$) ppm. MALDI TOF 4B.2a: $\text{C}_{44}\text{H}_{47}\text{BCrN}_2\text{O}_5$ Calculated m/z 746.2978 Observed m/z 785.1725 $[\text{M}+\text{K}]^+$ 4B.2b: $\text{C}_{43}\text{H}_{46}\text{BCrN}_2\text{O}_4$ Calculated m/z 717.2950 Observed m/z 718.8778 $[\text{M}+\text{H}]^+$

4B.5.3. Synthesis of 4B.3: A mixture of $[\text{W}(\text{CO})_6]$ (176 mg, 0.5 mmol) and 4B.1 (277 mg, 0.5



mmol) was irradiated for 4 h at room temperature in toluene (30 mL). The solution was stirred for 4 h, filtered through a sintered glass frit under an argon atmosphere, and the solvent was removed under vacuum. Concentrated dark yellow solution kept at room temperature. Dark yellow single crystals suitable for X-ray analysis were grown in toluene at room temperature. Yield: 68.3 % (300 mg). M.P. 260 °C.

^1H NMR (400 MHz, C_6D_6) δ 7.54 (d, J = 8.4 Hz, 2H, aromatic C-H), 7.07 – 6.83 (m, 10H, aromatic C-H), 6.78 (d, J = 7.8 Hz, 2H, aromatic C-H), 6.59–6.45 (m, 4H, aromatic C-H), 2.78 (dd, J = 13.6, 6.8 Hz, 2H, $\underline{\text{CH}}(\text{CH}_3)_2$), 2.61 (dt, J = 13.5, 6.7 Hz, 2H, $\underline{\text{CH}}(\text{CH}_3)_2$), 1.50 (d, J = 6.8 Hz, 6H, $\text{CH}(\underline{\text{CH}_3})_2$), 0.86 (d, J = 6.8 Hz, 6H, $\text{CH}(\underline{\text{CH}_3})_2$), 0.67 (dd, J = 13.8, 6.7 Hz, 12H, $\text{CH}(\underline{\text{CH}_3})_2$), -0.82 (b, 3H, $\underline{\text{BH}_3}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6) δ 199.53 (s, CO), 190.78 (s, CO), 145.14 (s, aromatic C), 144.93 (s, aromatic C), 131.01 (s, aromatic C), 130.73 (s, aromatic C), 130.33–130.13 (m, aromatic C), 129.55 (s, aromatic C), 128.99 (d, J = 5.4 Hz, aromatic C), 125.06 (s, aromatic C), 124.56 (s, aromatic C), 124.16 (s, aromatic C), 29.07 (s, $\underline{\text{CH}}(\text{CH}_3)_2$), 28.61 (s, $\underline{\text{CH}}(\text{CH}_3)_2$), 24.49 (s, $\text{CH}(\underline{\text{CH}_3})_2$), 23.41 (s, $\text{CH}(\underline{\text{CH}_3})_2$), 23.15 (s,

CH(CH₃)₂), 22.74 (s, CH(CH₃)₂) ppm. ¹¹B NMR (129 MHz, C₆D₆) δ -40.48 (s) ppm. MALDI TOF C₄₄H₄₇BWN₂O₅ Calculated m/z 878.3082 Observed m/z 917.5914 [M+K]⁺

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Chapter 5: Summary of the Thesis and Future Directions

5.1 Summary of the thesis

Transition-metal complexes featuring isolable N-heterocyclic silylene (NHSi) ligands represent a rapidly growing field with broad implications for modern chemistry. These ligands have redefined coordination chemistry with both transition and coinage metals, opening new opportunities for developing highly efficient and versatile catalytic systems for organic transformations. In parallel, the exploration of abnormal N-heterocyclic carbenes (*a*NHCs) as ligands has shown remarkable potential in the design of photoactive emitters, underscoring their relevance in materials science and photophysical applications. Together, these studies contribute to advancing sustainable catalysis and functional material development

5.1.1 Reactivity of phosphine base hybrid silylene ligand.

In the first section of this thesis, the focus is on investigating the reactivity of phosphine–base hybrid silylene ligands with 3d-transition metal halide complexes. The synthesis and characterisation of these complexes reveal their distinct redox behaviour and magnetic properties. Most of the phosphine–base hybrid silylene-3d-transition metal halide complexes are paramagnetic at room temperature and exhibit superparamagnetism at low temperatures. An exception is observed for the nickel complexes, which display superparamagnetic behaviour at both room and low temperatures. Additionally, the reactivity of these ligands with group 11 metal salts has been explored to gain deeper insights into the electronic factors influencing their coordination modes. Together, these studies provide a fundamental understanding of the electronic and magnetic properties that govern the coordination chemistry of phosphine–base hybrid silylene ligands.

5.1.2 Reactivity of organoazide toward Si(II) compounds

This section investigates the reactivity of low-valent silicon species (hybrid silylenes, bis-silylenes, and disilenes) towards organoazides, highlighting how ligand design governs the formation and stabilisation of Si-N multiple bonds. These findings provide key insights into bonding and product selectivity, paving the way for developing new ligand frameworks to access novel Si-N multiple bond species. The results offer valuable insights and demonstrate that appropriately tuned ligands can even enable the isolation of nitrene species from Si(II) compounds and organoazide reactions without requiring external reduction.

5.1.3 Coinage metal complexes with aNHC ligands and their photophysical properties.

The subsequent section deals with the synthesis and comprehensive characterisation of coinage metal complexes bearing abnormal N-heterocyclic carbene (*a*NHC) ligands. These complexes display a carbene-metal-amide framework, which is challenging to prepare due to the thermodynamic stability of *a*NHC carbene. Notably, they exhibit remarkable photophysical properties, including tunable emission characteristics, which make them promising candidates for the development of luminescent materials and advanced optoelectronic devices. this thesis endeavours to fully harness the capabilities of these complexes for optoelectronic applications and explore their broader potential in advanced material design.

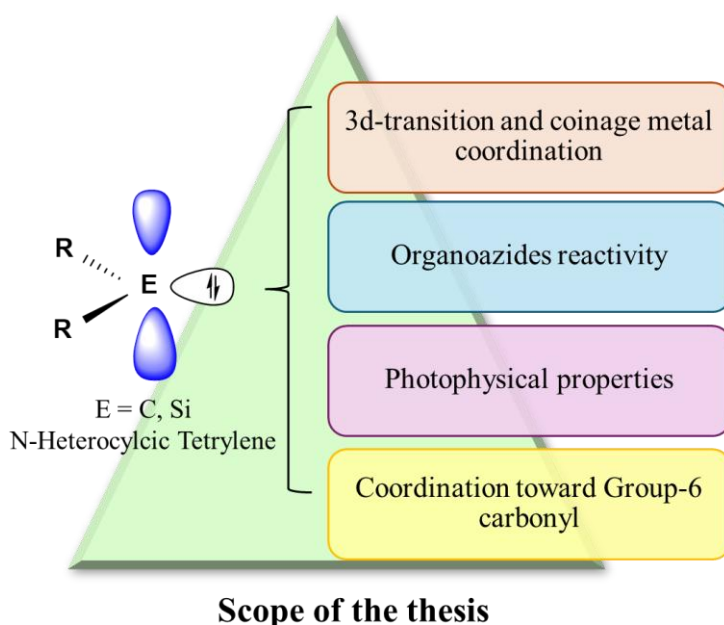


Figure 5.1. Overview of the work presented in this thesis.

5.2 Conclusion and future directions.

This thesis highlights the crucial role of low-valent main group ligands, particularly N-heterocyclic tetrylene (NHTs), in shaping modern synthetic chemistry. By systematically exploring their diverse coordination modes, reactivity patterns, and applications, this work seeks to inspire further research in the field. Future directions may involve designing novel synthetic routes to access derivatisation of *a*NHCs (either on the ligand or on the donor side), chiral *a*NHCs, establishing detailed structure-property relationships, and incorporating *a*NHCs into advanced technologies such as nanocomposites and sustainable energy systems. Collectively, this thesis presents a comprehensive study of transition-metal complexes bearing

isolable NHSi and aNHCs ligands, offering valuable insights that pave the way for versatile reactivity and photoemitters.

I am among those who think that science has great beauty

~Marie Curie, Nobel prize in Physics, 1903 and in Chemistry, 1911.

2A.A.1 Crystallographic data for complexes 2A.1, 2A.3-2A.6.

Table 2A.A.1: Crystallographic data for complexes 2A.1, 2A.3 and 2A.4

Identification code	2A.1	2A.3	2A.4
Empirical formula	C ₃₆ H ₄₆ N ₃ P Si ₂	C ₃₆ H ₄₆ Br ₂ Fe N ₃ P Si ₂	C ₃₆ H ₄₆ Br ₂ Co N ₃ P Si ₂ , C ₇ H ₈
Formula weight	607.91 g/mol	823.56 g/mol	918.77 g/mol
Temperature	100 (2) K	100 (2) K	100 (2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	P-1	Pna2 ₁	P-1
Unit cell dimensions	a = 9.765 (3) Å	a = 22.1324 (17) Å	a = 9.8244 (6) Å
	b = 9.838 (3) Å	b = 17.3481 (13) Å	b = 9.8926 (7) Å
	c = 17.729 (5) Å	c = 9.7904 (7) Å	c = 24.7495 (17) Å
	α = 84.161 (8) ^o	α = 90 ^o	α = 90.024 (2) ^o
	β = 88.298 (8) ^o	β = 90 ^o	β = 98.996 (2) ^o
	γ = 86.944 (9) ^o	γ = 90 ^o	γ = 117.081 (2) ^o
Volume	1691.4 (9) Å ³	3759.1 (5) Å ³	2108.3 (2) Å ³
Z	2	4	2
Density (calculated)	1.194 g/cm ³	1.455 g/cm ³	1.447 g/cm ³
Absorption coefficient	0.181 mm ⁻¹	2.663 mm ⁻¹	2.431 mm ⁻¹
F (000)	652.0	1688.0	946
Theta range for data collection	2.28 to 21.61 ^o	2.35 to 21.66 ^o	2.32 to 28.15 ^o
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -21 ≤ l ≤ 20	-27 ≤ h ≤ 27, -21 ≤ k ≤ 21, -12 ≤ l ≤ 12	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -33 ≤ l ≤ 33
Reflection collected	33056	156827	86460

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Independent reflections	5959 [R(int) = 0.2039]	7846 [R(int) = 0.1507]	10526 [R(int) = 0.0673]
Coverage of independent reflections	99.9%	99.9%	99.9%
Function minimized	$\Sigma w(\text{Fo}_2 - \text{Fc}_2)^2$	$\Sigma w(\text{Fo}_2 - \text{Fc}_2)^2$	$\Sigma w(\text{Fo}_2 - \text{Fc}_2)^2$
Data/ restraints /parameters	5959/0/389	7846/0/415	10526/0/479
Goodness-of-fit on F^2	1.012	1.017	1.102
Δ/σ max	0.000	0.001	0.001
Final R indices	3087 data; [I>2 σ (I)] R1 = 0.0662, wR2 = 0.1034	5826 data; [I>2 σ (I)] R1 = 0.0482, wR2 = 0.0802	8186 data; [I>2 σ (I)] R1 = 0.0513, wR2 = 0.0878
	all data, R1 = 0.1698, wR2 = 0.1318	all data, R1 = 0.0867, wR2 = 0.0903	All data, R1 = 0.0779, wR2 = 0.0948
Largest diff. peak and hole	0.297 and -0.365 eÅ ⁻³	0.788 and -0.568 eÅ ⁻³	1.882 and -1.706 eÅ ⁻³
R.M.S deviation from mean	0.068 eÅ ⁻³	0.085 eÅ ⁻³	0.104 eÅ ⁻³

Table 2A.A.2: Crystallographic data for complexes **2A.5** and **2A.6**

Identification Code	2A.5	2A.6
Empirical formula	C ₃₆ H ₄₆ Cl ₂ Ni N ₃ P Si ₂	C ₃₉ H ₅₂ Br ₂ N ₃ Ni P Si ₂
Formula weight	737.50 g/mol	868.48 g/mol
Temperature	100 (2) K	100 (2) K
Wavelength	0.71703 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
Unit cell dimensions	a = 17.4035 (11) Å	a = 11.140 (3) Å
	b = 9.5185 (6) Å	b = 11.463 (3) Å
	c = 46.185 (3) Å	c = 17.227 (5) Å

Appendix of Chapter 2A

	$\alpha = 90^\circ$	$\alpha = 74.289 (9)^\circ$
	$\beta = 106.340 (4)^\circ$	$\beta = 83.051 (9)^\circ$
	$\gamma = 90^\circ$	$\gamma = 85.336 (6)^\circ$
Volume	7341.8 (8) Å ³	2099.4 (10) Å ³
Z	8	2
Density (calculated)	1.334 g/cm ³	1.374 g/cm ³
Absorption coefficient	0.813 mm ⁻¹	2.490 mm ⁻¹
F (000)	3104.0	896
Theta range for data collection	2.30 to 27.76°	2.32 to 26.28°
Index ranges	-20 ≤ h ≤ 20, -11 ≤ k ≤ 11, -54 ≤ l ≤ 54	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -21 ≤ l ≤ 21
Reflection collected	114634	33056
Independent reflections	6461 [R(int) = 0.1410]	5959 [R(int) = 0.2039]
Coverage of independent reflections	100%	100%
Function minimized	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$
Data/ restraints /parameters	6461/0/415	8667/0/444
Goodness-of-fit on F ²	1.234	1.049
Δ/σ max	0.000	0.001
Final R indices	5357 data; [I > 2σ(I)] R1 = 0.0622, wR2 = 0.0932	6636 data; [I > 2σ(I)] R1 = 0.0400, wR2 = 0.0827
	all data, R1 = 0.0826, wR2 = 0.0981	all data, R1 = 0.0633, wR2 = 0.0901
Largest diff. peak and hole	0.431 and -0.630 eÅ ⁻³	0.832 and -0.608 eÅ ⁻³
R.M.S deviation from mean	0.084 eÅ ⁻³	0.095 eÅ ⁻³

2A.A.2 NMR spectroscopic data for complexes 2A.1-2A.6.

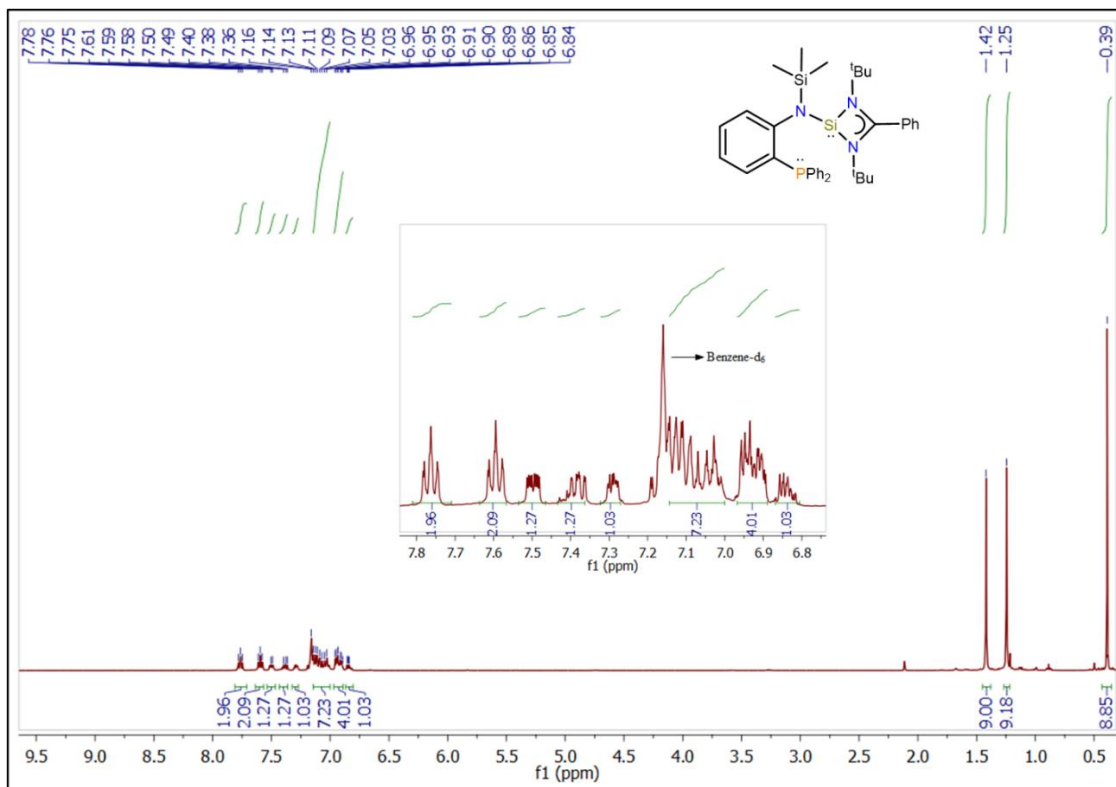


Figure 2A.A.1. ¹H NMR spectrum of 2A.1 (C₆D₆, 400 MHz, 298 K)

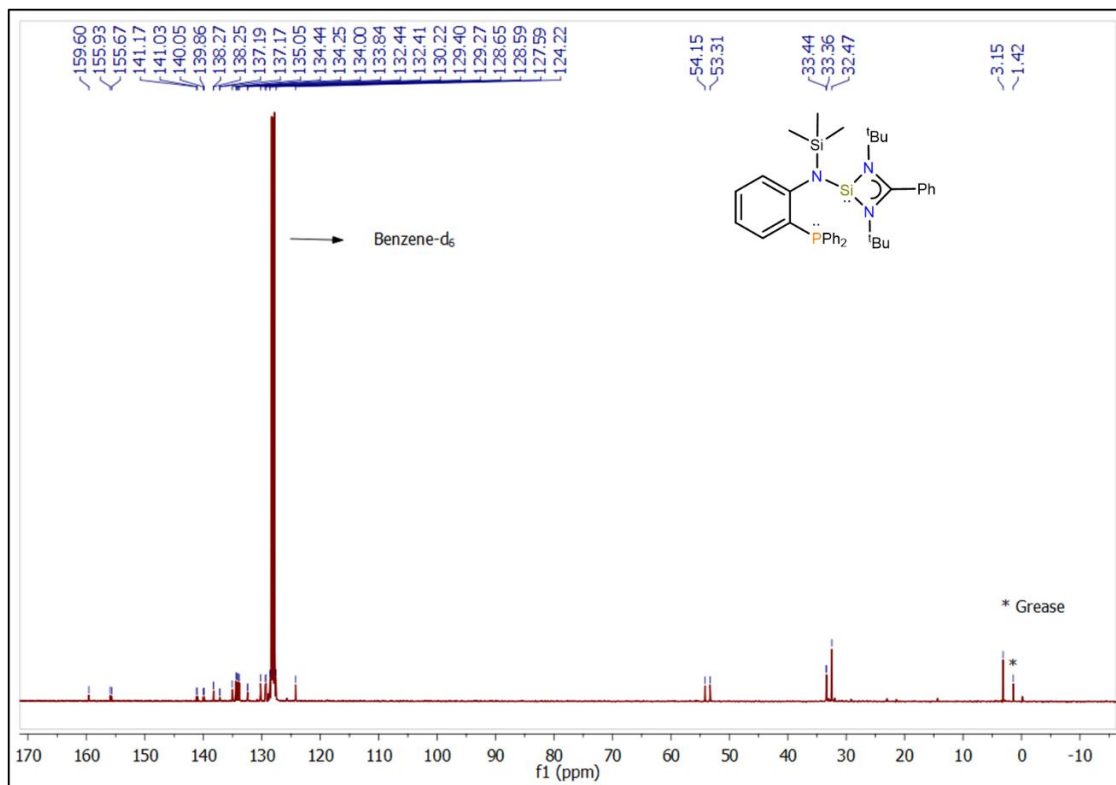


Figure 2A.A.2. ¹³C {¹H} NMR spectrum of 2A.1 (C₆D₆, 100.613 MHz, 298 K)

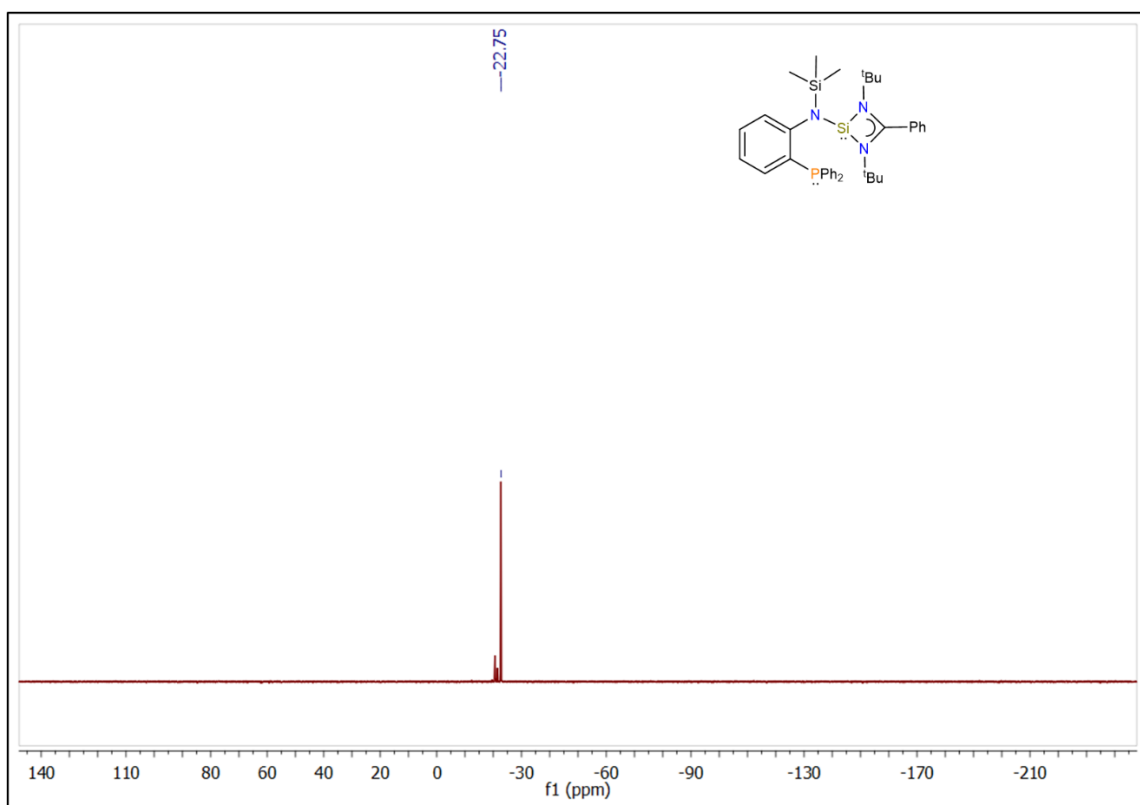


Figure 2A.A.3. $^{31}\text{P}\{^1\text{H}\}$ full NMR spectrum of 2A.1 (C_6D_6 , 161.97 MHz, 298 K)

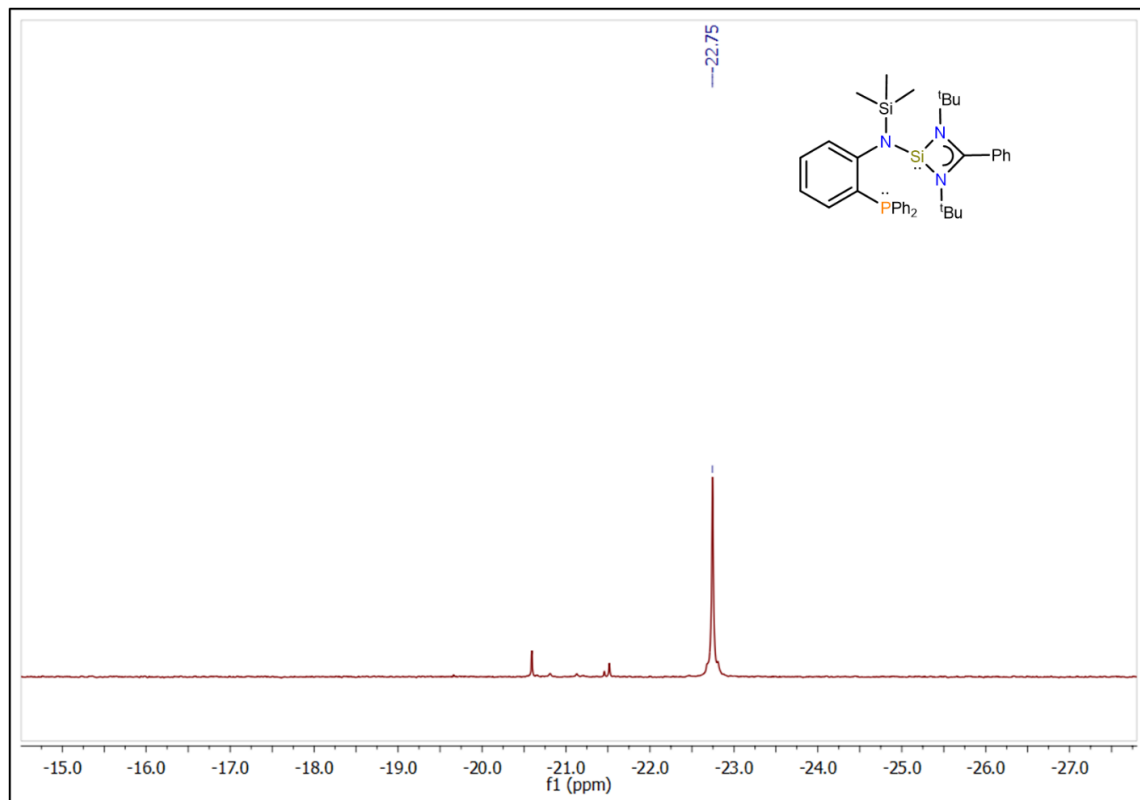


Figure 2A.A.4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2A.1 (C_6D_6 , 161.97 MHz, 298 K)

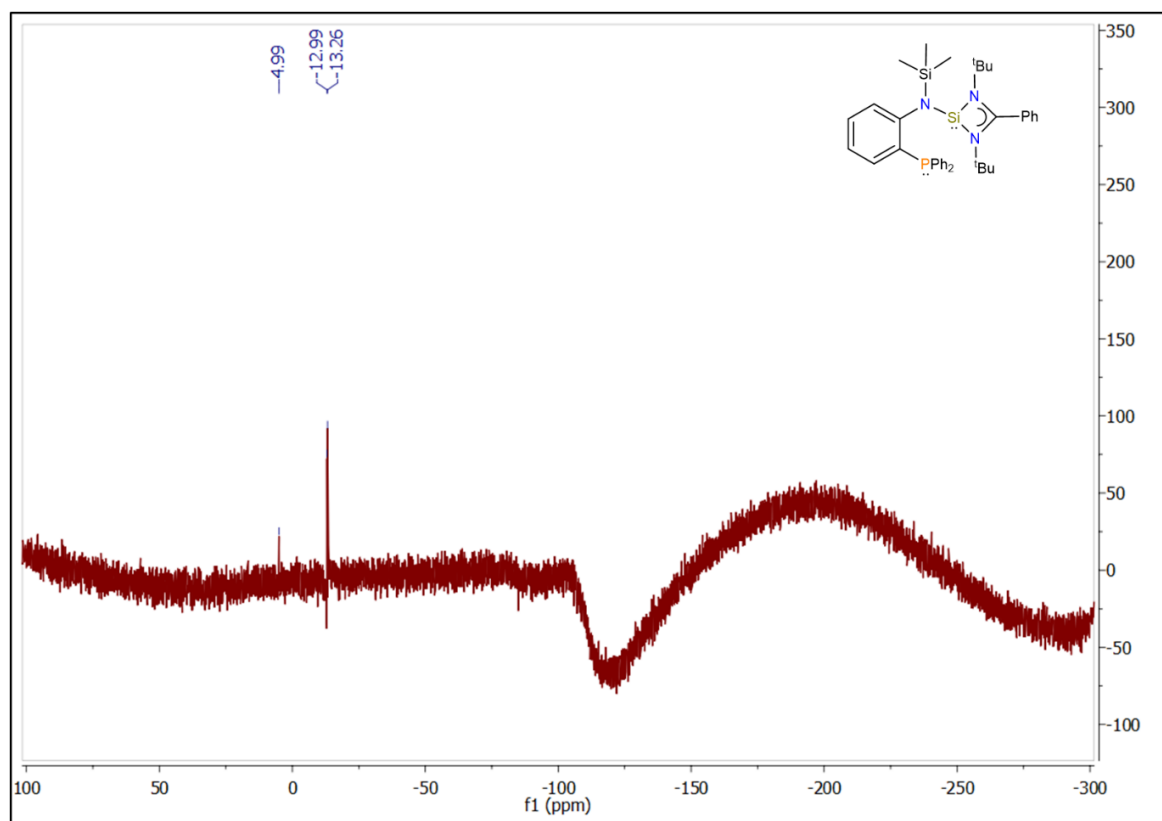


Figure 2A.A.5. $^{29}\text{Si}\{^1\text{H}\}$ full NMR spectrum of **2A.1** (C_6D_6 , 79.49 MHz, 298 K)

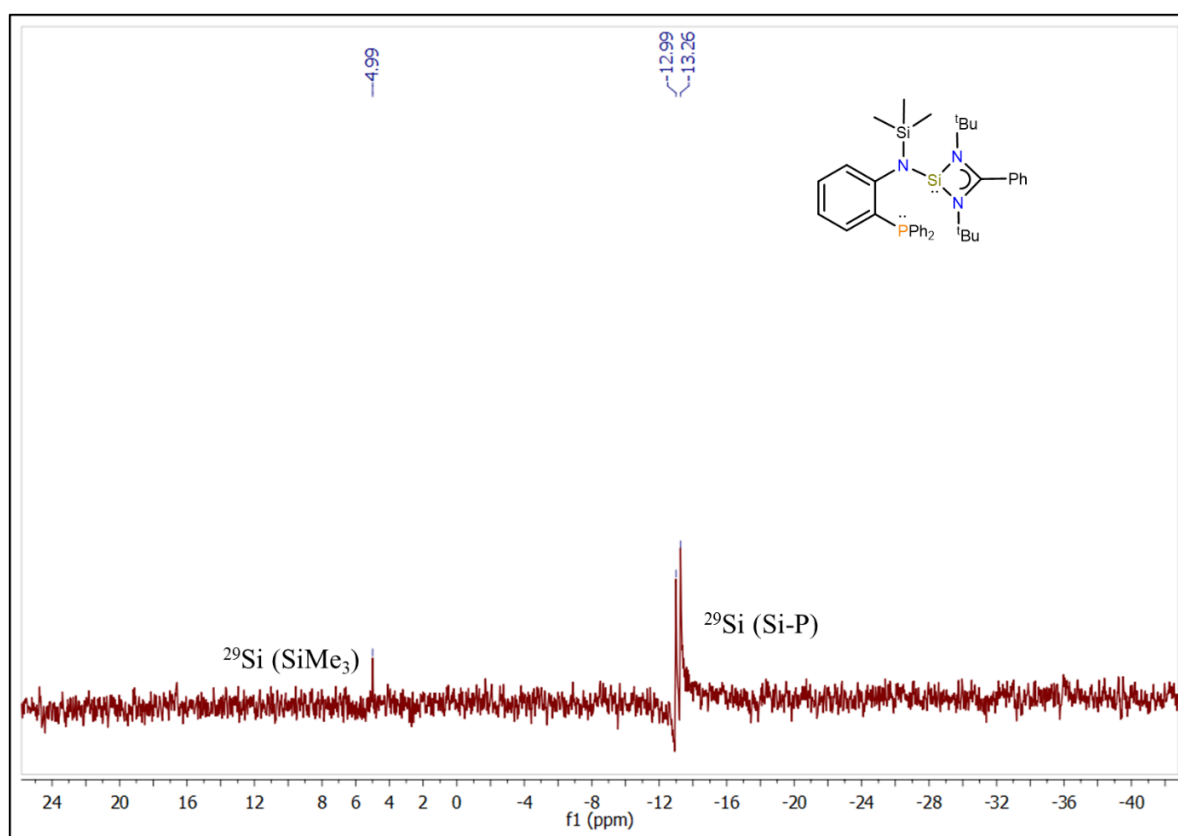


Figure 2A.A.6. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2A.1** (C_6D_6 , 79.49 MHz, 298 K)

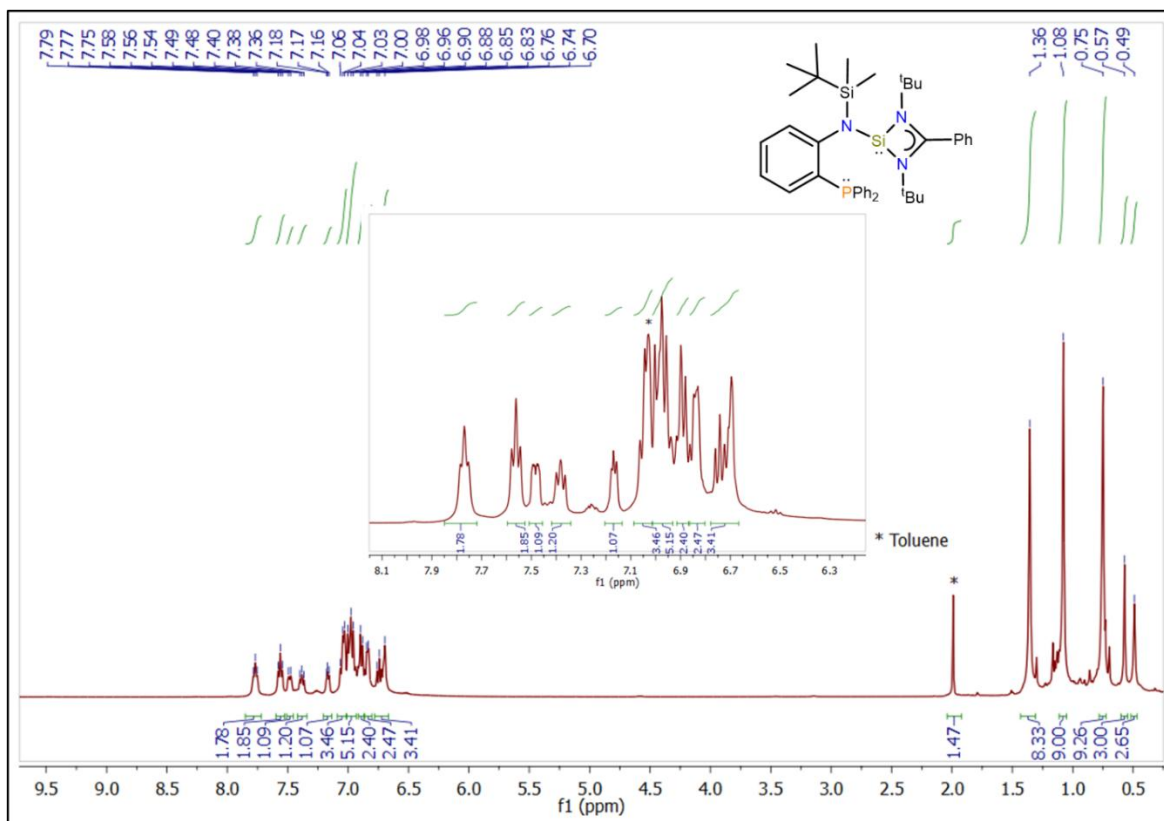


Figure 2A.A.7. ¹H NMR spectrum of **2A.2** (C₆D₆, 400 MHz, 298 K)

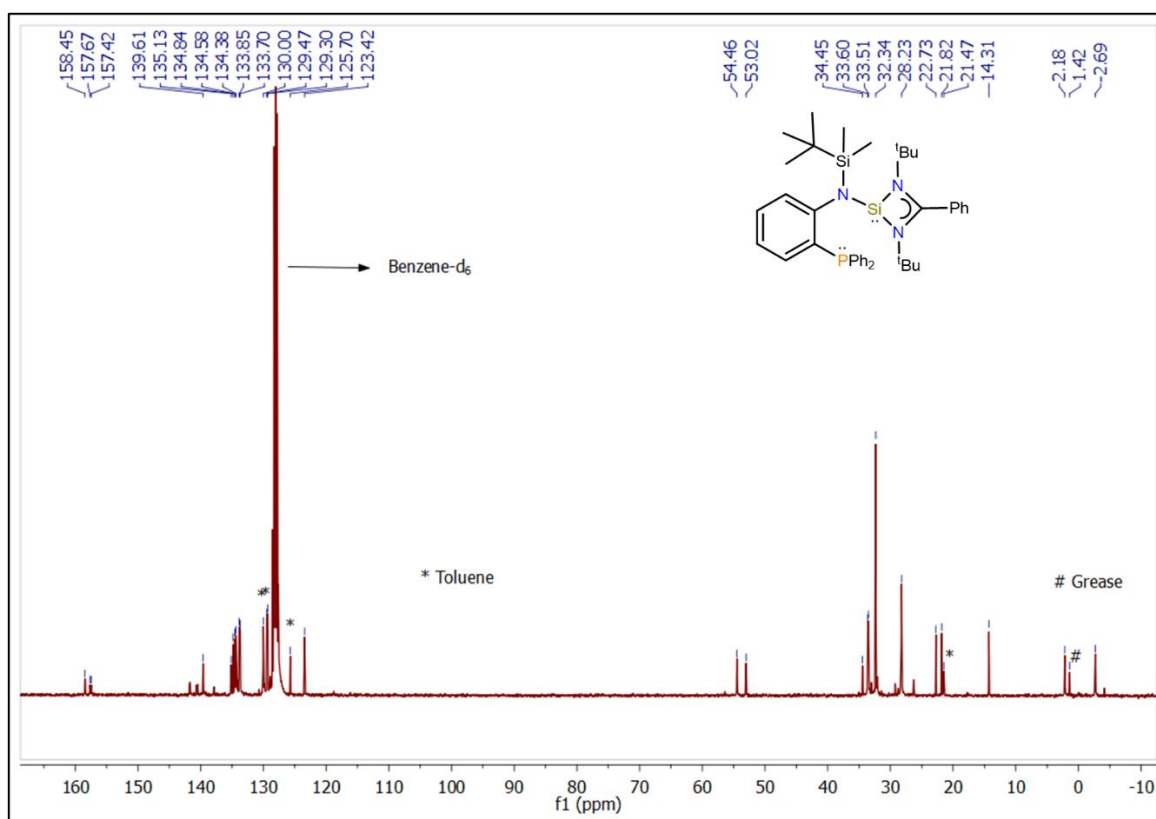


Figure 2A.A.8. ¹³C{¹H} NMR spectrum of **2A.2** (C₆D₆, 100.613 MHz, 298 K)

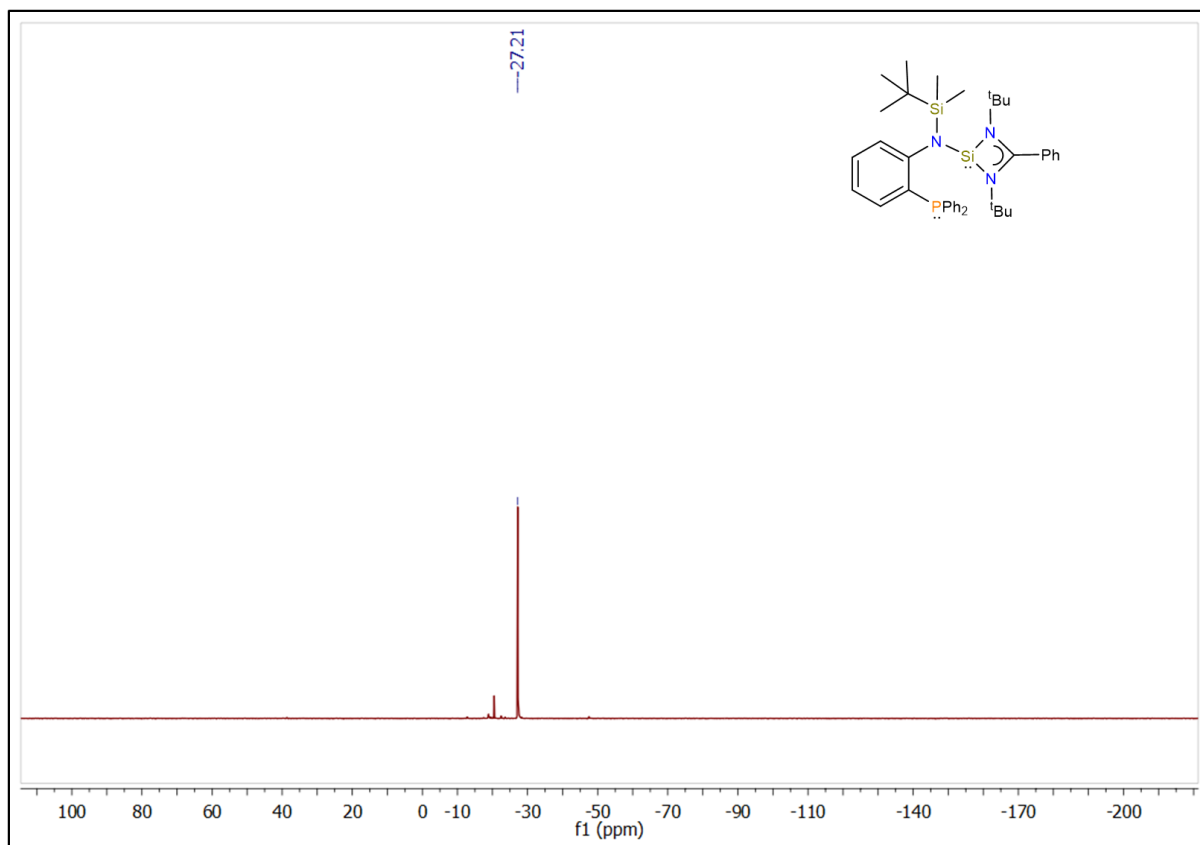


Figure 2A.A.9. $^{31}\text{P}\{^1\text{H}\}$ full NMR spectrum of 2A.2 (C_6D_6 , 161.97 MHz, 298 K)

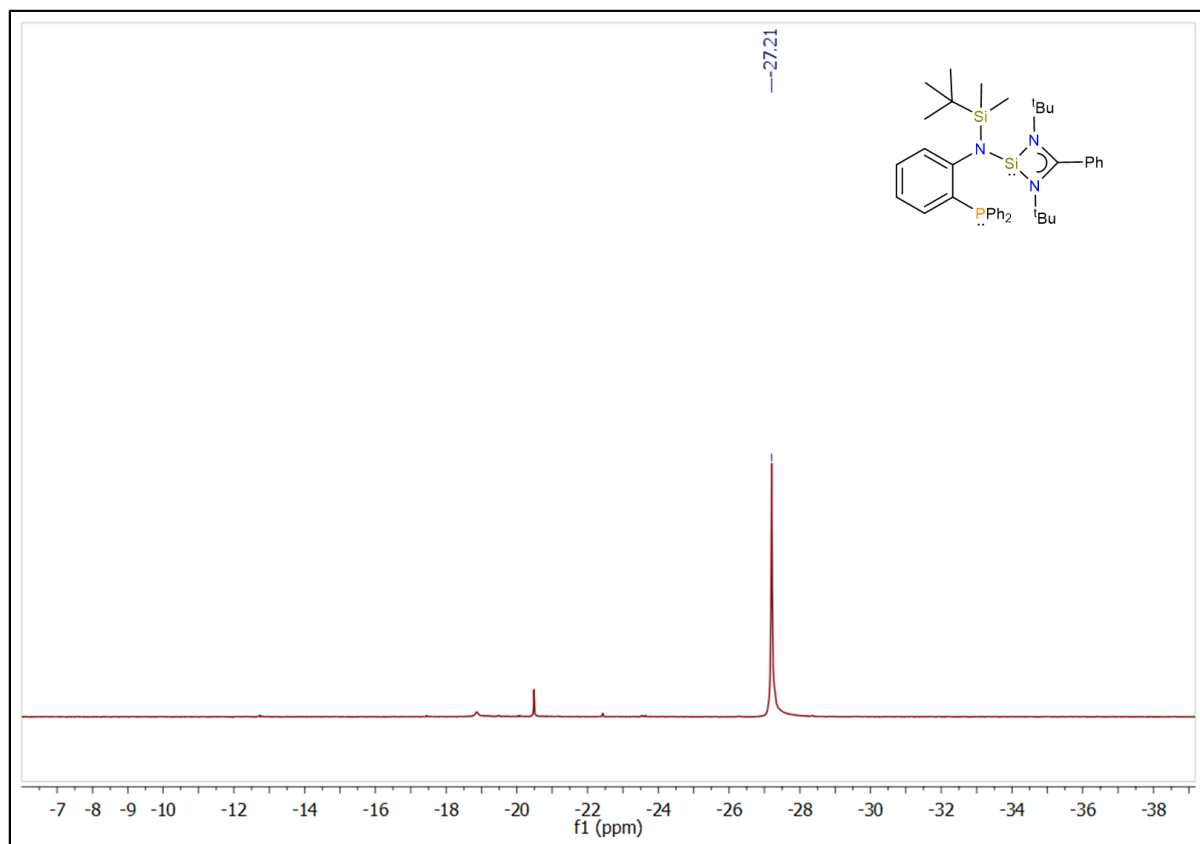


Figure 2A.A.10. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2A.2 (C_6D_6 , 161.97 MHz, 298 K)

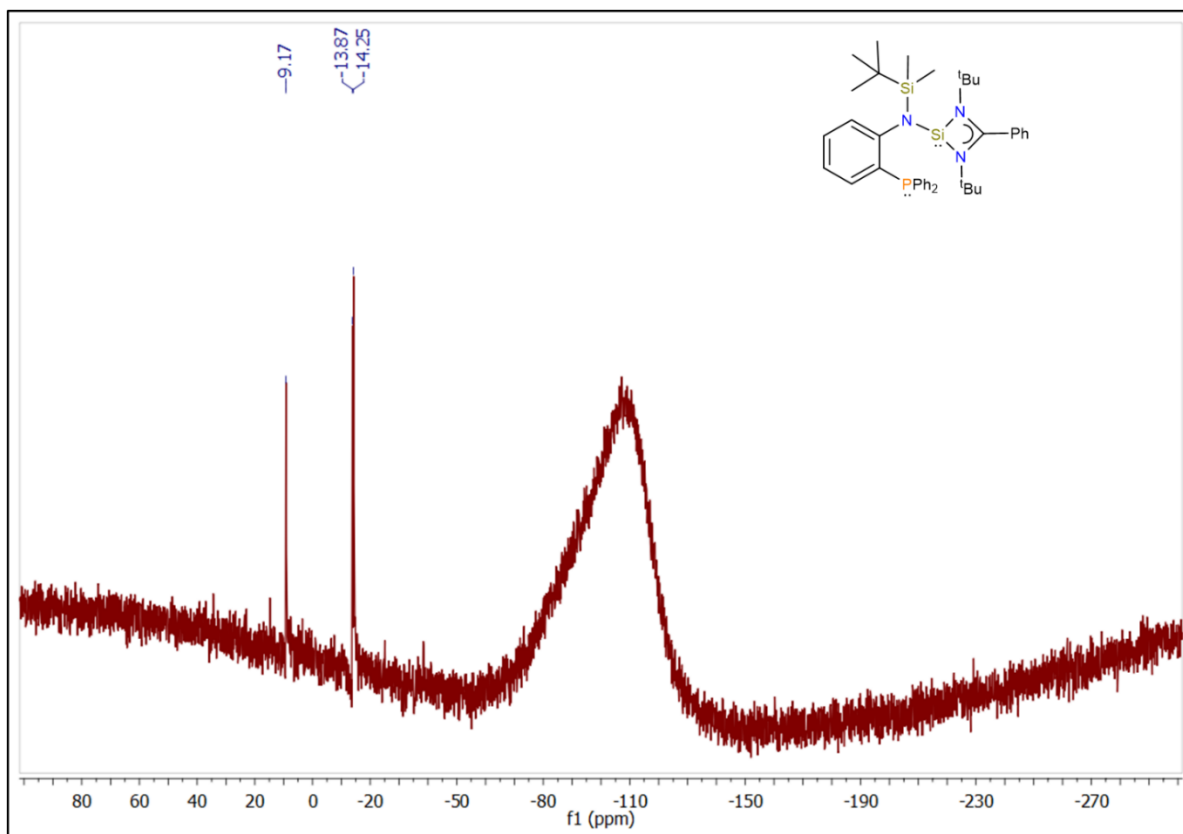


Figure 2A.A.11. $^{29}\text{Si} \{^1\text{H}\}$ NMR spectrum of **2A.2** (C_6D_6 , 79.49 MHz, 298 K)

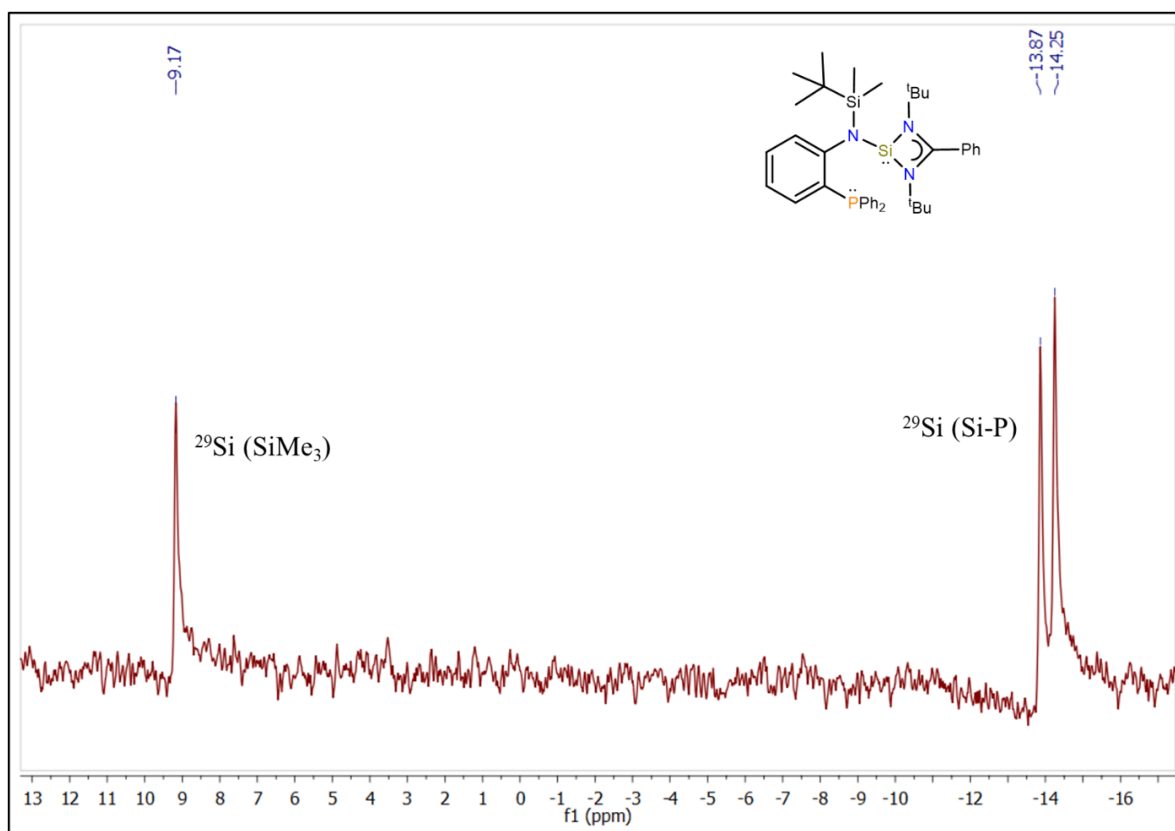


Figure 2A.A.12. $^{29}\text{Si} \{^1\text{H}\}$ NMR spectrum of **2A.2** (C_6D_6 , 79.49 MHz, 298 K)

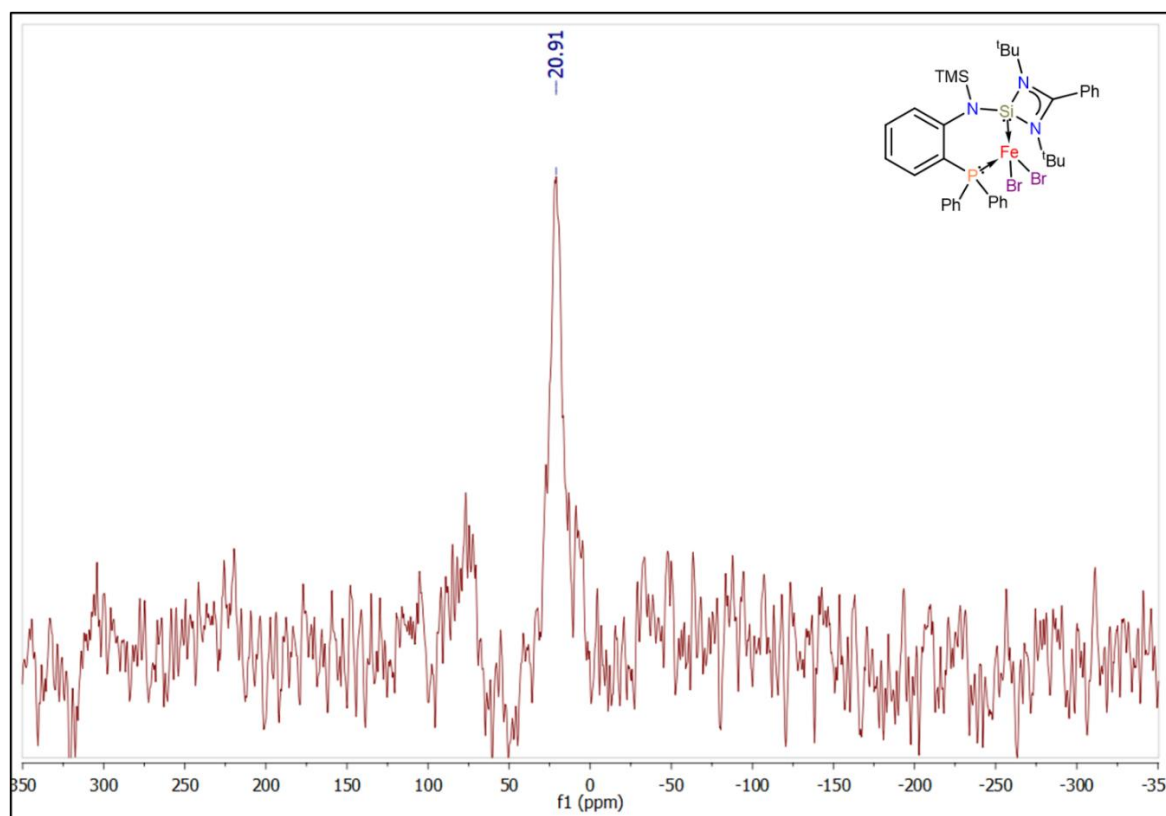


Figure 2A.A.13. ^{31}P static and magic angle spinning (MAS) NMR spectra of complex **2A.3**

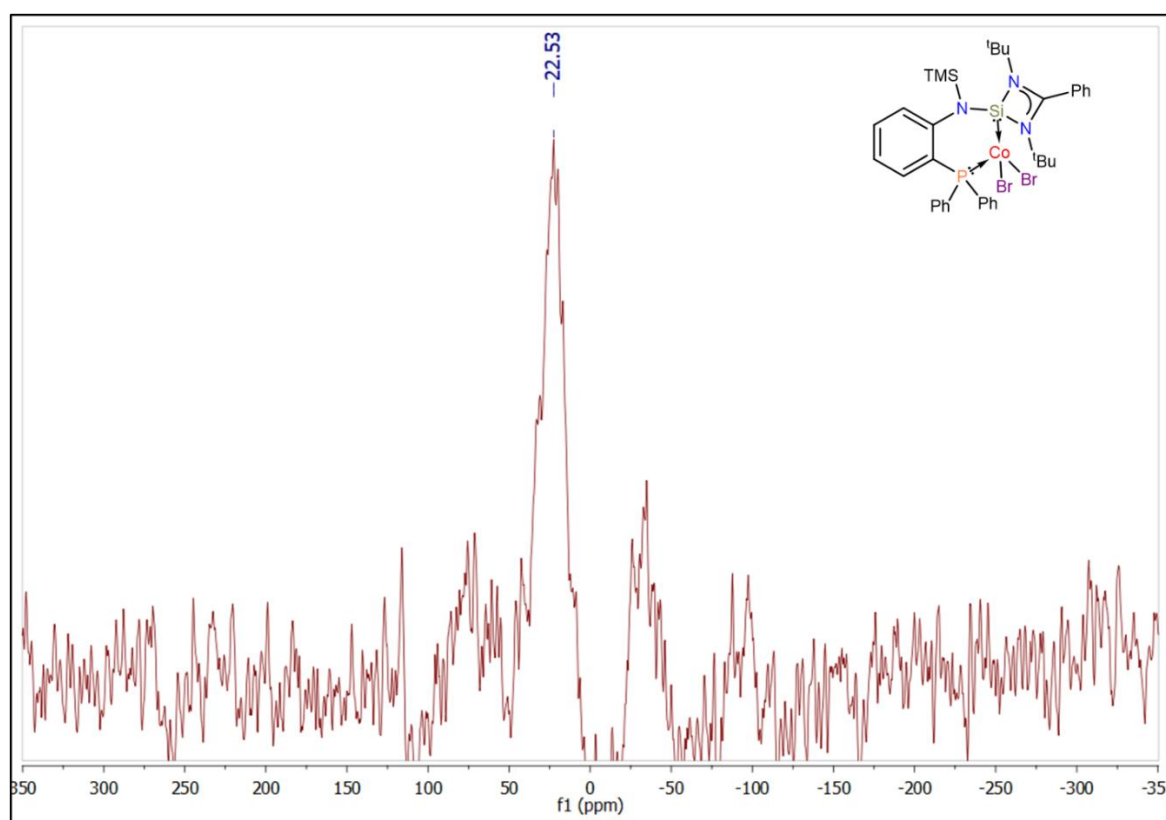


Figure 2A.A.14. ^{31}P static and magic angle spinning (MAS) NMR spectra of complex **2A.4**

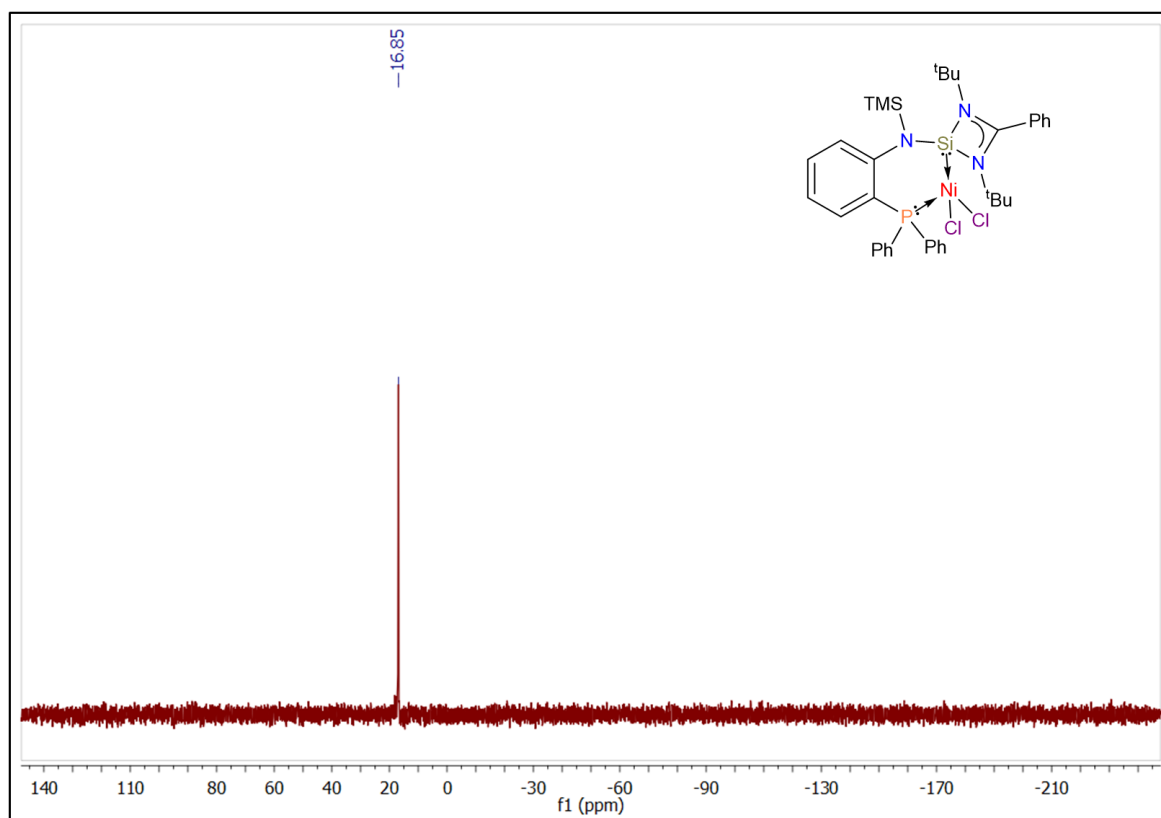


Figure 2A.A.15. $^{31}\text{P}\{^1\text{H}\}$ full NMR spectrum of **2A.5** (CDCl_3 , 161.97 MHz, 298 K)

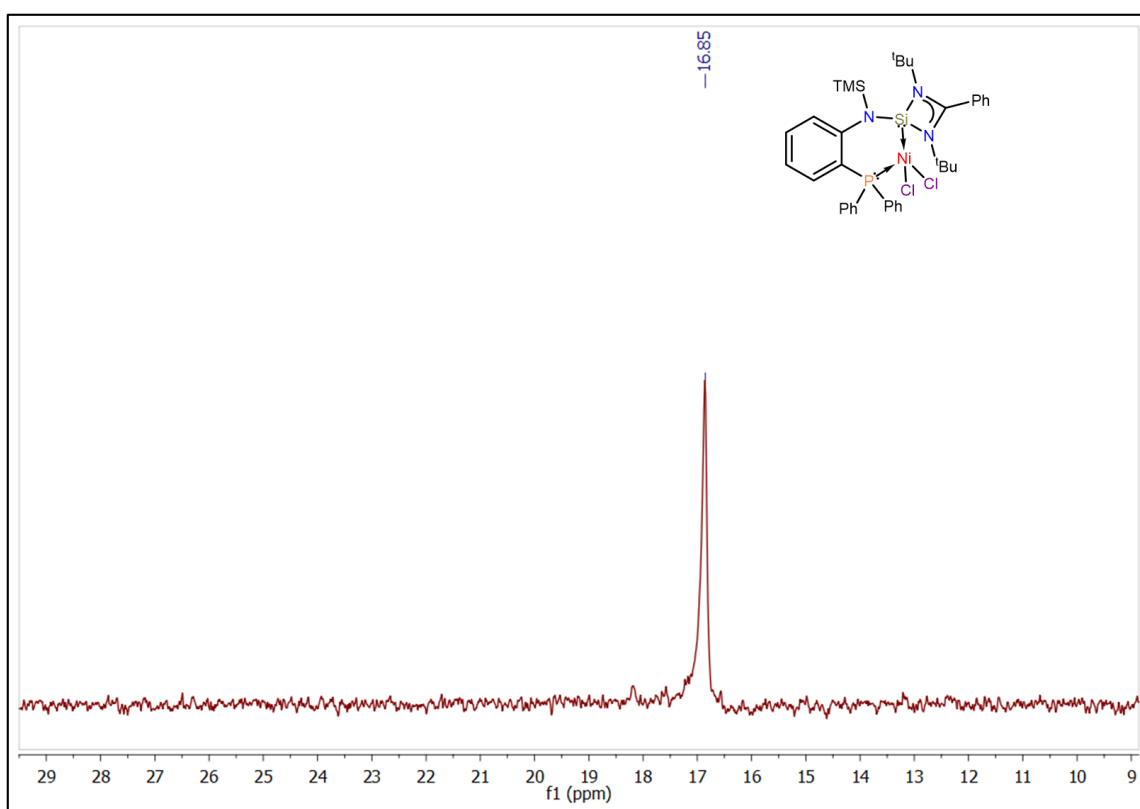


Figure 2A.A.16. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2A.5** (CDCl_3 , 161.97 MHz, 298 K)

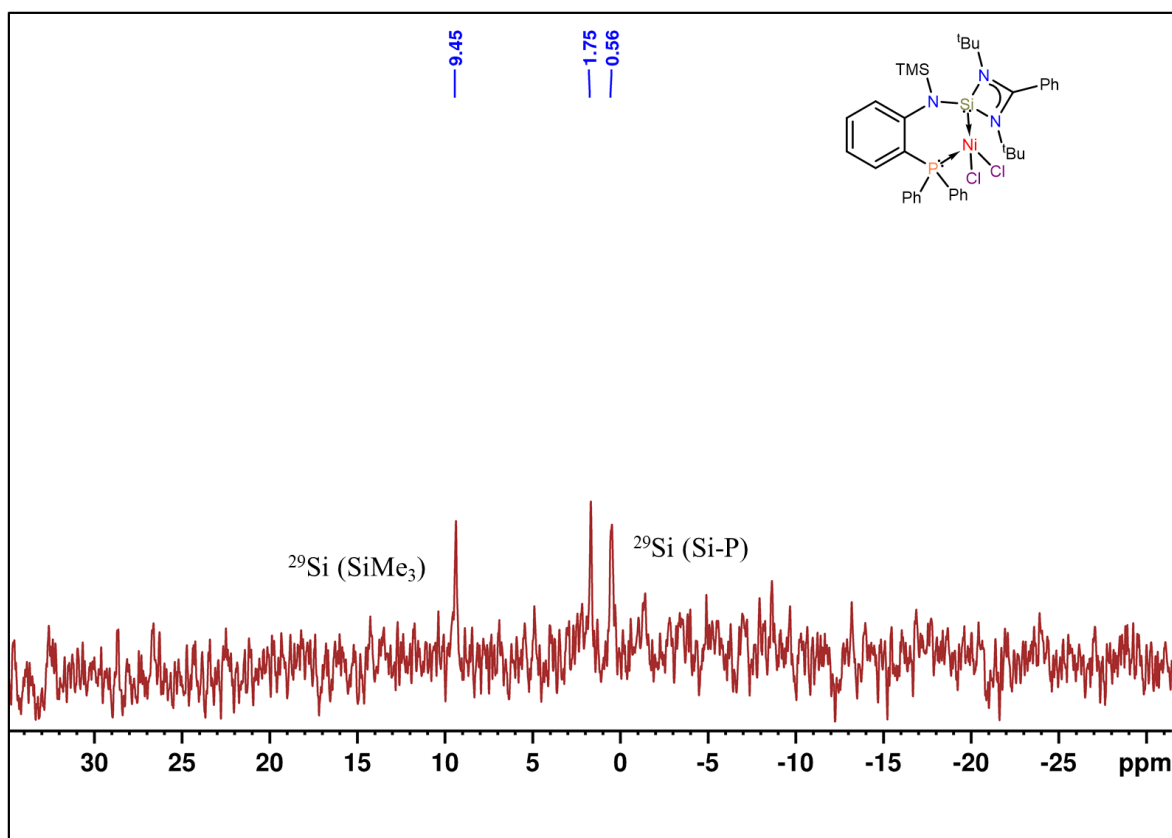


Figure 2A.A.17. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2A.5** (CDCl_3 , 79.49 MHz, 298 K)

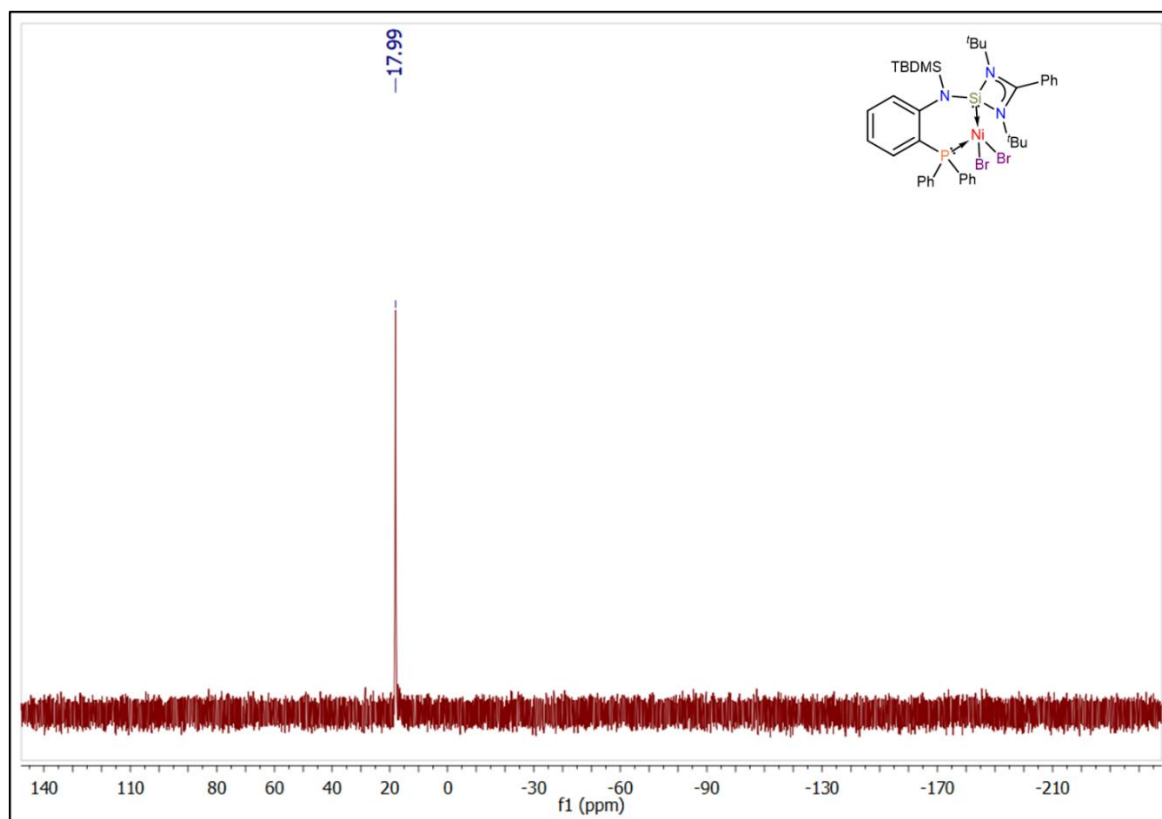


Figure 2A.A.18. $^{31}\text{P}\{^1\text{H}\}$ full NMR spectrum of **2A.6** (CDCl_3 , 161.97 MHz, 298 K)

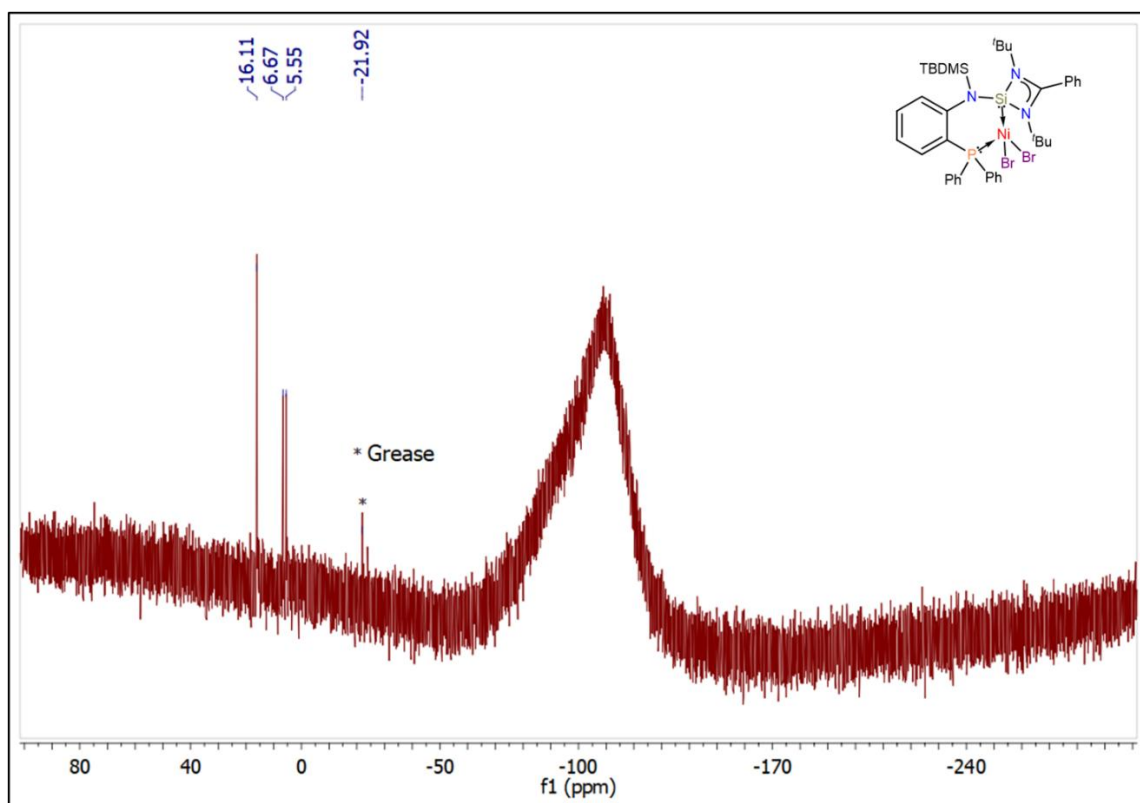


Figure 2A.A.19. $^{29}\text{Si}\{^1\text{H}\}$ NMR full spectrum of **2A.6** (CDCl_3 , 79.49 MHz, 298 K)

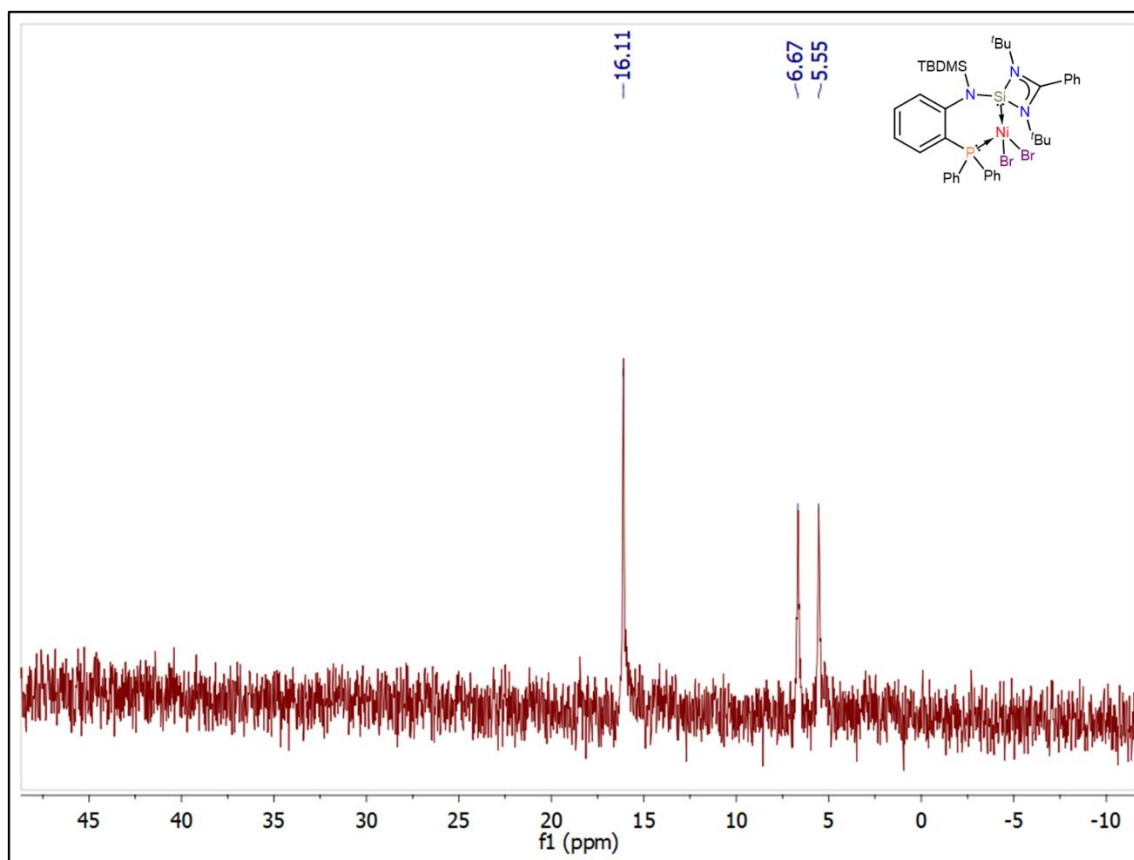


Figure 2A.A.20. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2A.6** (CDCl_3 , 79.49 MHz, 298 K)

2A.A.3. Calculation of four-coordinate geometry index (τ_4) for 2A.3-2A.6

τ_4 parameter was developed for four-coordinate structures like τ_5 . τ_5 is a commonly used method to predict the possible geometry in five coordinated complexes.^{S4a} If the structure is square planar, then $\tau_4 = 0$; for tetrahedral structures, $\tau_4 = 1$ and other feasible geometries with their respective τ_4 are discussed below.

Table 2A.A.3. τ_4 value with its possible geometries

Geometry	τ_4
Tetrahedral (T_d)	1.00
Trigonal pyramidal	0.85
Seesaw (C_{2v} , $\theta_6 = 90^\circ$)	0.64
Seesaw (C_{2v} , $\theta_6 = 109.5^\circ$)	0.50
Seesaw (C_{2v} , $\theta_6 = 154.4^\circ$)	0.18
Seesaw (C_{2v} , $\theta_6 = 170^\circ$)	0.07
Square planar (D_{4h})	0.00

Houser's and co-workers proposed a simple method to calculate the geometry index for four coordinate complexes, τ_4 , influenced by Addison and Reedjik's five-coordinate τ_5 index.

$$\tau_4 = \frac{360^\circ - (\alpha + \beta)}{141^\circ}$$

α and β are the two largest θ angles in the four coordinate species.

Okuniewski's and co-workers proposed another method due to little difference in α and β angle in the previous approach ($\tau_4' \leq \tau_4$).

$$\tau_4' = \frac{\beta - \alpha}{360^\circ - \theta} + \frac{180^\circ - \beta}{180^\circ - \theta}$$

For Complex 2A.3

$\alpha = 115.22$ and $\beta = 120.49$

$$\tau_4 = \frac{360^\circ - (115.22^\circ + 120.49^\circ)}{141^\circ}$$

$$\tau_4 = \frac{360^\circ - 235.71^\circ}{141^\circ}$$

$$\tau_4 = 0.881$$

For Complex 2A.4

$\alpha = 119.19$ and $\beta = 141.52$

$$\tau_4 = \frac{360^\circ - (119.19^\circ + 141.52^\circ)}{141^\circ}$$

$$\tau_4 = \frac{360^{\circ} - 260.71^{\circ}}{141^{\circ}}$$

$$\tau_4 = 0.704$$

For Complex 2A.5

$\alpha = 156.06$ and $\beta = 162.96$

$$\tau_4 = \frac{360^{\circ} - (156.06^{\circ} + 162.96^{\circ})}{141^{\circ}}$$

$$\tau_4 = \frac{360^{\circ} - 319.02^{\circ}}{141^{\circ}}$$

$$\tau_4 = 0.28$$

For Complex 2A.6

$\alpha = 153.01$ and $\beta = 156.62$

$$\tau_4 = \frac{360^{\circ} - (153.01^{\circ} + 156.26^{\circ})}{141^{\circ}}$$

$$\tau_4 = \frac{360^{\circ} - 309.63^{\circ}}{141^{\circ}}$$

$$\tau_4 = 0.357$$

2A.A.4. Cyclic voltammetry of the ligand 2A.1 and complex 2A.6

Cyclic voltammetry was performed in a non-aqueous electrolyte medium (*t*-butyl-ammonium-hexafluorophosphate used as electrolyte), **2A.1** was dissolved in tetrahydrofuran and **2A.6** in DCM under an atmosphere of argon in a glovebox. Data collection was done by Ω Metrohm Dropsens portable, multi-Potentiostat/Galvanostat. μ Stat 8000, μ Stat 8000P, μ Stat 4000, μ Stat 4000P are the different models. Also, μ STAT 8000 can be used in Multichannel mode, with up to eight (8) working electrodes sharing one auxiliary electrode and one reference electrode. For all the measurements, we used Drop View 8400 Software. The working electrode was a glassy carbon electrode, the counter electrode was a platinum coil, and the reference electrode was the platinum pseudo reference containing $n\text{-Bu}_4\text{NPF}_6$ (0.5 M) as electrolyte. Ferrocene was added as an internal standard separately, and all potentials were referenced to the Fc^+/Fc couple. A slow scan rate (50 mV s^{-1}) in the potential window of 3 to -3 V was used to scrutinize the electrochemical oxidation-reduction of complexes **2A.1** and **2A.6**.

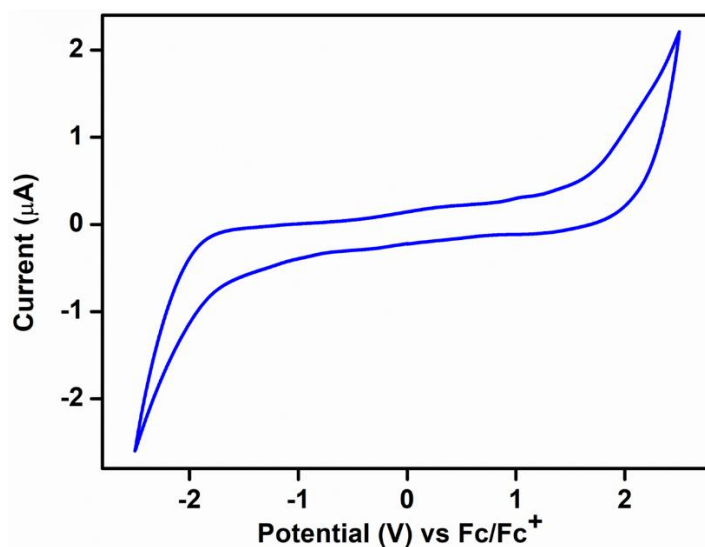


Figure 2A.A.21. Cyclic voltammogram of complex **2A.1** in THF with 0.05 M *t*-butylammonium-hexafluorophosphate. The working electrode was a glassy carbon electrode, the counter electrode was a platinum coil, and the reference electrode was the platinum pseudo reference. Ferrocene was added as an internal standard separately, and all potentials were referenced to the Fc/Fc^+ couple. Scan rate = 50 mV s^{-1} .

Observation: The oxidation and reduction potential of ligand **2A.1** is distinctly different compared to their complexes. There is no oxidation peak, and reduction is observed in ligand **2A.1**. This implies that the ligand is redox inactive. The coordination with metal induces redox-active properties.

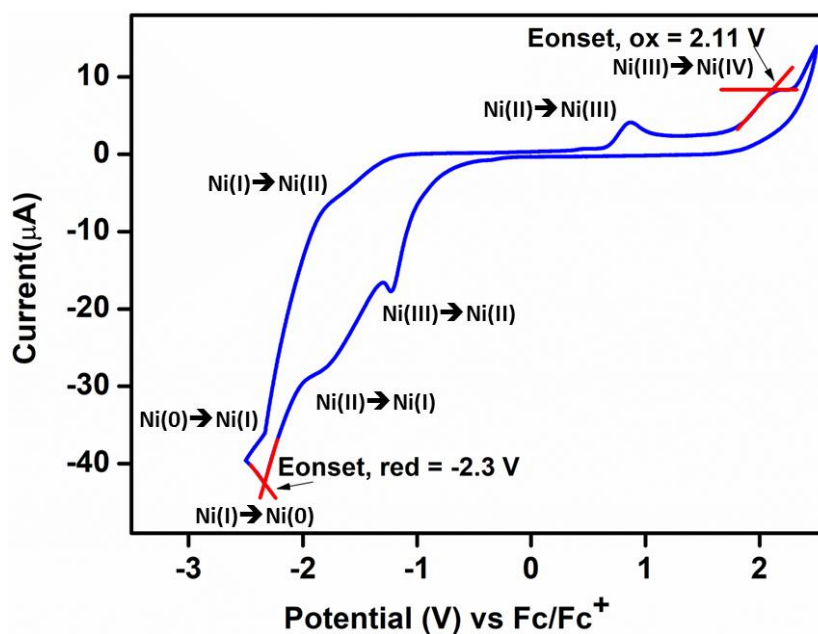


Figure 2A.A.22. Cyclic voltammogram of complex **2A.6** in DCM with 0.05 M *t*-butylammonium-hexafluorophosphate. The working electrode was a glassy carbon electrode, the counter electrode was a platinum coil, and the reference electrode was the platinum pseudo reference. Ferrocene was added as an internal standard separately, and all potentials were referenced to the Fc/Fc^+ couple. Scan rate = 50 mV s^{-1} .

Observation: For nickel complex **2A.6**, CV was performed in dichloromethane (Figure S28). Two reversible redox events with reduction peaks at $E_{\text{pc}} = -1803 \text{ mV}$ and $E_{\text{pc}} = 2333 \text{ mV}$ were assigned to $\text{Ni(II)} \rightarrow \text{Ni(I)}$ and $\text{Ni(I)} \rightarrow \text{Ni(0)}$ with corresponding oxidation peaks at $E_{\text{pa}} = -2333 \text{ mV}$ and $E_{\text{pa}} = -1819 \text{ mV}$ for $\text{Ni(0)} \rightarrow \text{Ni(I)}$ and $\text{Ni(I)} \rightarrow \text{Ni(II)}$, respectively. The reduction peak at $E_{\text{pa}} = -1233 \text{ mV}$ is assigned to $\text{Ni(III)} \rightarrow \text{Ni(II)}$ electron transfer event. The oxidation peak at positive potential corresponds to $\text{Ni(II)} \rightarrow \text{Ni(IV)}$ one-electron oxidation with $E_{\text{pa}} = 875 \text{ mV}$, and at extreme positive potential corresponds to $\text{Ni(III)} \rightarrow \text{Ni(IV)}$ with 2123 mV .

2A.A.5. UV visible absorption spectra of the ligand **2A.1** and complex **2A.6**

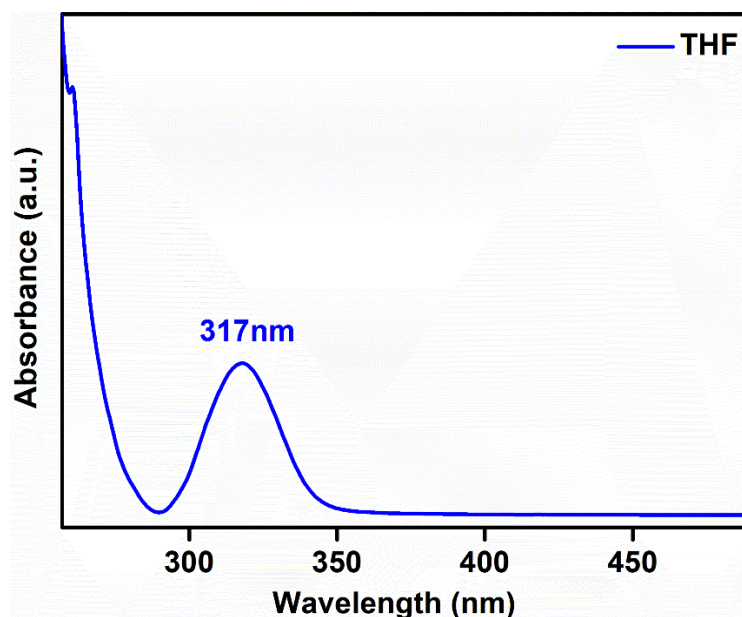


Figure 2A.A.23. UV visible absorption spectra of the ligand **2A.1**

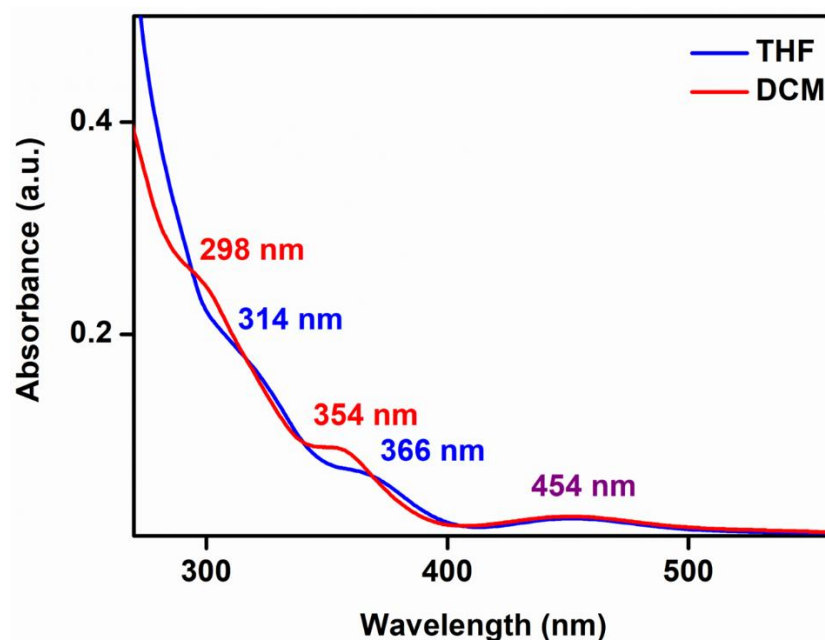


Figure 2A.A.24. UV visible absorption spectra of the Complex 2A.6

2A.A.6. Thermogravimetric analysis of the compounds 3-6

The thermogravimetric analyses (TGA) were performed using the PerkinElmer STA-6000 thermogravimetric analyser at a heating rate of 10 °C/min in a nitrogen atmosphere. In the case of complex **2A.3** (Figure S31), 29.53% weight loss is accounted for amidinate moiety, followed by 24.22 % for TMS {trimethylsilyl amide}. For complex **2A.4** and **2A.5**, 44.94% and 52.94% are for amidinate, and trimethylsilyl amide, respectively. A similar observation was made in the case of complex **2A.6**, 51.86% weight loss is for amidinate and *tert*-butyldimethylsilyl amide. The further gradual decrease of the weight loss in the complexes may be due to the removal of chlorine atoms as HCl gas.

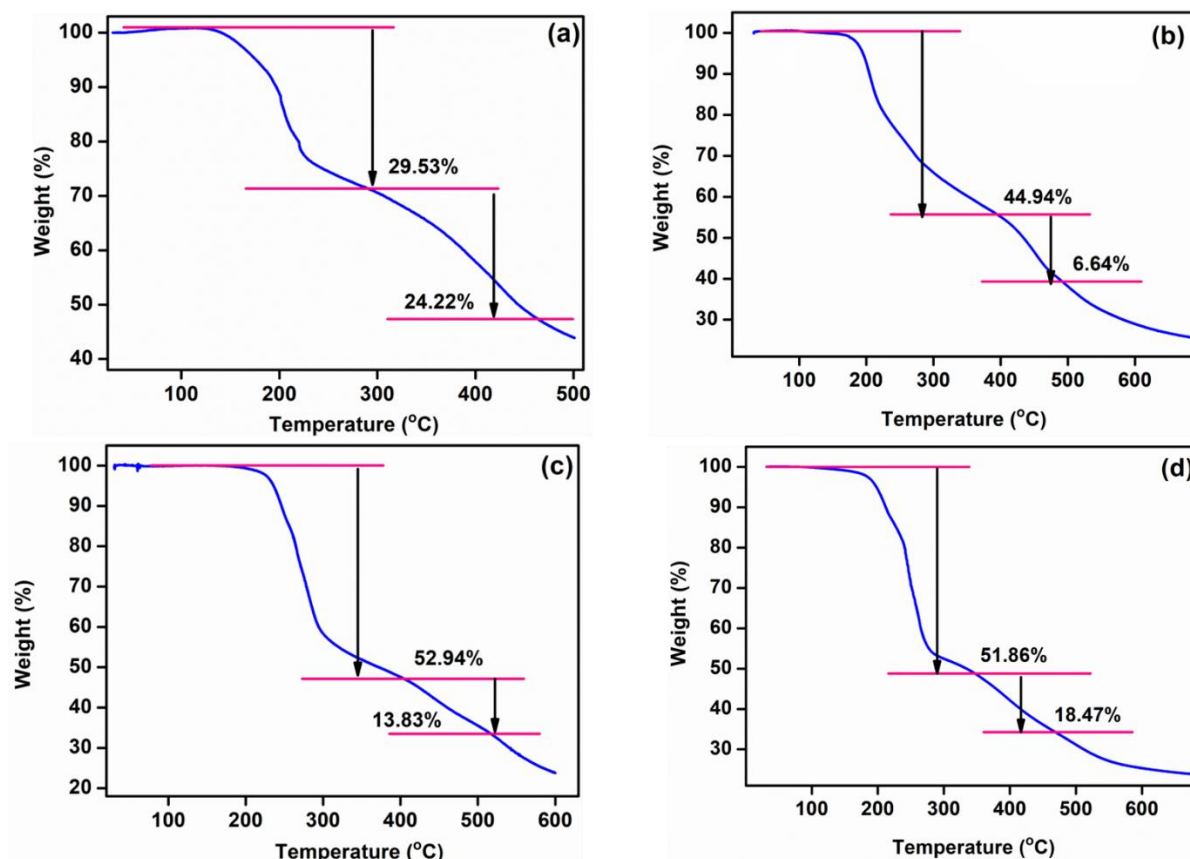


Figure 2A.A.25. Thermogravimetric analysis of complex **2A.3** (a), **2A.4** (b), **5** (c), and **2A.6** (d).

2A.A.7. Magnetic studies of the compounds 2A.3-2A.6

Magnetic measurements of the samples were carried out using a Quantum Design make Magnetic Property Measurement System (MPMS). The following complex magnetic measurements were carried out on the samples using the SQUID and VSM modes of the instrument.

1. Magnetization versus magnetic field at two different temperatures (5 K and 300 K) up to a maximum magnetic field of 6 Tesla (60 kOe). [kOe= kilo oersted]
2. The Magnetization of the samples was recorded as a function of temperature in the range 5-300 K, under:
 - a) Magnetic field of 100 Oe.
 - b) Zero field cooled (ZFC) and field cooled (FC) conditions

The samples were cooled in zero field to 5 K for ZFC measurements, and magnetization was measured while warming in a field of 100 Oe. For FC measurement, the samples were cooled from 300 K to 5 K in a magnetic field of 100 Oe, and the magnetization was measured while

warming in a field of 100 Oe. Before the measurement, instrument was calibrated using a standard sample of high-purity Palladium metal.

The calculation for the magnetic moment:

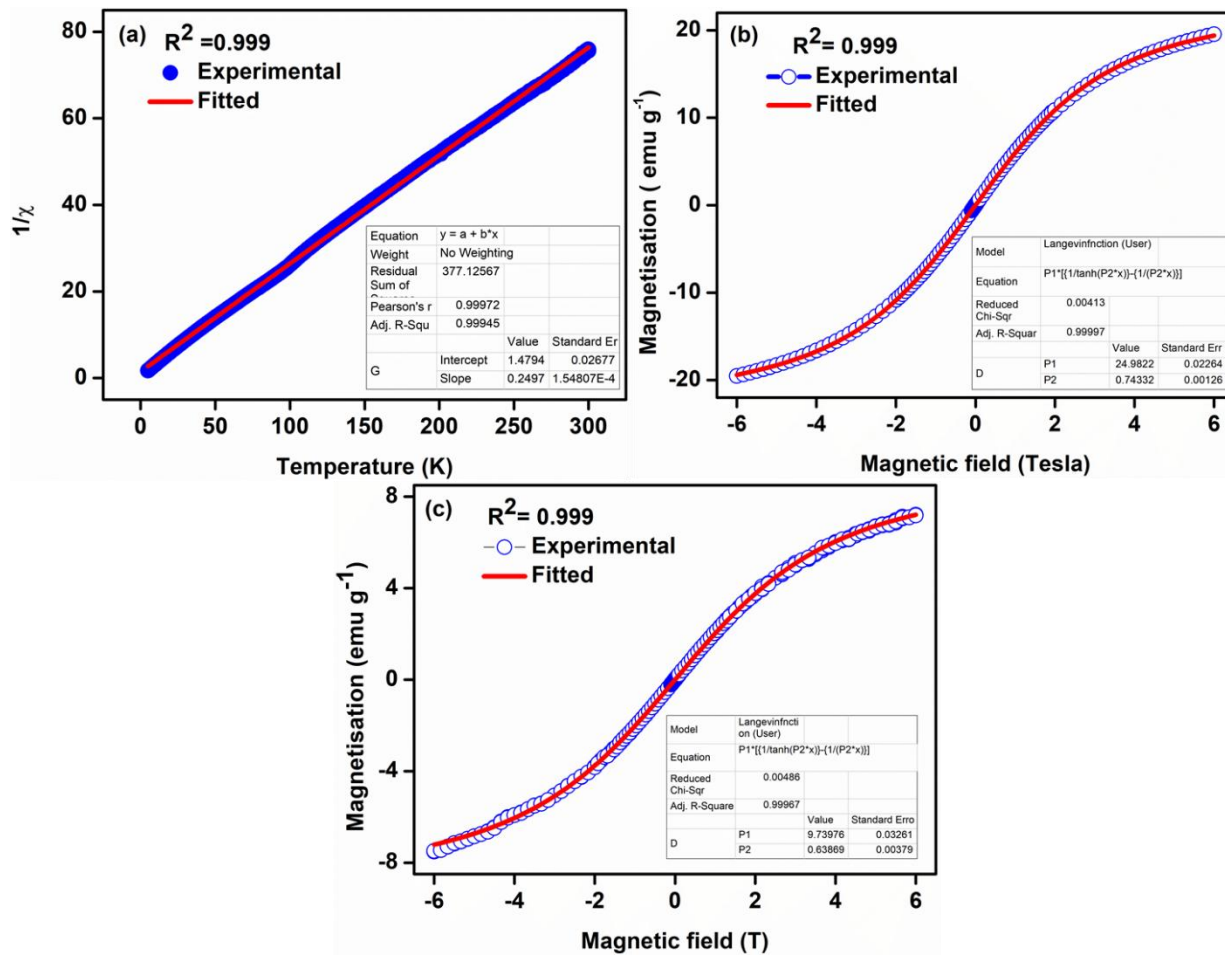


Figure 2A.A.26. (a) χ^{-1} vs. T plot fitted using Curie-Weiss model, (b) M vs. H plot for Complex 2A.3 at 5 K fitted using Langevin formula, and (c) M vs. H plot for Complex 2A.4 at 5 K fitted using Langevin formula. {M = Applied magnetic field, M = Magnetization}.

The Curie Weiss Law can be written as follows;

$$\chi = \frac{C}{T - T_c}$$

The Langevin equation can be written as

$$\frac{M}{M_o} = \coth \frac{\mu H}{K_b T} - \frac{K_b T}{\mu H}$$

Calculation summary:

1. For Complex 2A.3

Slope from the fitted plot, $1/C = 0.2497$

Hence $C = 4.004$

$$\begin{aligned}\text{Effective magnetic moment} &= 2.828(C)^{1/2} \\ &= 2.828 (4.004)^{1/2} \\ &= 5.6 \text{ Bohr Magnetron (BM)}\end{aligned}$$

2. For Complex 2A.3

From the Langevin fit of the M Vs H plot;

$$\mu / k_b T = 0.743 \text{ T}^{-1}$$

$$\mu = 0.743 \text{ T}^{-1} * k_b T$$

$$k_b = 1.38 * 10^{-16} \text{ erg/K}, T = 5 \text{ K}$$

$$\mu = 0.743 * 10^{-4} \text{ Oe}^{-1} * 1.38 * 10^{-16} \text{ erg/K} * 5 \text{ K}$$

$$\mu = 5.126 * 10^{-20} \text{ erg/Gauss}$$

$$\mu = 5.5 \text{ BM}$$

Expected magnetic moment for High Spin Fe(II) (4 unpaired electrons) is 4.8. *{Formula used is $n(n+2)$, where n = no. of unpaired electrons}*

Hence in case of complex **3**, we have Fe (II) in the high spin state with 4 unpaired electrons confirmed by the calculation of magnetic moment from both linear as well as Langevin fit.

2. For Complex 2A.4

From the Langevin fit of the M Vs H plot;

$$\mu / k_b T = 0.638 \text{ T}^{-1}$$

$$\mu = 0.638 \text{ T}^{-1} * k_b T$$

$$k_b = 1.38 * 10^{-16} \text{ erg/K}, T = 5 \text{ K}$$

$$\mu = 0.638 * 10^{-4} \text{ Oe}^{-1} * 1.38 * 10^{-16} \text{ erg/K} * 5 \text{ K}$$

$$\mu = 4.40 * 10^{-20} \text{ erg/Gauss}$$

$$\mu = 4.73 \text{ BM}$$

$1/\chi$ v/s T plot is not fit correctly by linear fit, so we used only Langevin fit to calculate the magnetic moment of complex **2A.4**. The expected magnetic moment value of Co(II) (HS) is 3.8 BM. However, our calculations show that the magnetic moment comes out to be 4.73 BM which is slightly on the higher side of the expected value. This difference in the expected and calculated value can be attributed to some mixing of orbitals in the sample. We cannot calculate the magnetic moment of nickel complex neither from the $1/\chi$ v/s T plot using Linear fit nor from the M v/s H plot using Langevin fit.

2A.A.8. Magnetic moment by using the Evan Method:

All manipulations were carried out in an inert gas atmosphere of dinitrogen using standard Schlenk techniques and a dinitrogen-filled glove box. Employing Evan's method, NMR spectra were recorded in CDCl_3 using Bruker 400 MHz spectrometer. *tert*-Butanol is the reference compound, and the residual peak is for CHCl_3 .

^1H NMR sample preparation:

- i. *tert*-Butanol and CDCl_3 for the reference in CDCl_3 .
- ii. Using complex *tert*-butanol and CDCl_3 for samples in CDCl_3 .

The equation for the magnetic moment:

$$\chi_m = \frac{6}{1000} \frac{1}{c} \frac{\Delta f}{f}$$

Where χ_m is the molar magnetic susceptibility of the transition metal complex, c is the concentration of the complex (mol/L), Δf is the shift in the frequency of the reference compound (Hz), and f is the frequency of the spectrometer (Hz).

The relationship between μ_{eff} and χ_m is the following:

$$\mu_{\text{eff}} = \sqrt{\frac{3k\chi_m T}{N\mu_0\mu_B^2}}$$

Where k = Boltzmann constant, N = Avogadro number, μ_0 = vacuum permeability, μ_B = Bohr magneton, T = Temperature in kelvin.

Using SI units of the constants, this expression is reduced to the following equation,

$$\mu_{\text{eff}} = 798 \sqrt{\chi_m T} = \sqrt{n(n+2)}$$

Where χ_m is the molar magnetic susceptibility determined earlier with the Evans method, T is the temperature in Kelvin, n is the number of unpaired electrons in the metal ions, and μ_{eff} = effective magnetic moment.

For complex 2A.3:

The standard peak of *tert*-butanol = 1.272 ppm

The shifted peak of *tert*-butanol with iron complex = 1.735 ppm

$$\Delta f = 1.735 - 1.272 \text{ ppm} = 0.463 \text{ ppm}$$

Convert it into Hz by multiplying with the frequency of the instrument

$$0.463 \times 400 = 185 \text{ Hz}$$

Concentration = 0.02 mol/L, $f = 400 \times 10^6 \text{ Hz}$

$$X_m = \frac{6}{1000} \times \frac{1}{0.02} \times \frac{185}{400 \times 10^6}$$

$$X_m = 13.89 \times 10^{-8} \text{ L/mol}$$

$$\mu_{\text{eff}} = 798 \sqrt{13.89 \times 10^{-8} \times 298}$$

$$\mu_{\text{eff}} = 798 \sqrt{4139 \times 10^{-8}}$$

$$\mu_{\text{eff}} = 5.1 \text{ BM}$$

For complex 2A.4:

The standard peak of *tert*-butanol = 1.272 ppm

The shifted peak of *tert*-butanol with cobalt complex = 1.565 ppm

$$\Delta f = 1.565 - 1.272 \text{ ppm} = 0.29 \text{ ppm}$$

Convert it into Hz by multiplying with the frequency of the instrument

$$0.29 \times 400 = 117 \text{ Hz}$$

Concentration = 0.02 mol/L, $f = 400 \times 10^6 \text{ Hz}$

$$X_m = \frac{6}{1000} \times \frac{1}{0.02} \times \frac{117}{400 \times 10^6}$$

$$X_m = 8.7 \times 10^{-8} \text{ L/mol}$$

$$\mu_{eff} = 798\sqrt{8.7 \times 10^{-8} \times 298}$$

$$\mu_{eff} = 798\sqrt{2619 \times 10^{-8}}$$

$$\mu_{eff} = 4.08 \text{ BM}$$

For complex 2A.5:

The standard peak of *tert*-butanol = 1.272 ppm

The shifted peak of *tert*-butanol with nickel complex = 1.326 ppm

$$\Delta f = 1.326 - 1.272 \text{ ppm} = 0.054 \text{ ppm}$$

Convert it into Hz by multiplying with the frequency of the instrument

$$0.05 \times 400 = 21.6 \text{ Hz}$$

Concentration = 0.02 mol/L, $f = 400 \times 10^6 \text{ Hz}$

$$X_m = \frac{6}{1000} \times \frac{1}{0.02} \times \frac{21.6}{400 \times 10^6}$$

$$X_m = 1.62 \times 10^{-8} \text{ L/mol}$$

$$\mu_{eff} = 798\sqrt{1.62 \times 10^{-8} \times 298}$$

$$\mu_{eff} = 798\sqrt{482.7 \times 10^{-8}}$$

$$\mu_{eff} = 1.75 \text{ BM}$$

For complex 2A.6:

The standard peak of *tert*-butanol = 1.272 ppm

The shifted peak of *tert*-butanol with nickel complex = 1.308 ppm

$$\Delta f = 1.308 - 1.272 \text{ ppm} = 0.036 \text{ ppm}$$

Convert it into Hz by multiplying with the frequency of the instrument

$$0.036 \times 400 = 14.4 \text{ Hz}$$

Concentration = 0.02 mol/L, $f = 400 \times 10^6 \text{ Hz}$

$$X_m = \frac{6}{1000} \times \frac{1}{0.02} \times \frac{14.4}{400 \times 10^6}$$

$$X_m = 1.08 \times 10^{-8} \text{ L/mol}$$

$$\mu_{eff} = 798 \sqrt{1.08 \times 10^{-8} \times 298}$$

$$\mu_{eff} = 798 \sqrt{321 \times 10^{-8}}$$

$$\mu_{eff} = 1.4 \text{ BM}$$

These magnetic moment values closely match the theoretical value, which is 4.8 BM for complex **2A.3**, 3.8 BM for complex **2A.4**, and 2.8 BM for complex **2A.5** and **2A.6** for the high spin.

For 238 K, the calculated magnetic moment is 4.96 BM for complex **2A.3**, 4.4 BM for complex **2A.4**, and 1.9 BM for complex **2A.5**.

Variable temperature (298 – 238 K) Evans method:

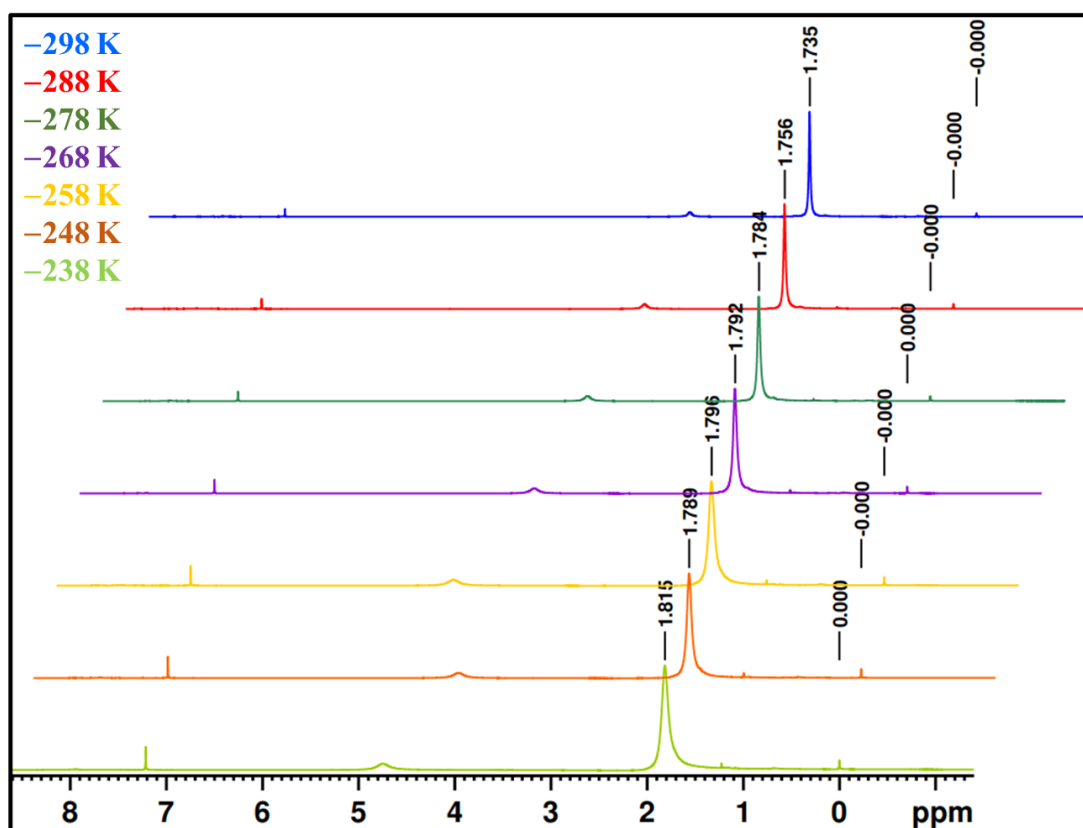


Figure 2A.A.27. Variable temperature of Evans method of complex **2A.3**.

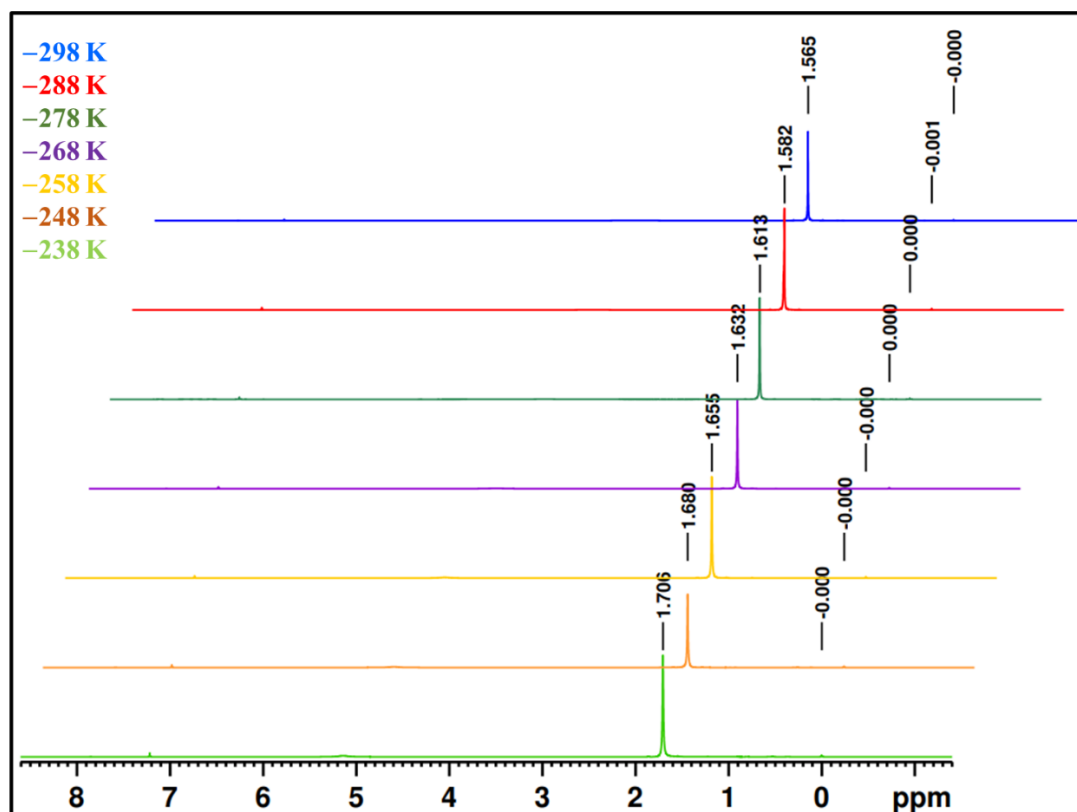


Figure 2A.A.28. Variable temperature of Evans method of complex 2A.4.

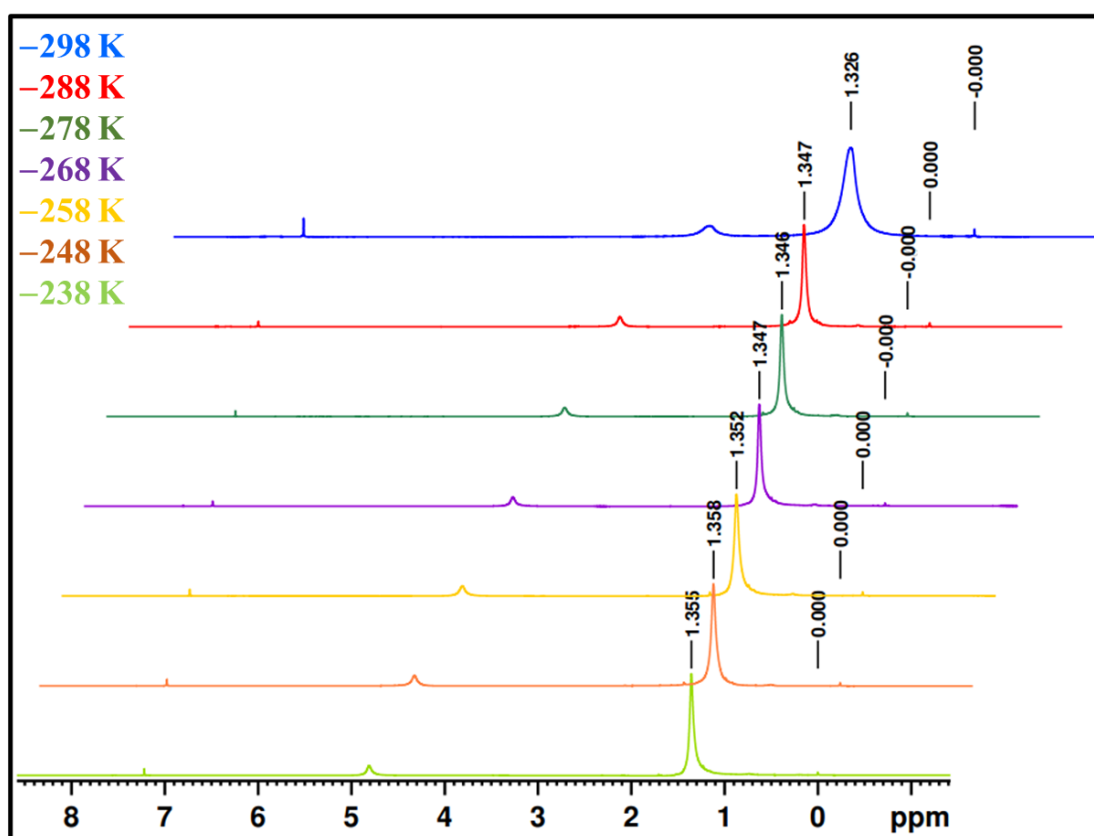
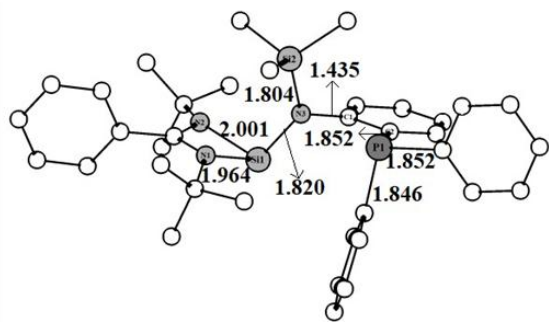


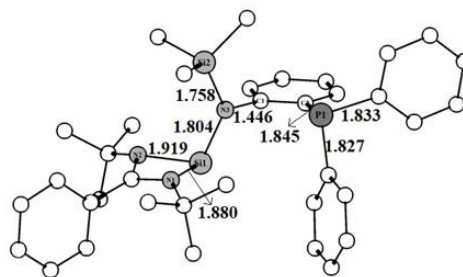
Figure 2A.A.29. Variable temperature of the Evans method of complex 2A.5

2A.A.9: Quantum Computational Studies

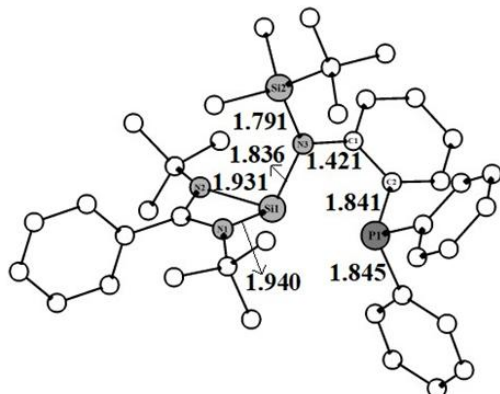
All geometry optimizations were carried out with Gaussian09[10] utilizing the generalized gradient approximation functional of Becke in conjunction with the correlation functional of Perdew (BP86). For describing dispersion interactions, Grimme's C6R-6 correction terms with a Becke-Johnson (BJ) damping function (D3(BJ)) were included in all optimisations. A def2-SVP basis set augmented with one set of polarisation functions was used for the geometry optimisation. All stationary points were characterised on the potential energy hypersurface by vibrational analysis as minima (all real frequencies). Single-point calculations were performed on the optimised geometries using the meta-GGA exchange functional M06 with a basis set having triple ζ -quality, augmented with two sets of polarisation functions (def2-TZVPP). Solvent-corrected energy estimations were done using the PCM model in solvent chloroform. Natural Bond Orbital (NBO version 3.1) analyses were performed at the M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory. The reaction energy (ΔE) was calculated by adding electronic energy at the M06/def2-TZVPP level of theory with zero-point correction calculated at the BP86-GD3BJ/def2-SVP level of theory. Corresponding to Gibbs free energy change (ΔG) was calculated by adding electronic energy at the M06/def2-TZVPP level of theory with zero-point correction for Gibbs free energy calculated at the BP86-GD3BJ/def2-SVP level of theory. Time-dependent density functional theory (TD-DFT) calculations were carried out at the M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory.^{S12} Solvent corrected calculations were carried out using the PCM model in DCM solvent for **2A.3-2A.5** and THF for ligand **2A.1**.



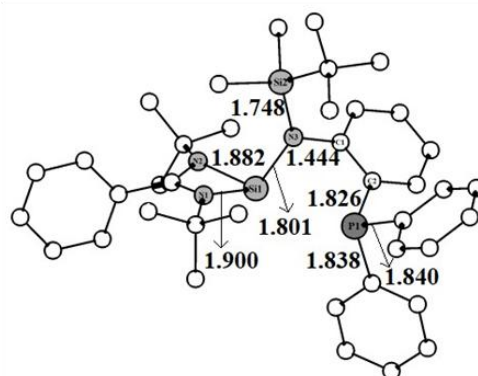
2A.1 ($\theta_{\text{Si/P}} = 86.21^\circ/56.80^\circ$)



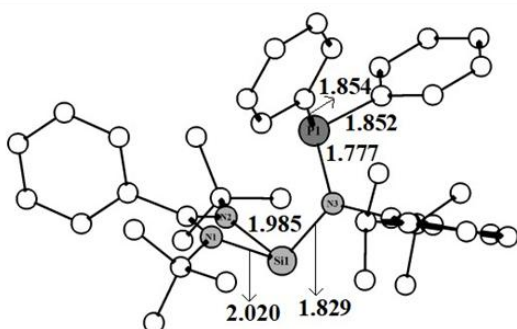
2A.1_{Exp} ($\theta_{\text{Si/P}} = 86.21^\circ/56.80^\circ$)



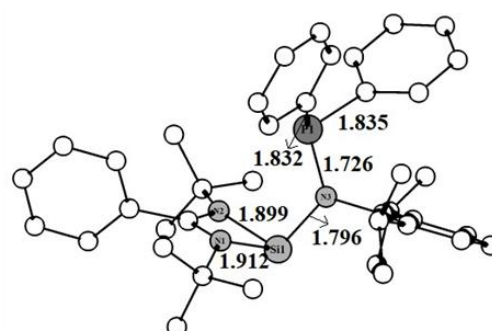
2A.2 ($\theta_{\text{Si/P}} = 80.06^\circ/51.89^\circ$)



2A.2_{Exp} ($\theta_{\text{Si/P}} = 75.98^\circ/54.28^\circ$)



2A.A ($\theta_{\text{Si/P}} = 91.79^\circ/47.84^\circ$)



2A.A_{Exp} ($\theta_{\text{Si/P}} = 82.07^\circ/43.29^\circ$)

Figure 2A.A.30. Optimised geometries of compounds **2A.1**, **2A.2**, and **2A.A** at the BP86-GD3BJ/def2-SVP level of theory; Given along are the pyramidalization angles around Si and P centers (360 - a sum of angles around the center); The experimental geometries of **2A.1**, **2A.2** and **2A.A** are given in the right side.

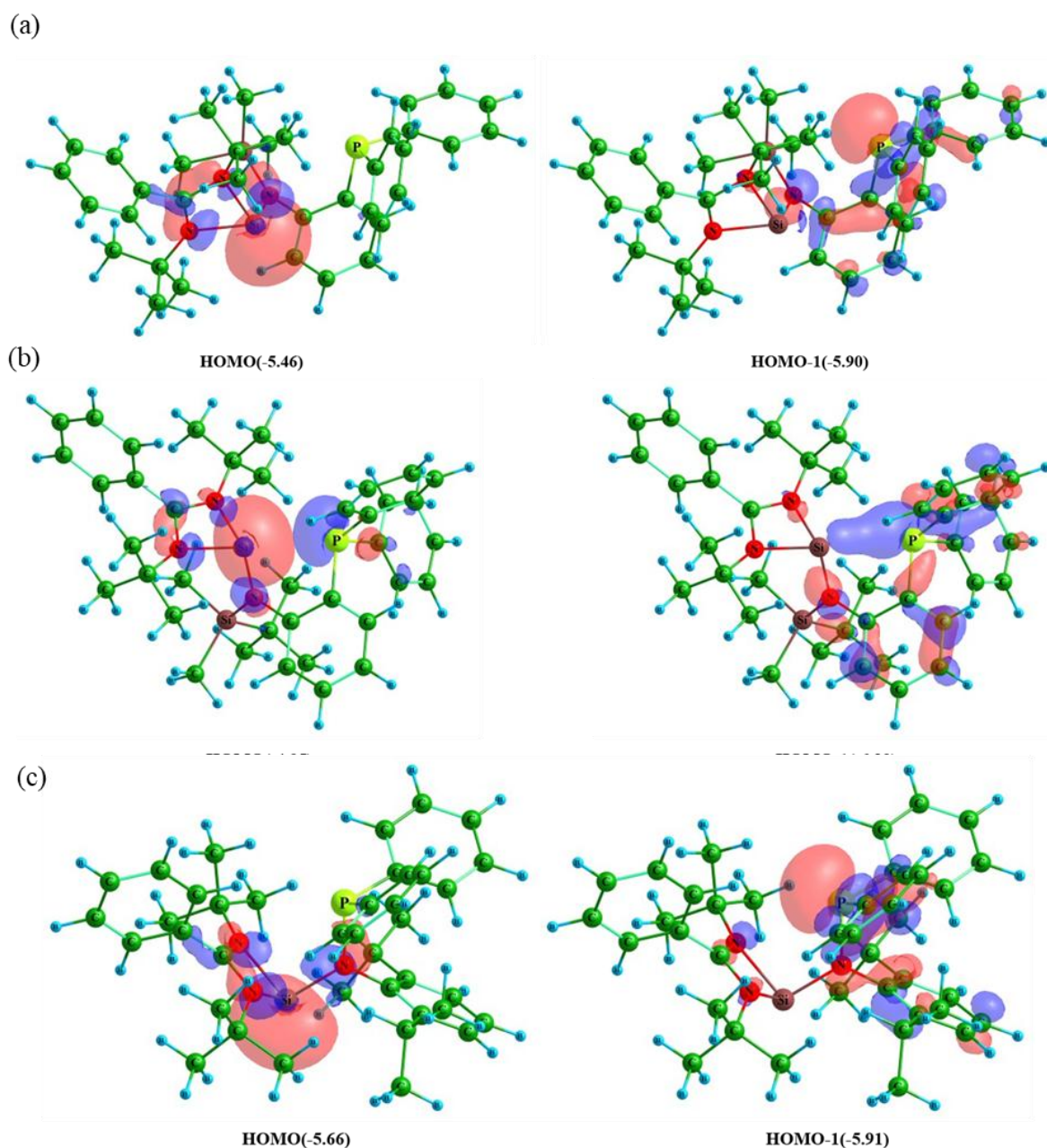


Figure 2A.A.31. Selected frontier molecular orbitals of (a) **2A.1**, (b) **2A.2**, and (c) **2A.A** at the M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory. Eigen values in eV in parenthesis. The isosurface value is 0.045.

Table 2A.A.4: Natural charge on Si, P, and bond orbital occupancy from NPA and NBO analysis of compounds **1**, **2**, and **A** at the M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory.

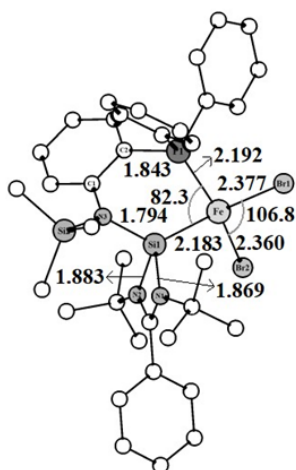
Appendix of Chapter 2A

	2A.1	2A.2	2A.A
qSi	1.18	1.21	1.18
qP	0.85	0.89	1.04
LP(Si)	1.90	1.70	1.94
LP(P)	1.89	1.79	1.90

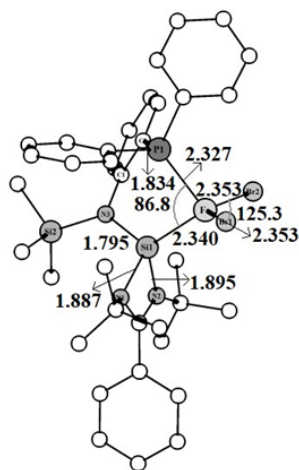
Table 2A.A.5: Results of different optimisations carried out for **3-5** in different spin states with either a square planar or tetrahedral initial guess geometry at the BP86-GD3BJ/def2-SVP level of theory. Converged geometry refers to the geometry around the metal center after a successful optimisation.

Compound	Initial guess geometry	Converged geometry
³2A.3	Square planar	³ 2A.3 – distorted square planar
³2A.3	Tetrahedral	³ 2A.3 – distorted square planar
⁵2A.3	Tetrahedral	⁵ 2A.3 – distorted tetrahedral
²2A.4	Square planar	² 2A.4 – distorted square planar
⁴2A.4	Square planar	⁴ 2A.4 – distorted tetrahedral
⁴2A.4	Tetrahedral	⁴ 2A.4 – distorted tetrahedral
³2A.5	Square planar	³ 2A.5 – distorted square tetrahedral
³2A.5	Tetrahedral	³ 2A.5 – distorted square tetrahedral

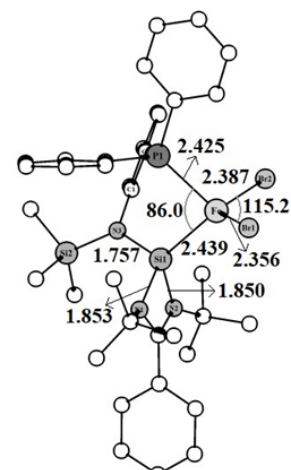
(A1)



³2A.3 (20.13; -21.03)

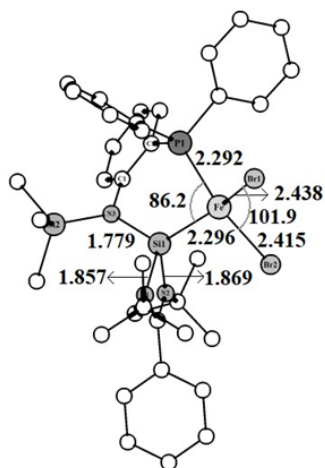


⁵2A.3 (0)

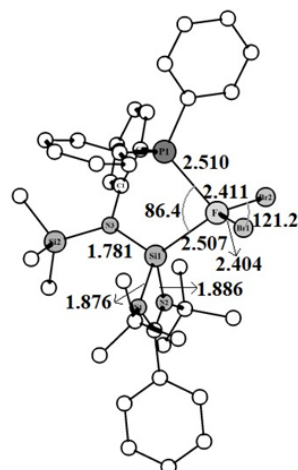


32A.Exp

B1)

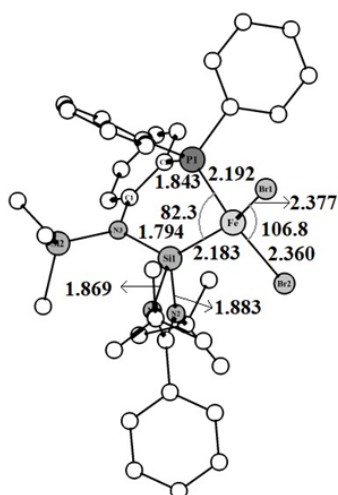


³2A.3-B3LYP (16.72)

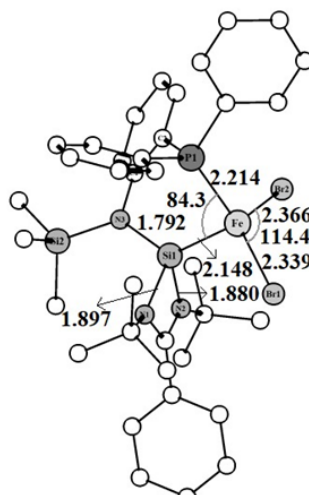


⁵2A.3-B3LYP (0)

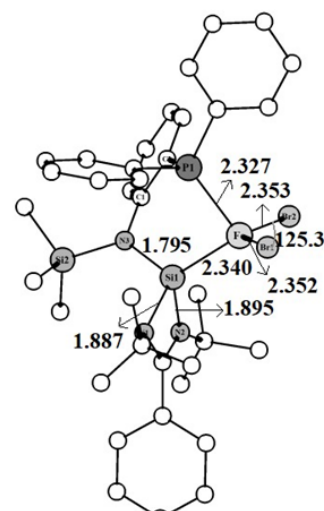
(C1)



³2A.3-SquarePlanar
(convg to ³2A.3)

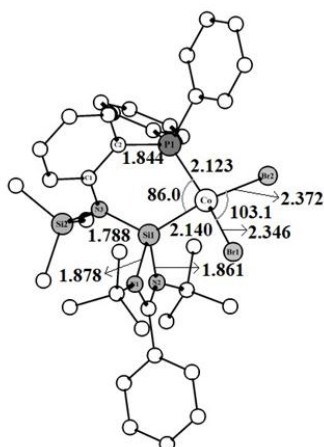


³2A.3-Tetrahedral
(convg to ³2A.3)

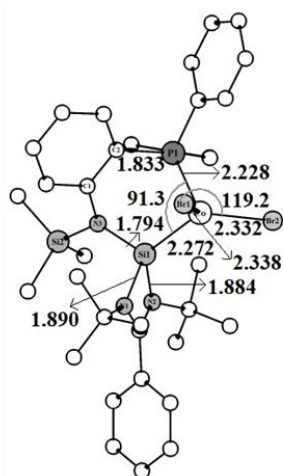


⁵2A.3-Tetrahedral
(convg to ⁵2A.3)

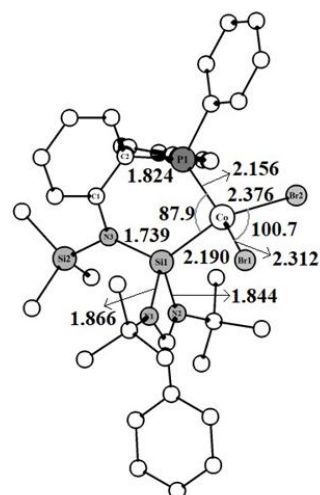
(A2)



²2A.4 (1.46; **2.56**)

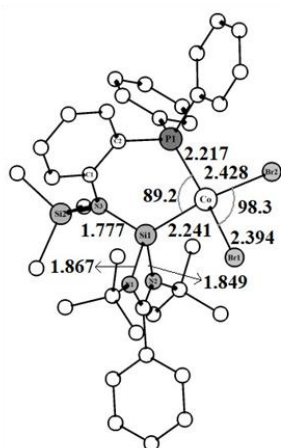


⁴2A.4 (0)

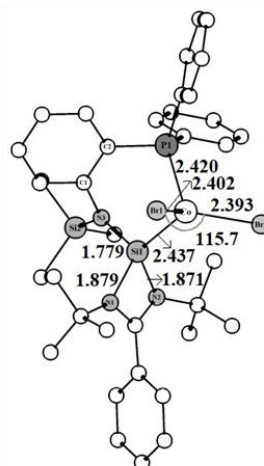


2A.4Exp

B2)

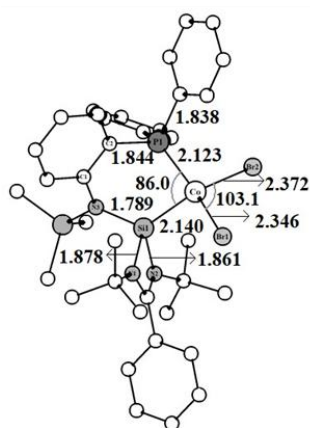


²2A.4-B3LYP (6.23)

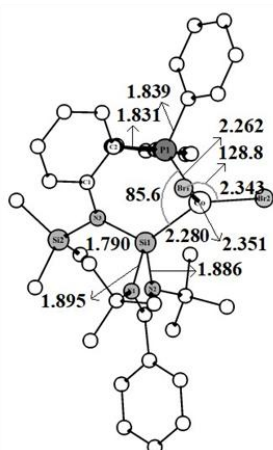


⁴2A.4-B3LYP (0)

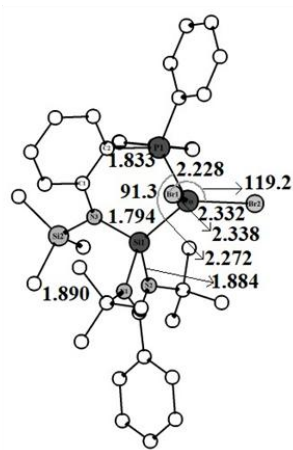
(C2)



²2A.4-SquarePlanar
(convg to ²2A.4)



⁴2A.4-SquarePlanar
(convg to ⁴2A.4)



⁴2A.4-Tetrahedral
(convg to ⁴2A.4)

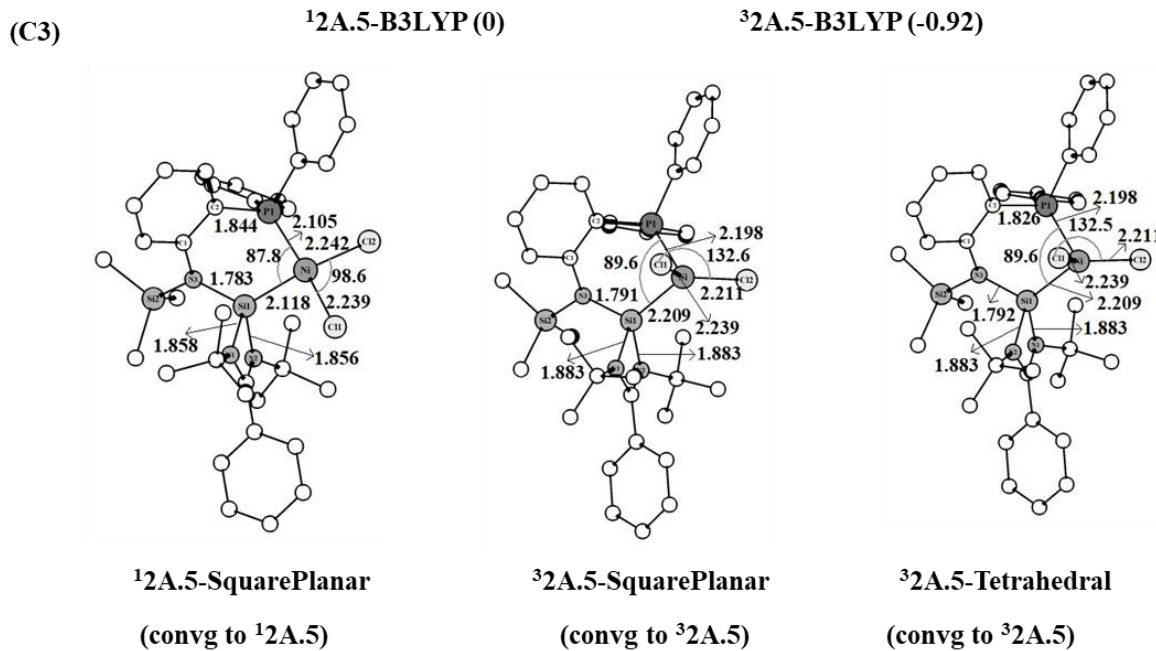
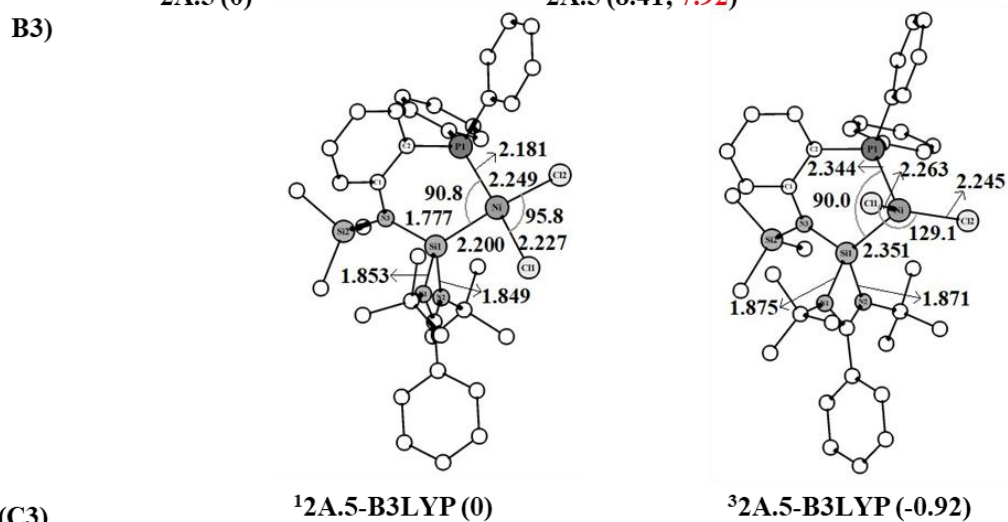
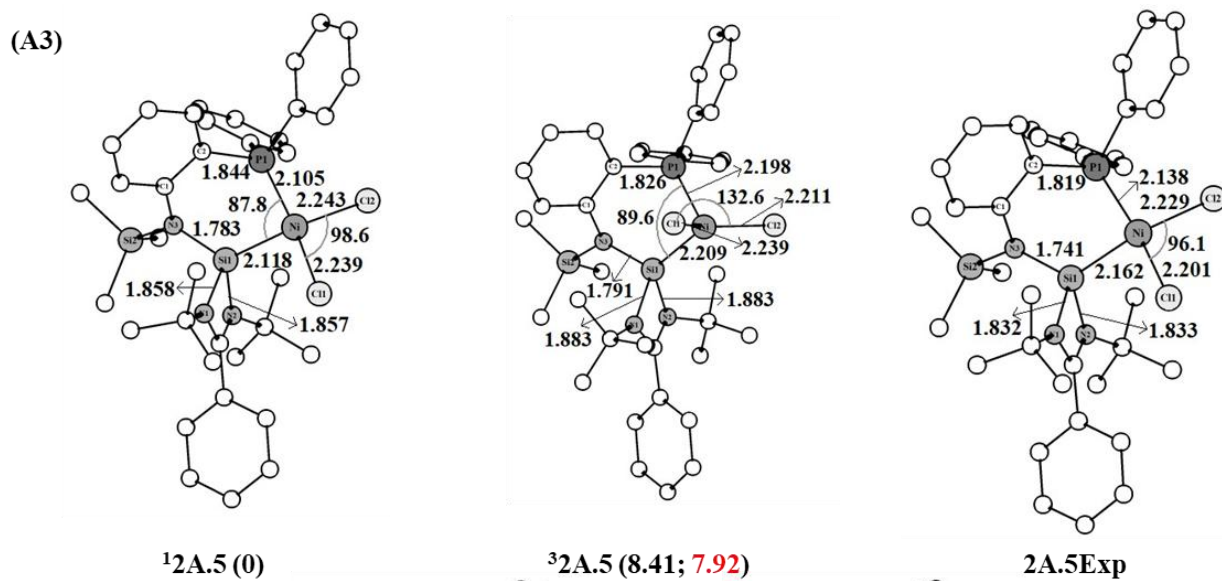


Figure 2A.A.32. Optimised geometries of compounds ⁿ2A.3 - ⁿ2A.5 (n = spin multiplicity) at BP86-GD3BJ/def2-SVP level of theory. Given along are the experimental geometries 32A.Exp-52A.Exp. A1-A3 are the optimised geometries of compounds 2A.3-2A.5 using experimental coordinates as an initial guess. B1-B3 are the optimised geometries of compounds 2A.3-2A.5 using experimental coordinates as an initial guess at the B3LYP/def2-TZVPP level of theory. C1-C3 are optimised geometries with either a square planar (ⁿN-SquarePlanar) or tetrahedral (ⁿN-Tetrahedral) geometry as an initial guess. Relative energies calculated in the gas phase (ΔE in black) and Gibbs free energy (ΔG in red) with respect to the most stable geometry for the respective compound (denoted as zero in parenthesis) are given along in parenthesis.

Table 2A.A.6: Reaction energy (ΔE) and Gibbs free energy (ΔG) for the formation of compounds 2A.3-2A.5 calculated by adding electronic energy from M06/def2-TZVPP and zero-point correction from BP86-GD3BJ/def2-SVP level of theory. Energies are given in kcal mol⁻¹

Compound	ΔE	ΔG
³ 2A.3	-50.04	-38.57
⁵ 2A.3	-70.17	-59.60
² 2A.4	-58.44	-46.67
⁴ 2A.4	-59.90	-49.23
¹ 2A.5	-70.53	-60.10
³ 2A.5	-62.12	-52.18

Table 2A.A.7: Natural spin density on metal center Fe, Co, Ni (M), halogen centers Br (in 2A.3 and 2A.4) and Cl (in 2A.5) (X1 and X2), P and Si centers for compounds 2A.3-2A.5 calculated at the M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory.

Compound	SM	Natural Spin Density					Total Spin Density
		M	X1	X2	P	Si	
2A.3	⁵ 2A.3	3.20	0.21	0.23	0.14	0.15	3.93
2A.4	² 2A.4	1.02	0.02	0.05	-0.02	-0.04	1.03
	⁴ 2A.4	2.22	0.19	0.21	0.14	0.17	2.93
2A.5	³ 2A.5	1.23	0.13	0.12	0.19	0.22	1.89

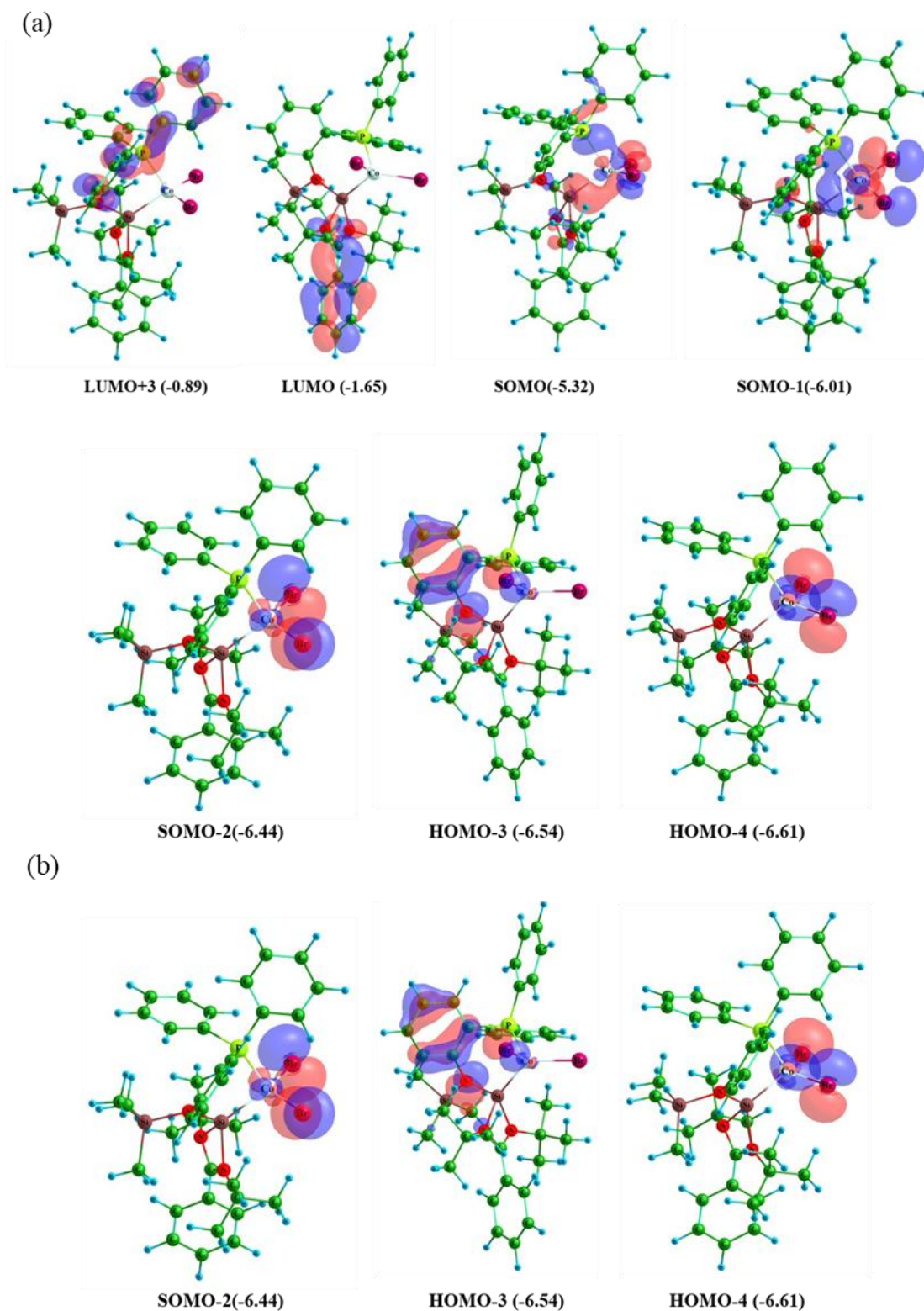


Figure 2A.A.33. Selected alpha frontier molecular orbitals of complexes (a) $^4\mathbf{2A.4}$ and (b) $^3\mathbf{2A.5}$ at the M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory. Eigenvalues in eV are given in parenthesis. The isosurface value is 0.045.

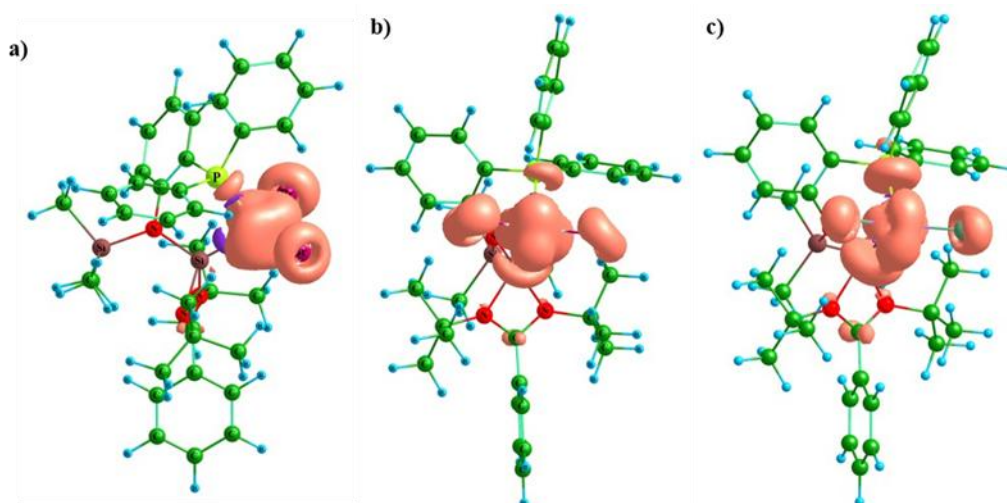


Figure 2A.A.34. Spin densities of compounds $^5\mathbf{2A.3}$, $^4\mathbf{2A.4}$, and $^3\mathbf{2A.5}$ at the M06-def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory. The isosurface value is 0.003.

Table 2A.A.8: Calculated SOMO-LUMO energy gaps (in eV) for complexes $\mathbf{2A.3-2A.5}$ in their LS and HS states at M06/def2-TZVPP//BP86-GD3BJ/def2-SVP level of theory.

Complex	$\Delta E_{\text{SOMO-LUMO}}$
$^5\mathbf{2A.3}$	3.65
$^2\mathbf{2A.4}$	3.93
$^4\mathbf{2A.4}$	3.67
$^1\mathbf{2A.5}$	4.19
$^3\mathbf{2A.5}$	3.63

2B.A.1 Crystallographic data for complexes 2B.2-2B.11.

Table 2B.A.1: Crystallographic data for complexes **2B.2-2B.4**

Identification code	2B.2	2B.3	2B.4
Empirical formula	C ₃₈ H ₄₈ N ₃ PSi	C ₈₈ H ₁₀₈ Cu ₂ N ₈ P ₂ S ₂ Si ₄	C ₉₀ H ₁₁₂ Br ₂ Cu ₂ N ₆ P ₂ Si ₂
Formula weight	605.85	1643.32	1682.87
Temperature/K	150.15	150.15	150.15
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	I4 ₁ /a	P2 ₁ /n	P2 ₁ /n
a/Å	19.654(3)	19.8639(14)	10.2412(19)
b/Å	19.654(3)	16.1925(13)	34.973(7)
c/Å	35.973(4)	28.217(2)	24.116(5)
α/°	90	90	90
β/°	90	108.507(2)	97.245(6)
γ/°	90	90	90
Volume/Å ³	13895(4)	8606.5(11)	8569(3)
Z	16	4	4
ρ _{calc} /g/cm ³	1.158	1.268	1.304
μ/mm ⁻¹	0.143	0.684	1.542
F(000)	5216.0	3472.0	3520.0
Crystal size/mm ³	0.162 × 0.153 × 0.148	0.222 × 0.213 × 0.188	0.142 × 0.133 × 0.112
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.98 to 50.146	3.926 to 50.236	3.886 to 50.338
Index ranges	-23 ≤ h ≤ 23, -23 ≤ k ≤ 23, -42 ≤ l ≤ 39	-23 ≤ h ≤ 21, -19 ≤ k ≤ 19, -33 ≤ l ≤ 33	-12 ≤ h ≤ 12, -41 ≤ k ≤ 41, -28 ≤ l ≤ 28
Reflections collected	117622	176662	219678
Independent reflections	6178 [R _{int} = 0.1506, R _{sigma} = 0.0548]	15300 [R _{int} = 0.1231, R _{sigma} = 0.0577]	15282 [R _{int} = 0.2631, R _{sigma} = 0.1220]
Data/restraints/parameters	6178/0/397	15300/0/847	15282/0/829
Goodness-of-fit on F ²	1.071	1.041	1.019
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0502, wR ₂ = 0.0947	R ₁ = 0.0561, wR ₂ = 0.1229	R ₁ = 0.0562, wR ₂ = 0.0997
Final R indexes [all data]	R ₁ = 0.0812, wR ₂ = 0.1046	R ₁ = 0.0873, wR ₂ = 0.1400	R ₁ = 0.1147, wR ₂ = 0.1143
Largest diff. peak/hole / e Å ⁻³	0.28/-0.38	0.71/-0.63	0.48/-0.47

Table 2B.A.2: Crystallographic data for complexes **2B.5-2B.7**

Identification code	2B.5	2B.6	2B.7
Empirical formula	C ₃₆ H ₄₆ AgClN ₃ PSi ₂	C _{45.88} H ₅₇ AgClN ₃ PSi	C ₃₆ H ₄₆ AgBrN ₃ PSi ₂
Formula weight	704.86	852.88	795.69
Temperature/K	150.15	150.15	150.15
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2 ₁ /c	P-1	P2 ₁ /c
a/Å	22.8863(19)	12.937(4)	22.870(5)
b/Å	9.7430(7)	14.323(5)	9.756(2)
c/Å	17.2213(14)	25.455(9)	17.206(4)
α/°	90	74.090(12)	90
β/°	107.428(2)	84.737(10)	106.933(6)
γ/°	90	78.340(11)	90
Volume/Å ³	3663.7(5)	4439(3)	3672.6(14)
Z	4	4	4
ρ _{calc} /g/cm ³	1.278	1.276	1.439
μ/mm ⁻¹	0.758	0.611	1.774
F(000)	1376.0	1785.0	1632.0
Crystal size/mm ³	0.277 × 0.269 × 0.256	0.247 × 0.236 × 0.215	0.277 × 0.263 × 0.256
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.73 to 50.29	3.858 to 50.352	4.572 to 50.222
Index ranges	-27 ≤ h ≤ 27, -11 ≤ k ≤ 10, -20 ≤ l ≤ 20	-15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -30 ≤ l ≤ 30	-27 ≤ h ≤ 27, -11 ≤ k ≤ 11, -20 ≤ l ≤ 20
Reflections collected	98160	183321	128190
Independent reflections	6540 [R _{int} = 0.0863, R _{sigma} = 0.0334]	15785 [R _{int} = 0.1037, R _{sigma} = 0.0501]	6548 [R _{int} = 0.0605, R _{sigma} = 0.0217]
Data/restraints/parameters	6540/0/397	15785/0/829	6548/0/406
Goodness-of-fit on F ²	1.074	1.053	1.062
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0497, wR ₂ = 0.1336	R ₁ = 0.0504, wR ₂ = 0.1050	R ₁ = 0.0263, wR ₂ = 0.0507
Final R indexes [all data]	R ₁ = 0.0620, wR ₂ = 0.1444	R ₁ = 0.0677, wR ₂ = 0.1112	R ₁ = 0.0371, wR ₂ = 0.0543
Largest diff. peak/hole / e Å ⁻³	0.86/-0.77	1.30/-1.58	0.50/-0.38

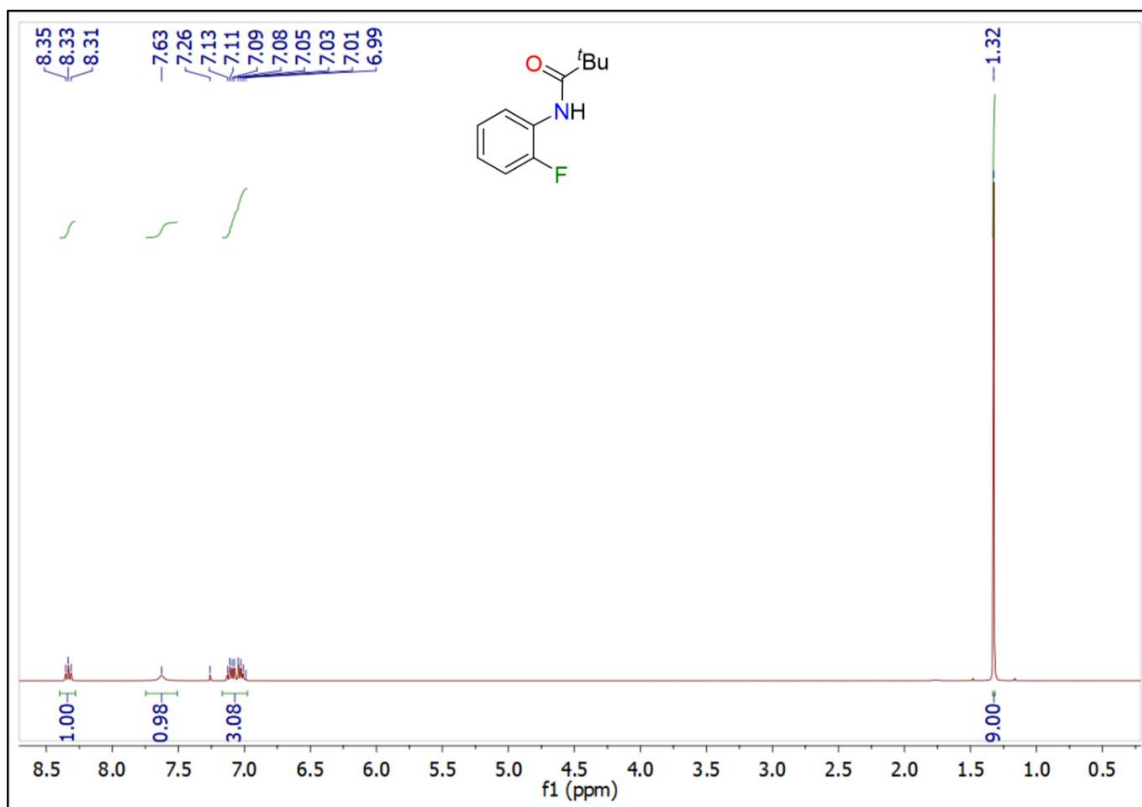
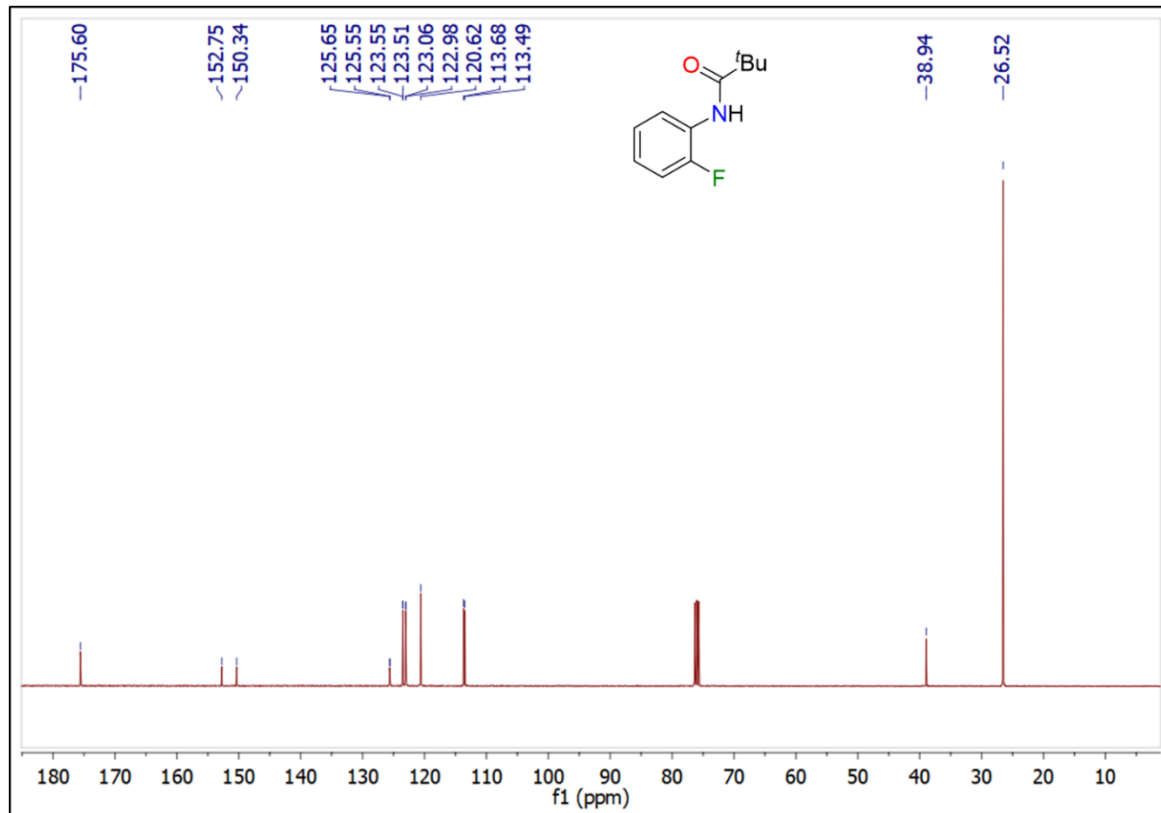
Table 2B.A.3: Crystallographic data for complexes **2B.8-2B.10**

Identification code	2B.8	2B.9	2B.10
Empirical formula	C ₃₇ H ₄₆ AgN ₄ PSi ₂	C ₅₃ H ₆₄ AgN ₄ PSi	C ₃₇ H ₄₈ AuCl ₃ N ₃ PSi ₂
Formula weight	741.80	924.01	925.25
Temperature/K	150.15	150.15	150.15
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P2 ₁ /c	Pca2 ₁	Cc
a/Å	22.978(3)	25.880(6)	18.0671(13)
b/Å	9.8305(11)	15.470(4)	12.8057(9)
c/Å	17.1285(19)	11.985(3)	17.5592(12)
α/°	90	90	90
β/°	108.627(3)	90	94.159(2)
γ/°	90	90	90
Volume/Å ³	3666.4(7)	4798(2)	4051.8(5)
Z	4	4	4
ρ _{calc} /g/cm ³	1.344	1.279	1.517
μ/mm ⁻¹	0.690	0.517	3.957
F(000)	1544.0	1944.0	1856.0
Crystal size/mm ³	0.175 × 0.169 × 0.156	0.148 × 0.131 × 0.129	0.346 × 0.325 × 0.311
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.546 to 50.288	4.104 to 50.226	4.458 to 50.234
Index ranges	-27 ≤ h ≤ 27, -11 ≤ k ≤ 11, -19 ≤ l ≤ 20	-30 ≤ h ≤ 30, -18 ≤ k ≤ 18, -14 ≤ l ≤ 14	-21 ≤ h ≤ 21, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	71039	60017	73480
Independent reflections	6536 [R _{int} = 0.1389, R _{sigma} = 0.0644]	8535 [R _{int} = 0.2263, R _{sigma} = 0.1728]	7170 [R _{int} = 0.0498, R _{sigma} = 0.0357]
Data/restraints/parameters	6536/6/415	8535/247/593	7170/61/462
Goodness-of-fit on F ²	1.037	1.085	1.045
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0475, wR ₂ = 0.1027	R ₁ = 0.0833, wR ₂ = 0.1242	R ₁ = 0.0255, wR ₂ = 0.0572
Final R indexes [all data]	R ₁ = 0.0776, wR ₂ = 0.1185	R ₁ = 0.1587, wR ₂ = 0.1461	R ₁ = 0.0284, wR ₂ = 0.0585
Largest diff. peak/hole / e Å ⁻³	0.82/-0.59	1.17/-0.52	0.99/-0.71

Table 2B.A.4: Crystallographic data for complexes **2B.11**

Identification code	2B.11
Empirical formula	C ₃₈ H ₄₈ AuClN ₃ PSi
Formula weight	838.27
Temperature/K	150.15
Crystal system	Monoclinic
Space group	P2 ₁ /c
a/Å	23.114(9)
b/Å	9.525(4)
c/Å	17.568(6)
α /°	90
β /°	102.386(11)
γ /°	90
Volume/Å ³	3778(3)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.474
μ/mm^{-1}	4.069
F(000)	1688.0
Crystal size/mm ³	0.241 × 0.238 × 0.215
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.642 to 50.098
Index ranges	-27 ≤ h ≤ 27, -11 ≤ k ≤ 11, -20 ≤ l ≤ 20
Reflections collected	151069
Independent reflections	6670 [R_{int} = 0.0657, R_{sigma} = 0.0191]
Data/restraints/parameters	6670/0/415
Goodness-of-fit on F ²	1.070
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0195, wR_2 = 0.0469
Final R indexes [all data]	R_1 = 0.0230, wR_2 = 0.0488
Largest diff. peak/hole / e Å ⁻³	0.66/-0.83

2B.A.2 NMR spectrum for 2B.2-2B.11.

Figure 2B.A.1. ¹H NMR spectrum of **2B.L'** (CDCl₃, 400 MHz, 298 K)Figure 2B.A.2. ¹³C{¹H} NMR spectrum of **2B.L'** (CDCl₃, 100.613 MHz, 298 K)

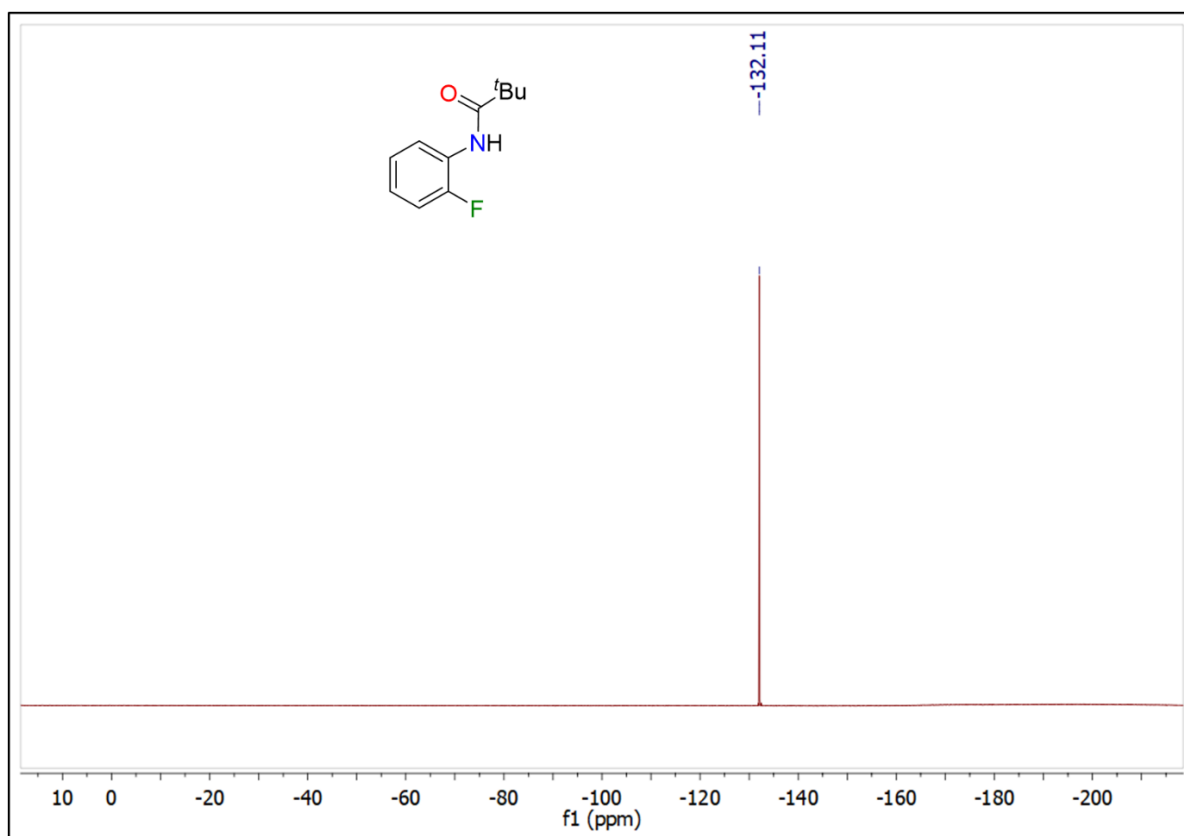


Figure 2B.A.3. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **2B.L'** (CDCl_3 , 376.49 MHz, 298 K)

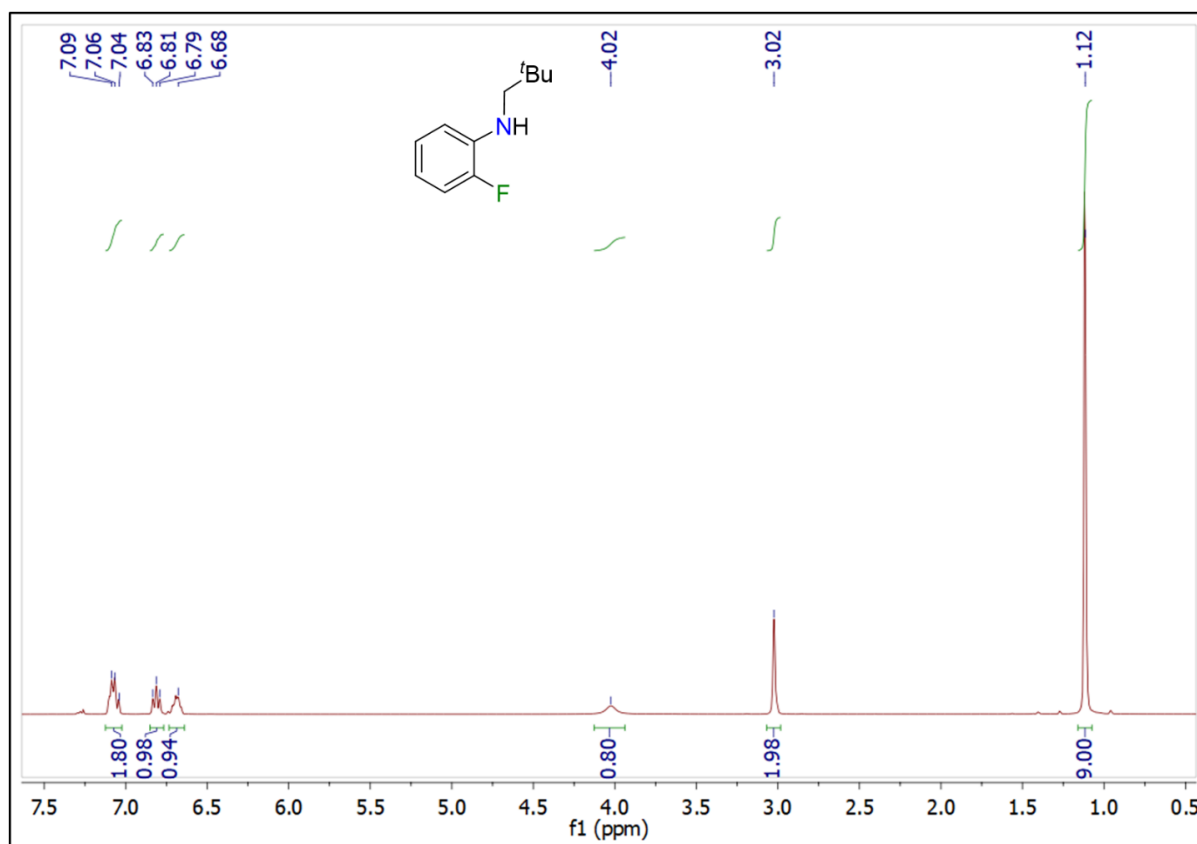


Figure 2B.A.4. ^1H NMR spectrum of **2B.L''** (CDCl_3 , 400 MHz, 298 K)

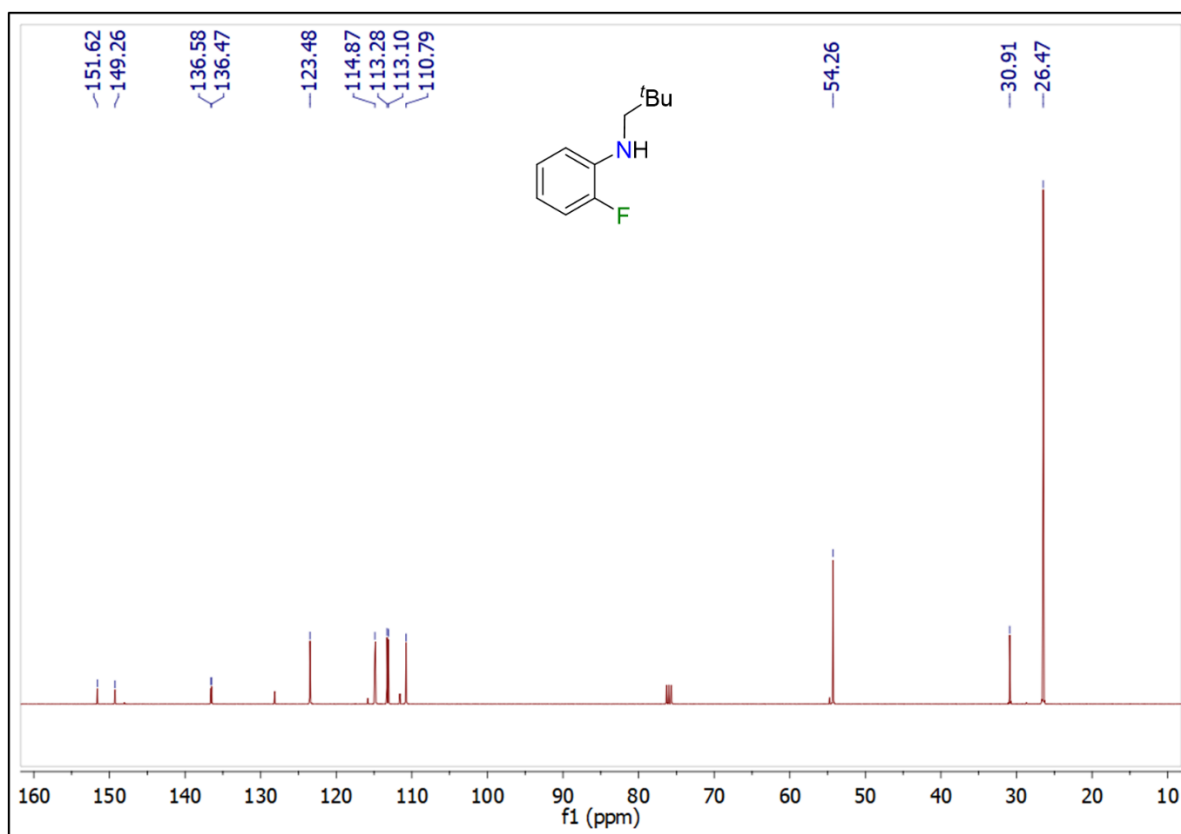


Figure 2B.A.5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2B.L''** (CDCl₃, 100.613 MHz, 298 K)

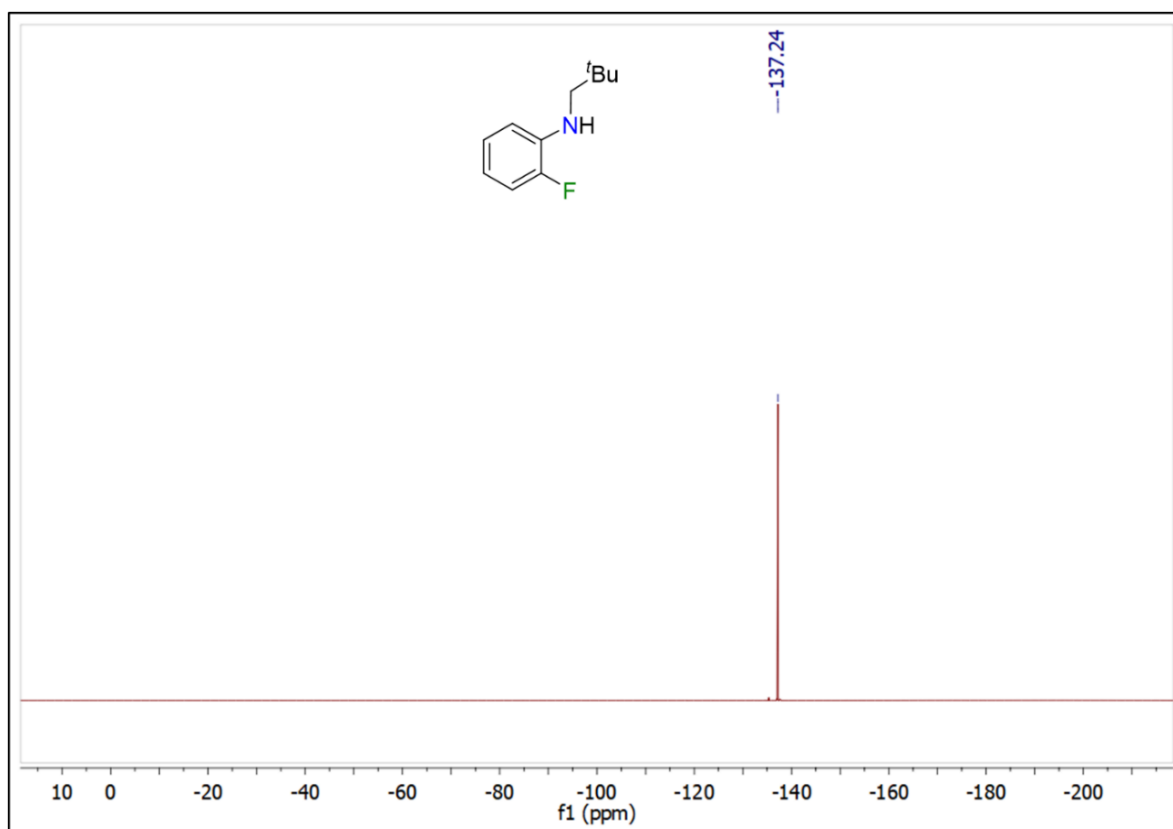


Figure 2B.A.6. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **2B.L''** (CDCl₃, 376.49 MHz, 298 K)

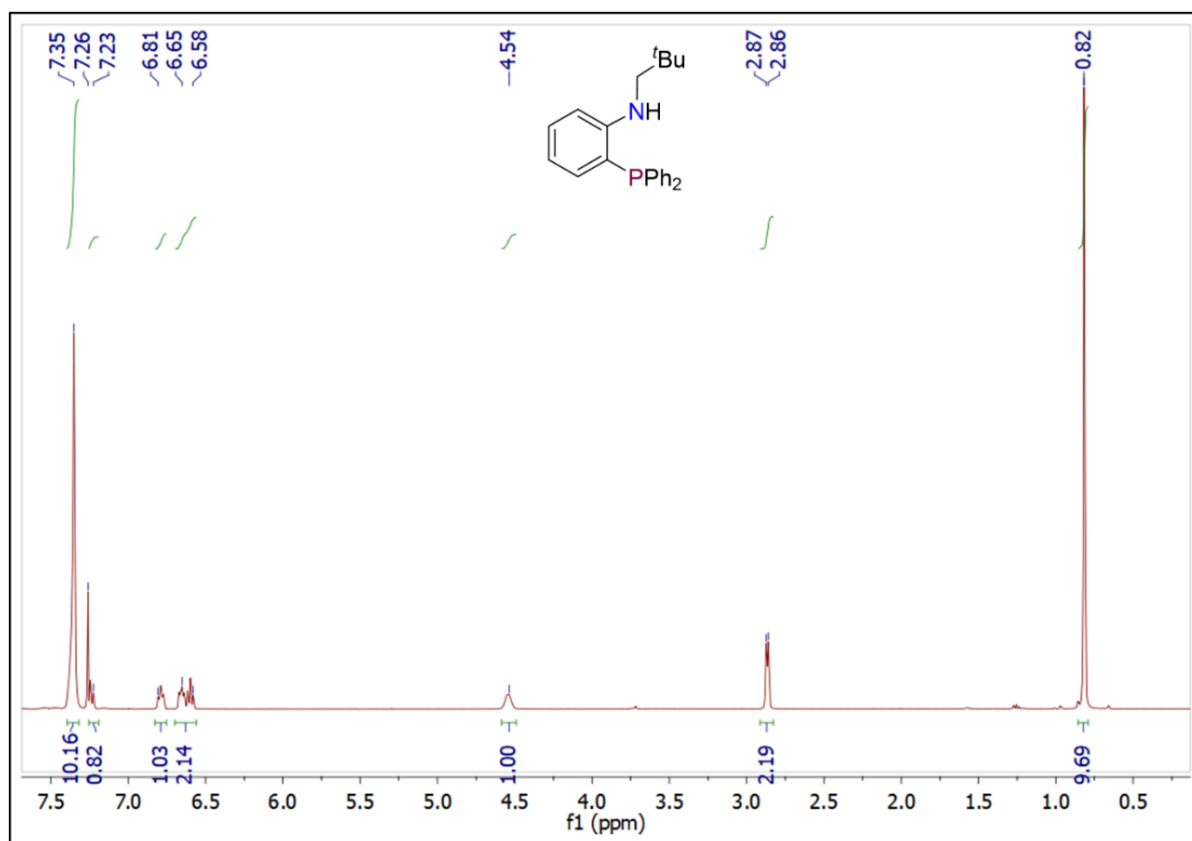


Figure 2B.A.7. ¹H NMR spectrum of **2B.L1** (CDCl₃, 400 MHz, 298 K)

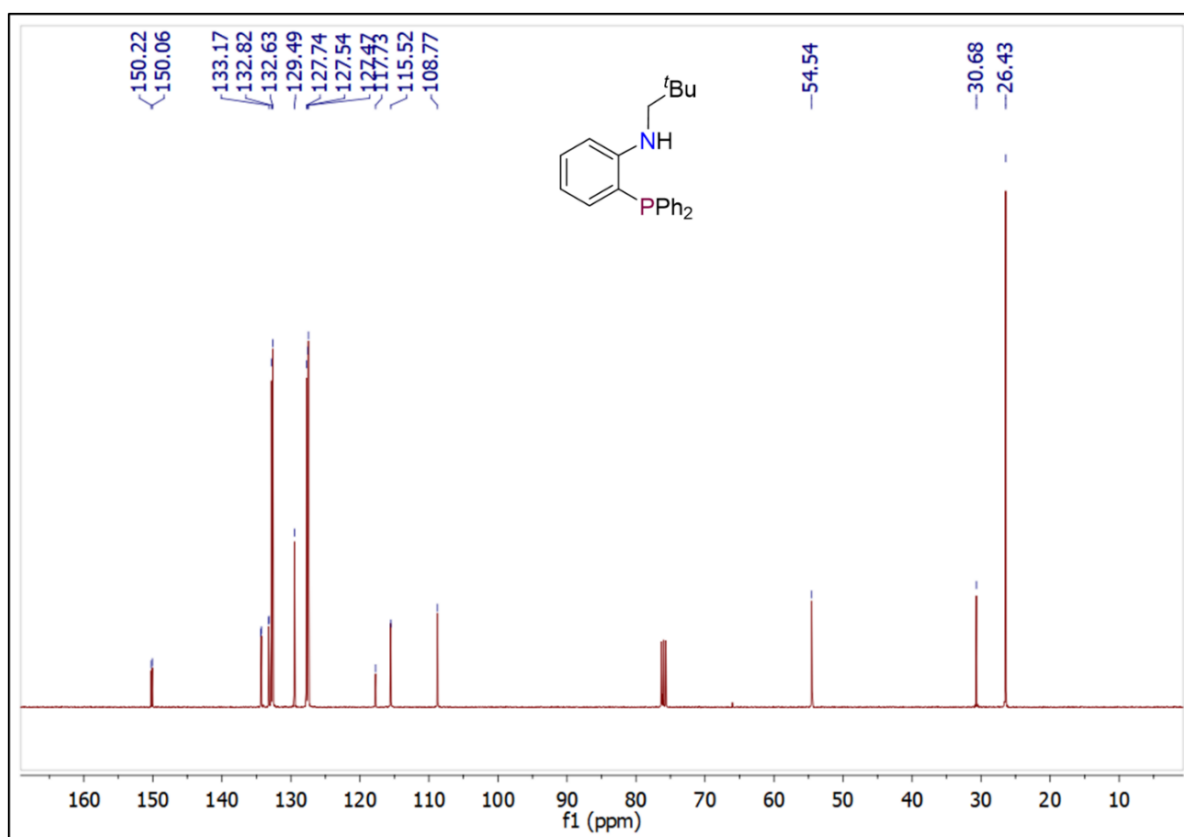


Figure 2B.A.8. ¹³C{¹H} NMR spectrum of **2B.L1** (CDCl₃, 100.613 MHz, 298 K)

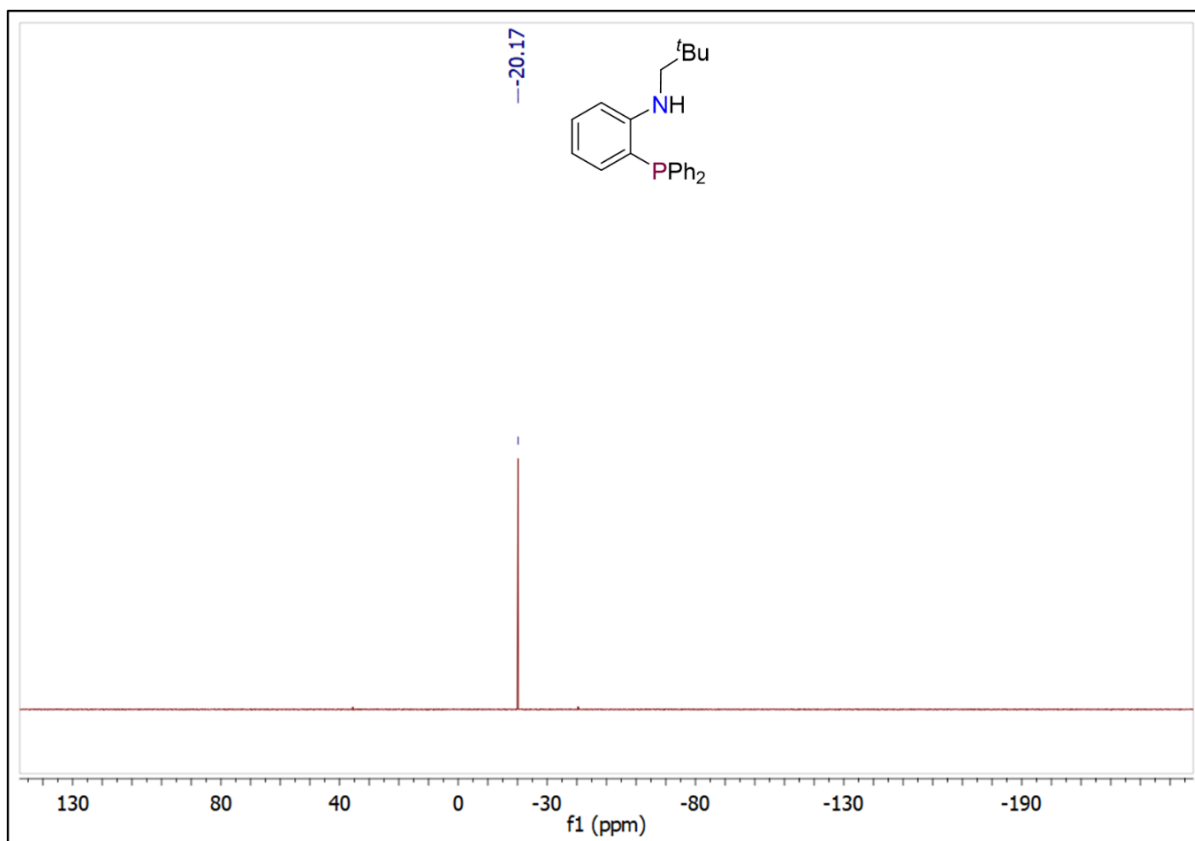


Figure 2B.A.9. $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2B.L1** (CDCl₃, 161.97 MHz, 298 K)

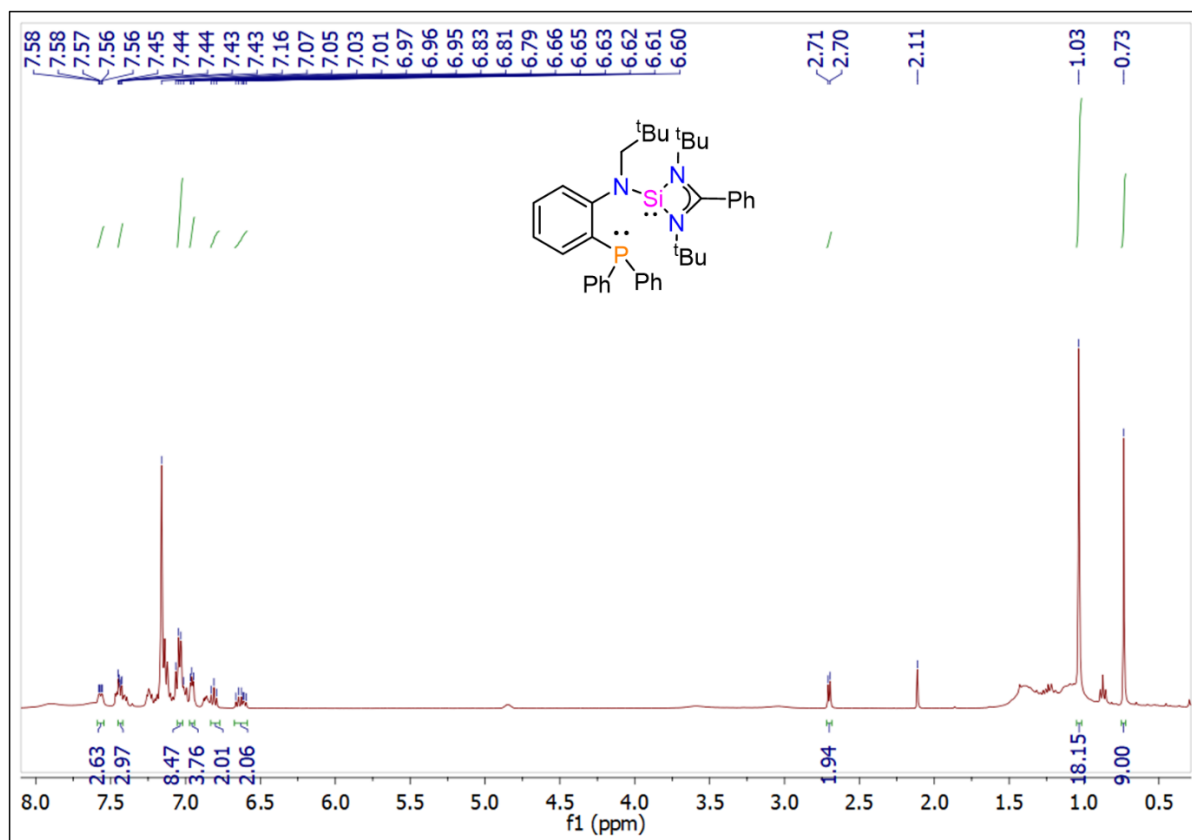


Figure 2B.A.10. ^1H NMR spectrum of **2B.2** (C₆D₆, 400 MHz, 298 K)

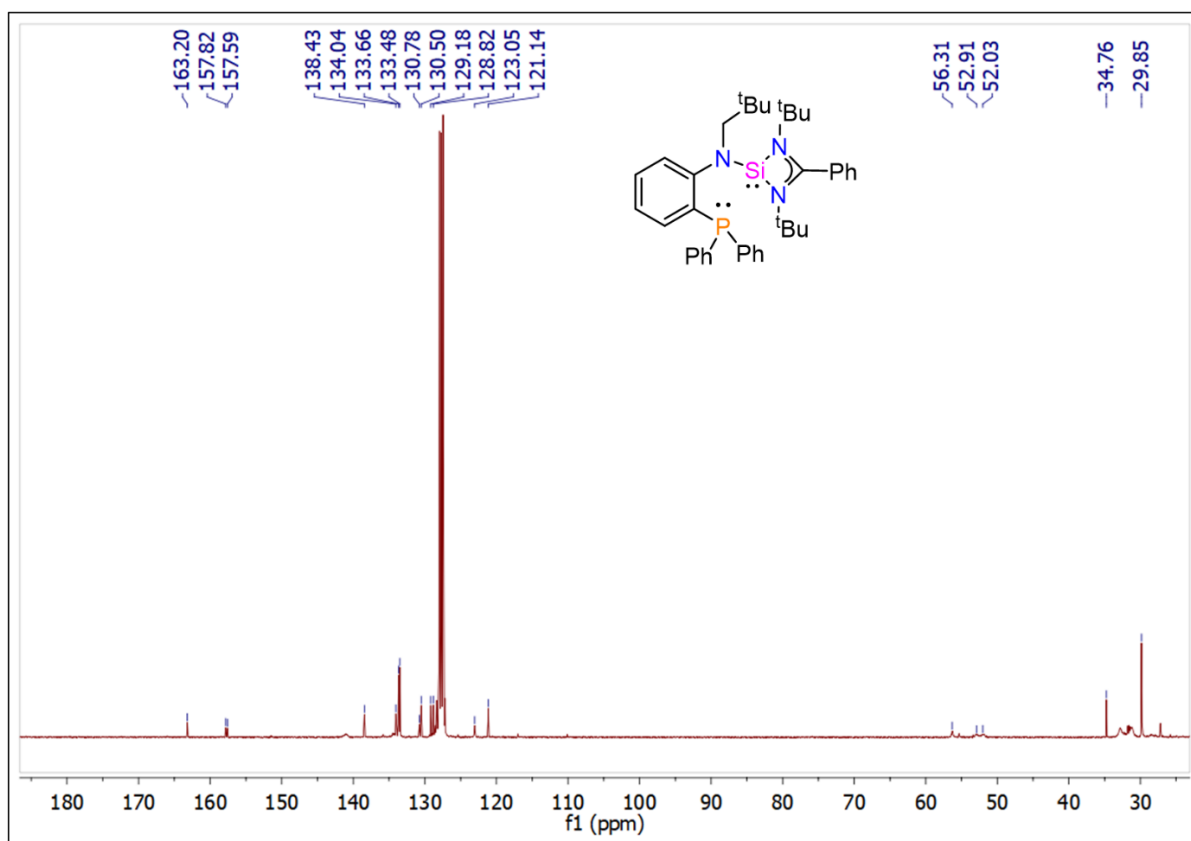


Figure 2B.A.11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2B.2** (C_6D_6 , 100.613 MHz, 298 K)

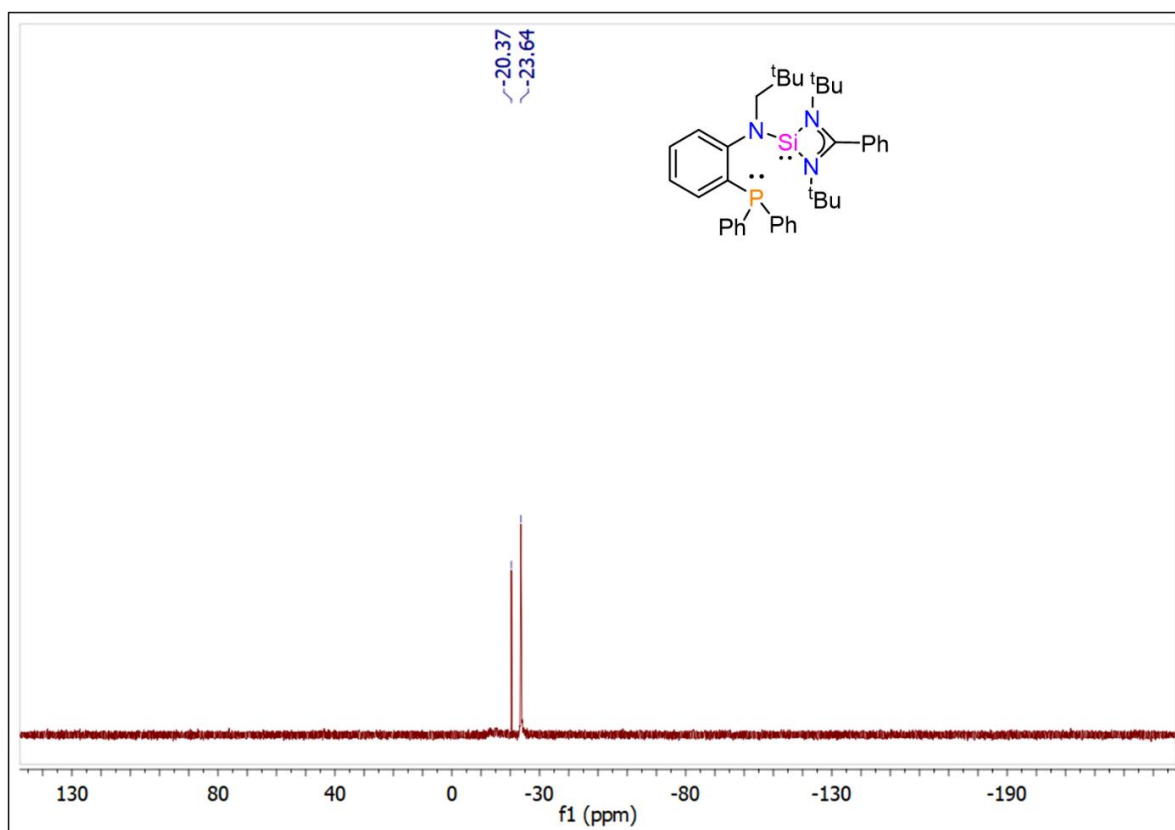


Figure 2B.A.12. $^{31}\text{P}\{^1\text{H}\}$ full NMR spectrum of **2B.2** (C_6D_6 , 161.97 MHz, 298 K)

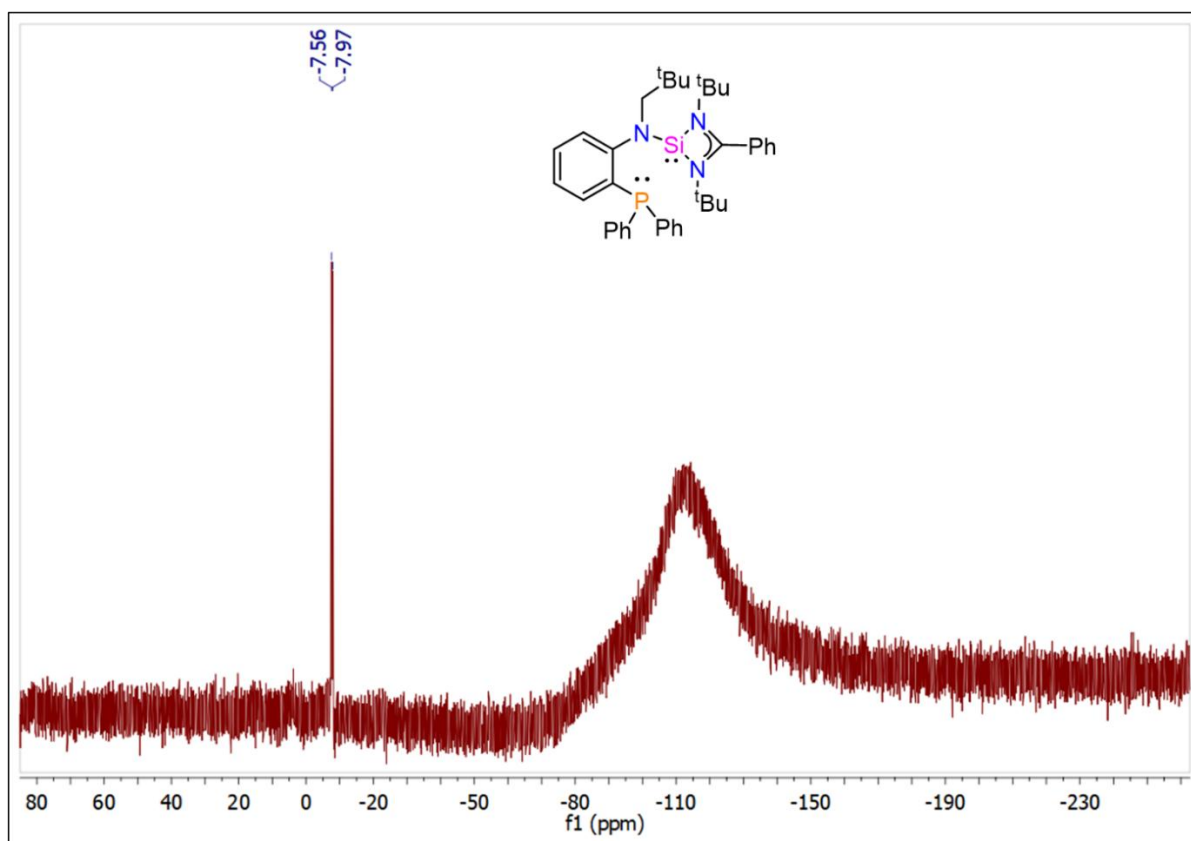


Figure 2B.A.13. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2B.2** (C_6D_6 , 79.49 MHz, 298 K)

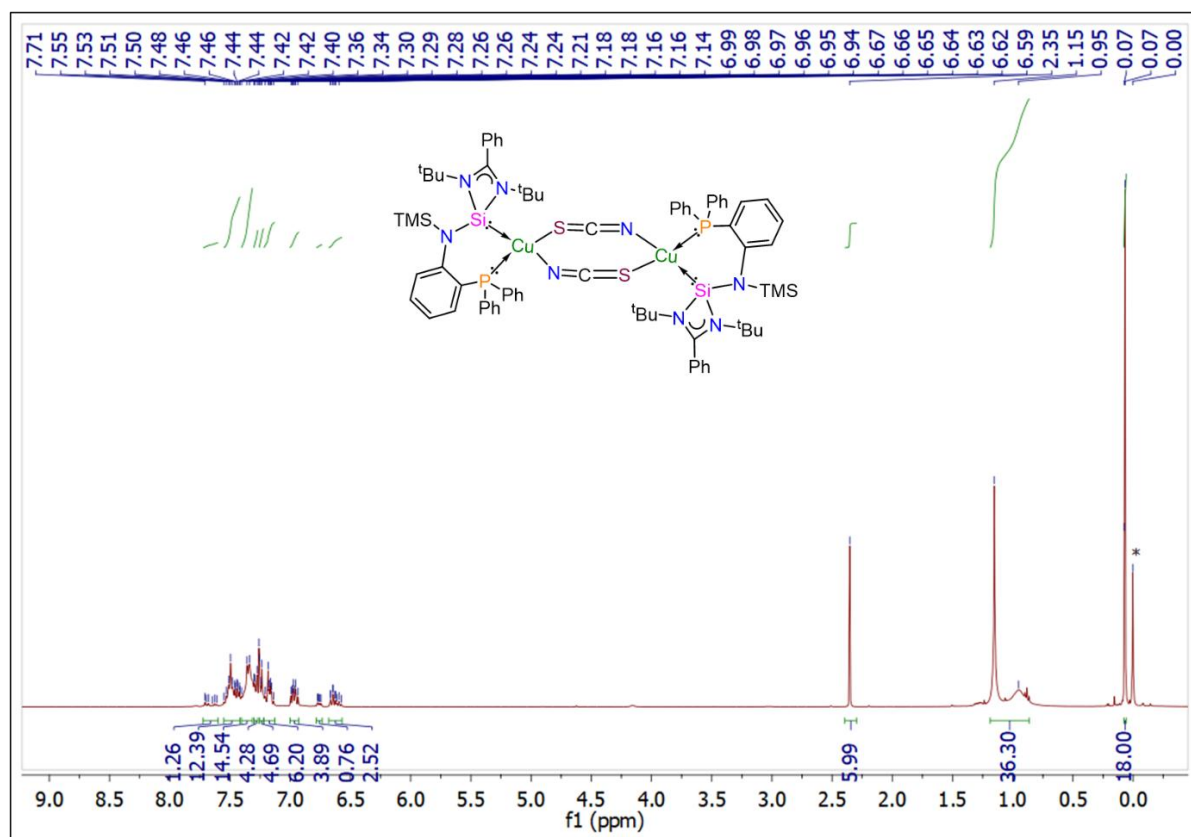


Figure 2B.A.14. ^1H NMR spectrum of **2B.3** (CDCl_3 , 400 MHz, 298 K), *Grease

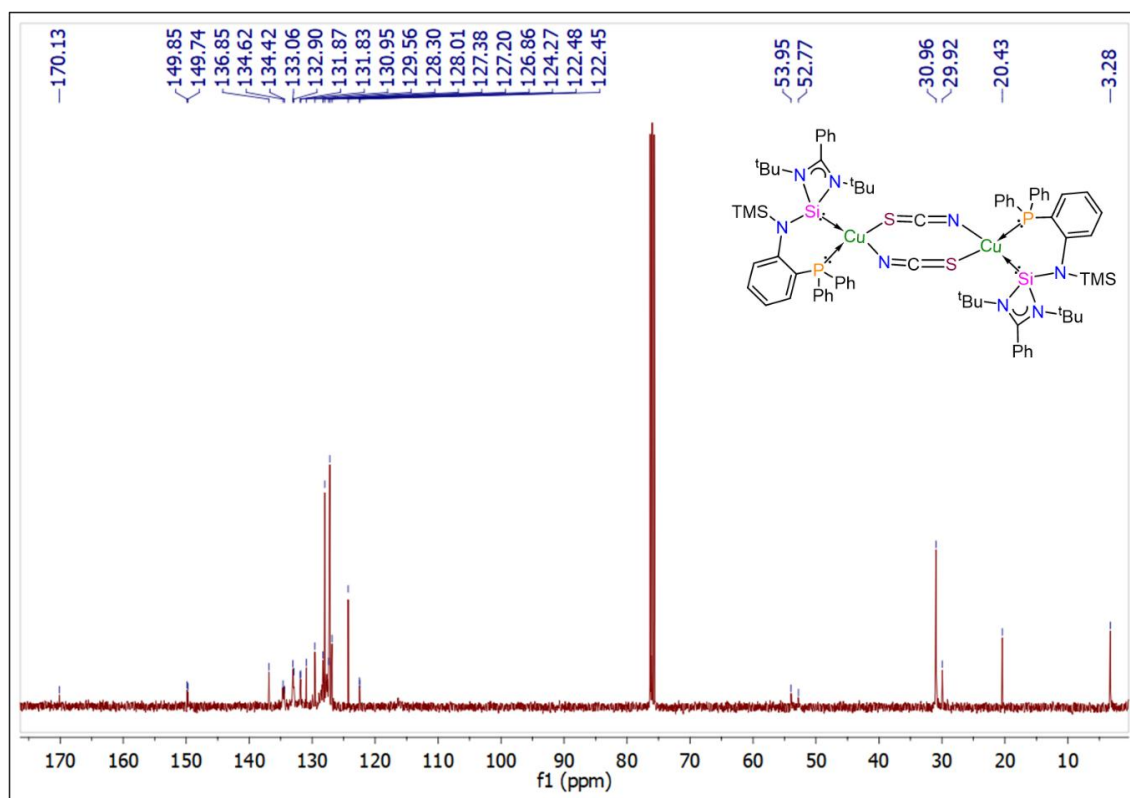


Figure 2B.A.15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2B.3** (CDCl₃, 100.613 MHz, 298 K)

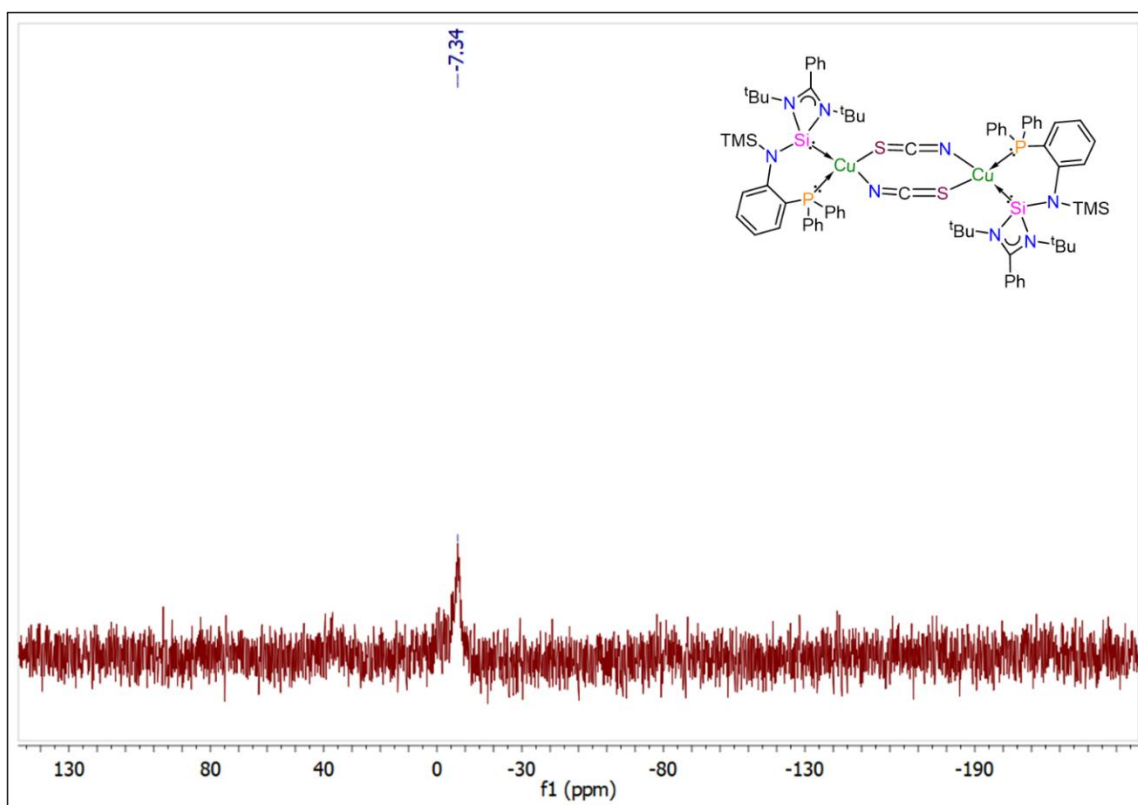


Figure 2B.A.16. $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2B.3** (CDCl₃, 161.97 MHz, 298 K)

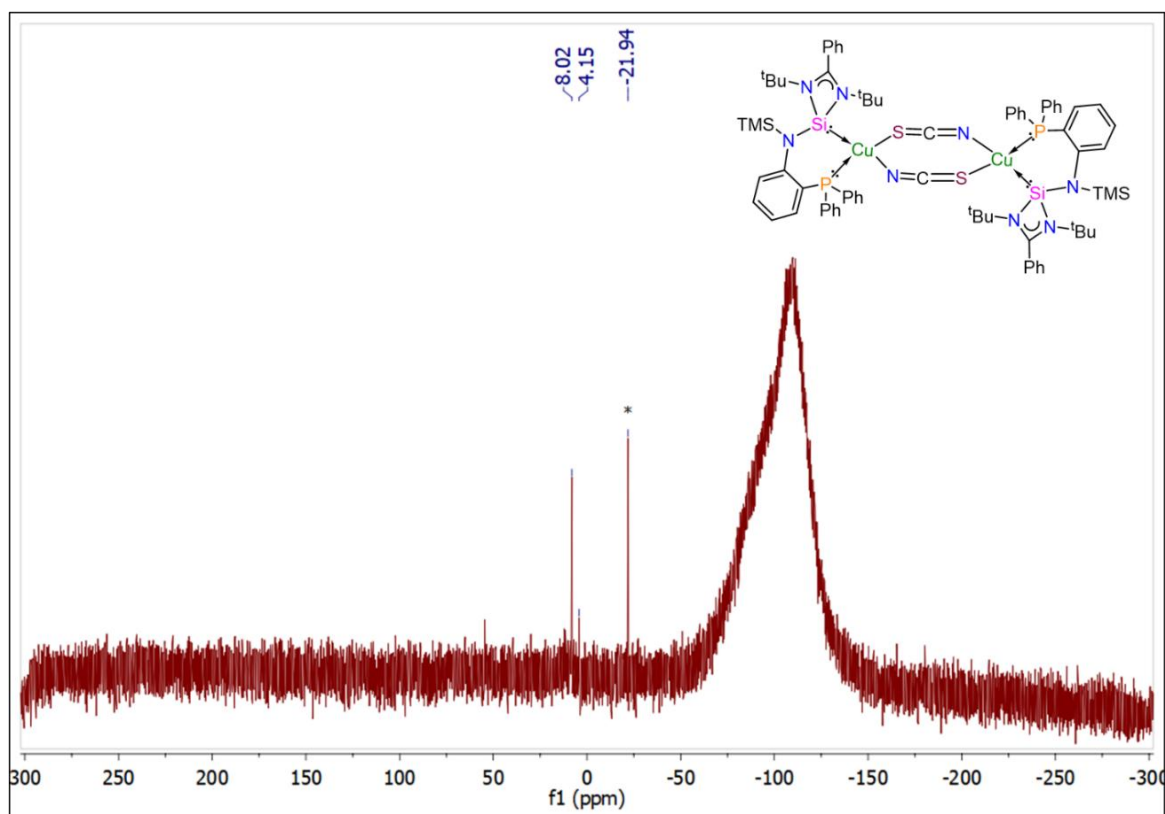


Figure 2B.A.17. $^{29}\text{Si}\{^1\text{H}\}$ full NMR spectrum of **2B.3** (CDCl_3 , 79.49 MHz, 298 K) *Grease

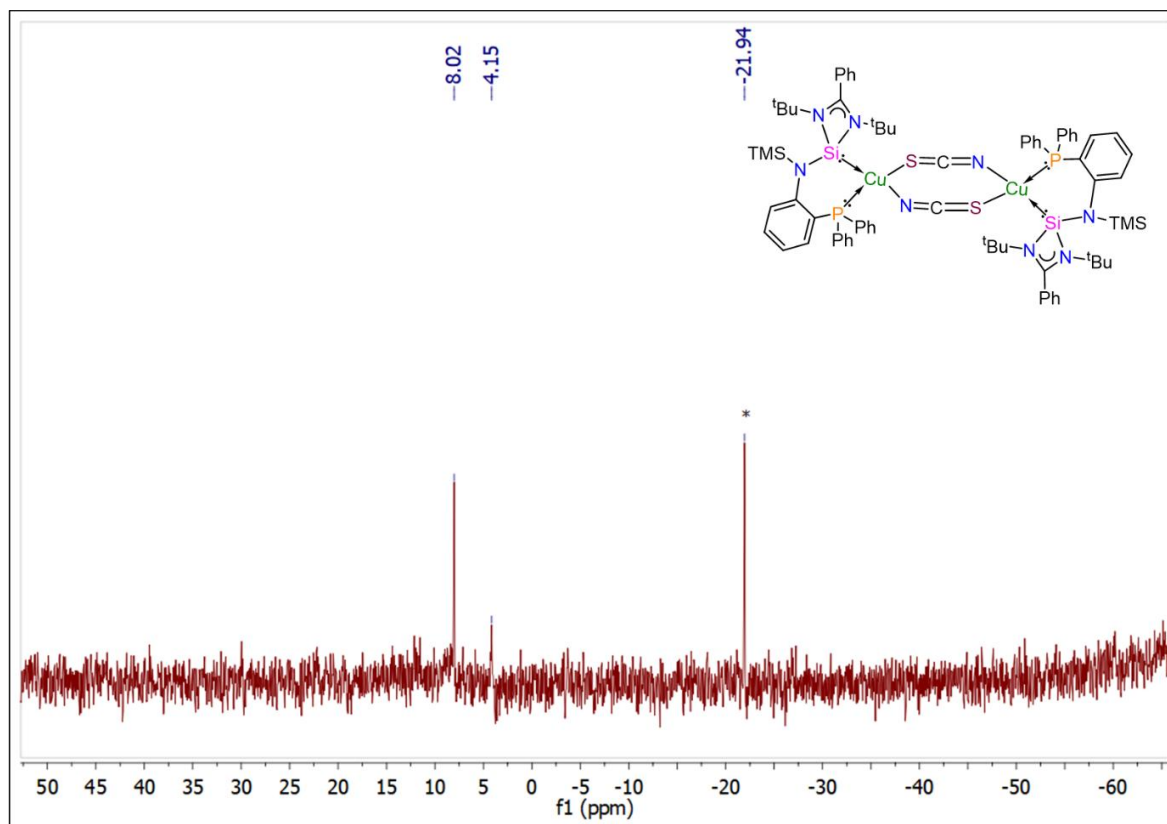


Figure 2B.A.18. $^{29}\text{Si}\{^1\text{H}\}$ zoomed NMR spectrum of **2B.3** (CDCl_3 , 79.49 MHz, 298 K) *Grease

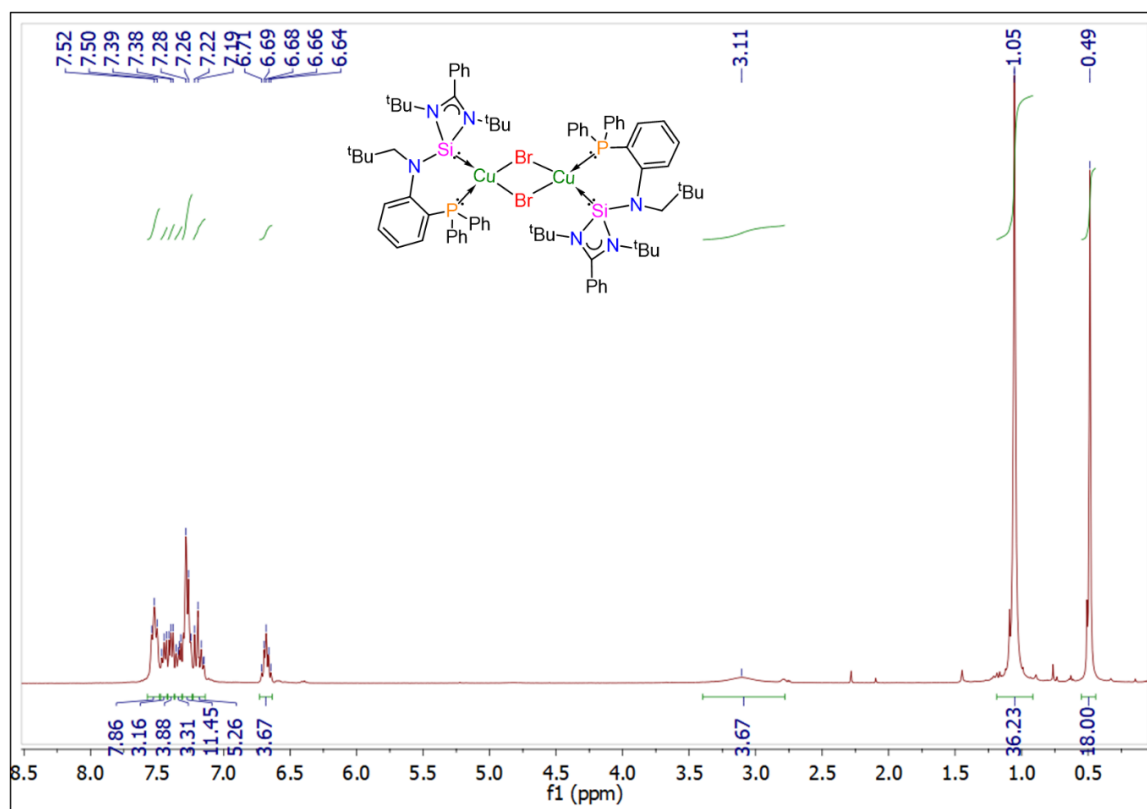


Figure 2B.A.19. ¹H NMR spectrum of **2B.4** (CDCl₃, 400 MHz, 298 K)

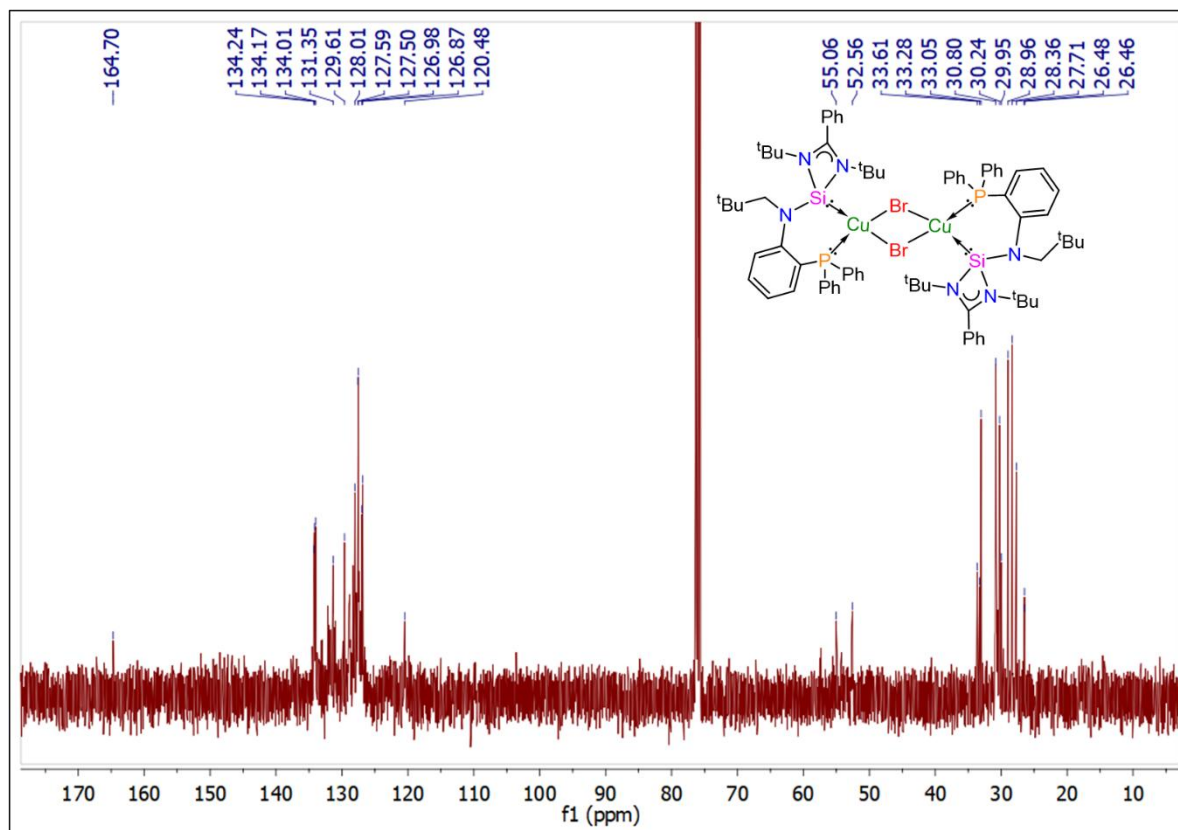


Figure 2B.A.20. ¹³C{¹H} NMR spectrum of **2B.4** (CDCl₃, 100.613 MHz, 298 K)

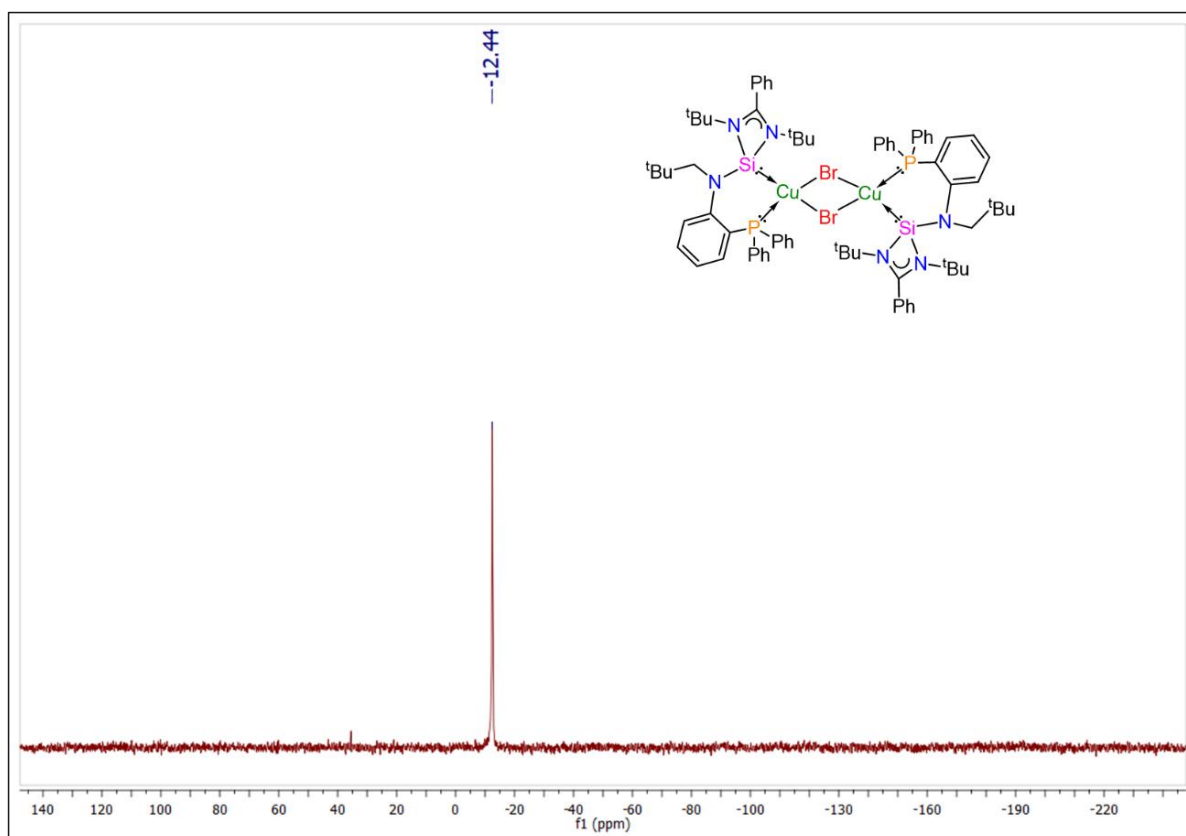


Figure 2B.A.21. $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2B.4** (CDCl_3 , 161.97 MHz, 298 K)

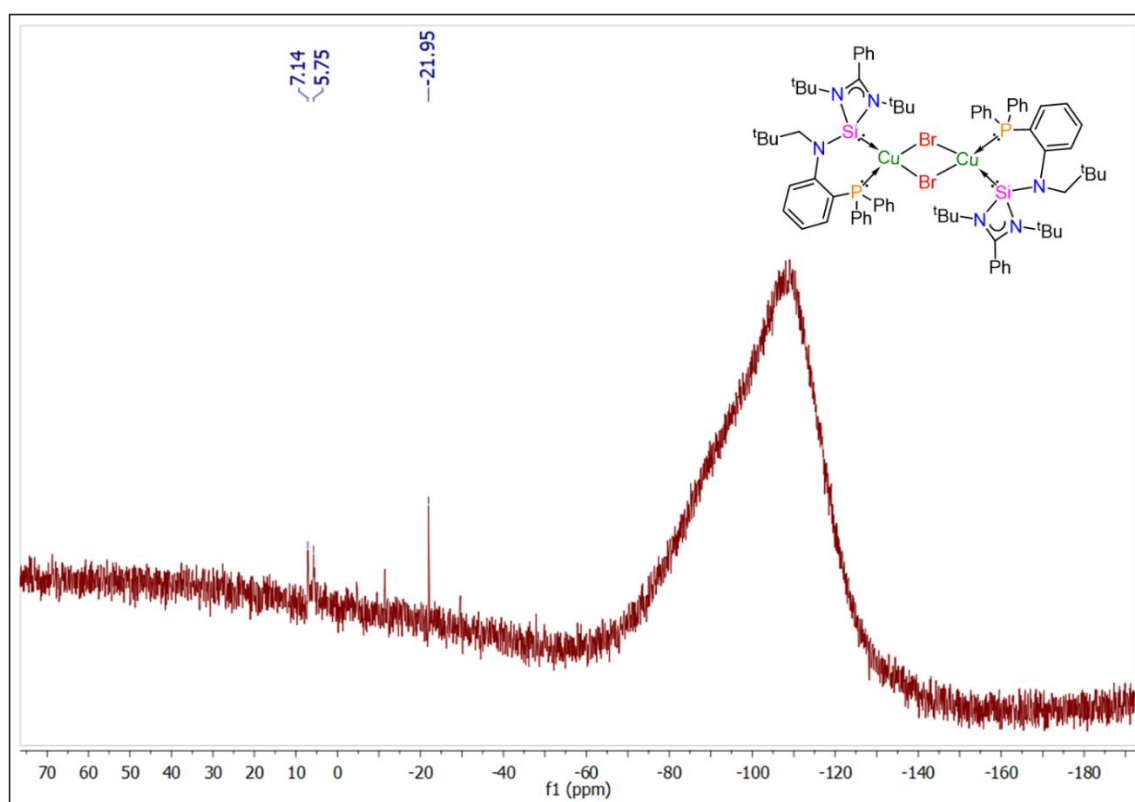


Figure 2B.A.22. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2B.4** (CDCl_3 , 79.49 MHz, 298 K)

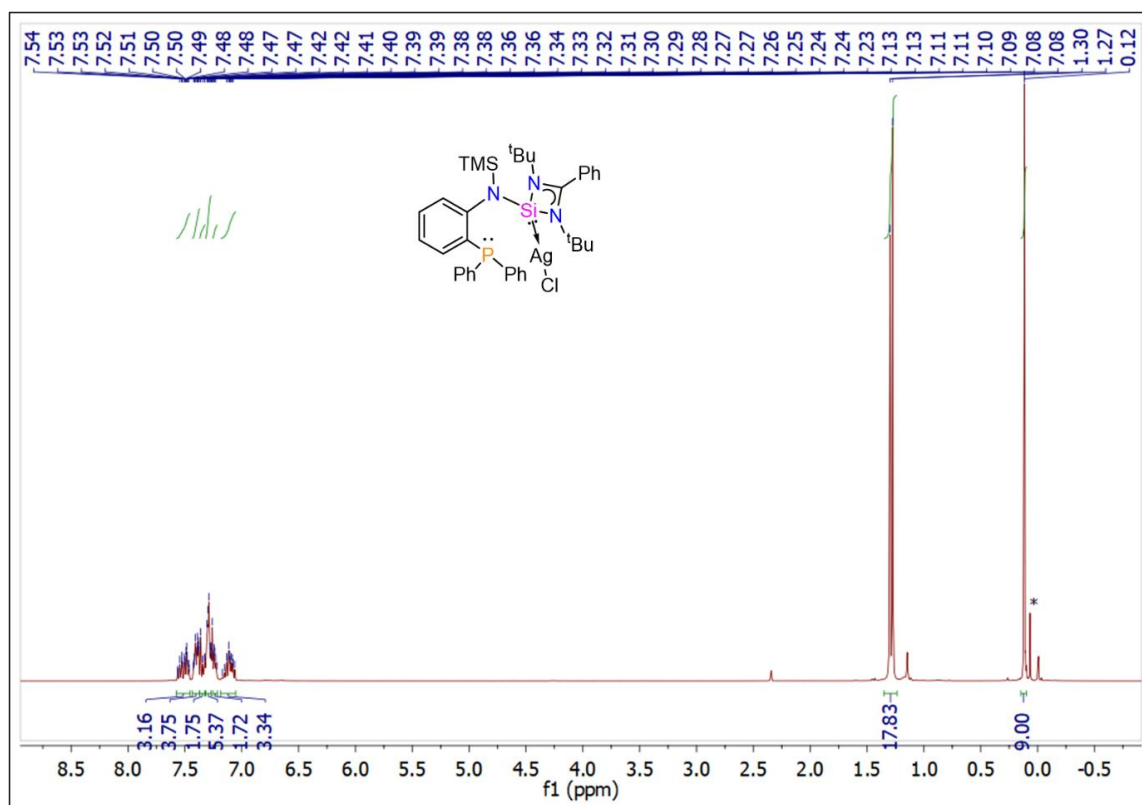


Figure 2B.A.23. ¹H NMR spectrum of **2B.5** (CDCl₃, 400 MHz, 298 K) *Grease

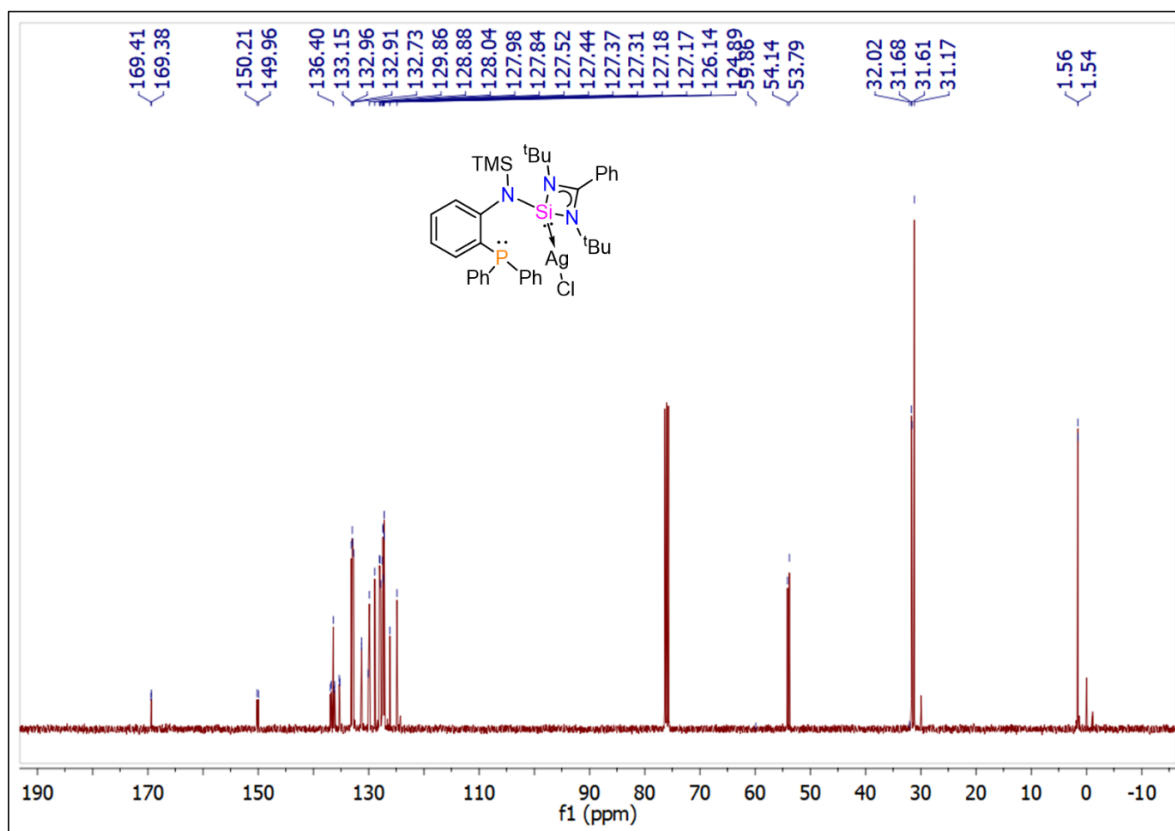


Figure 2B.A.24. ¹³C{¹H} NMR spectrum of **2B.5** (CDCl₃, 100.613 MHz, 298 K)

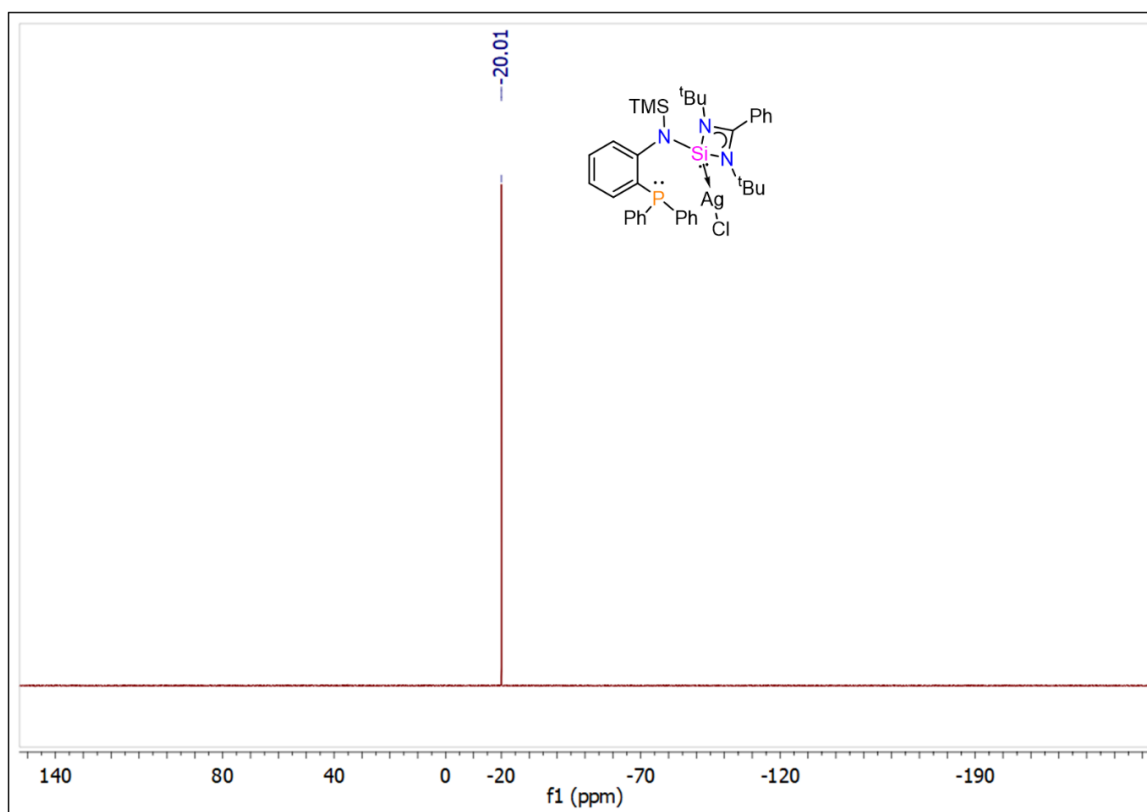


Figure 2B.A.25. $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2B.5** (CDCl₃, 161.97 MHz, 298 K)

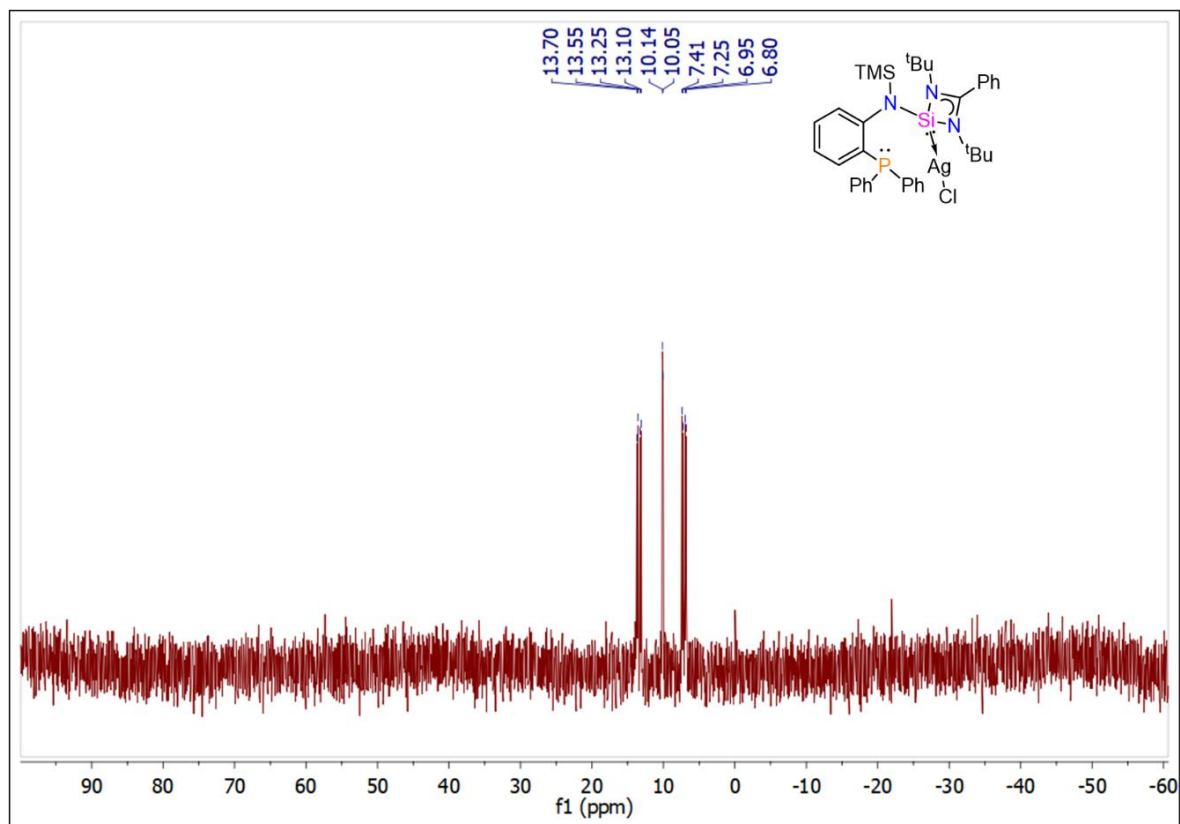


Figure 2B.A.26. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2B.5** (CDCl₃, 79.49 MHz, 298 K)

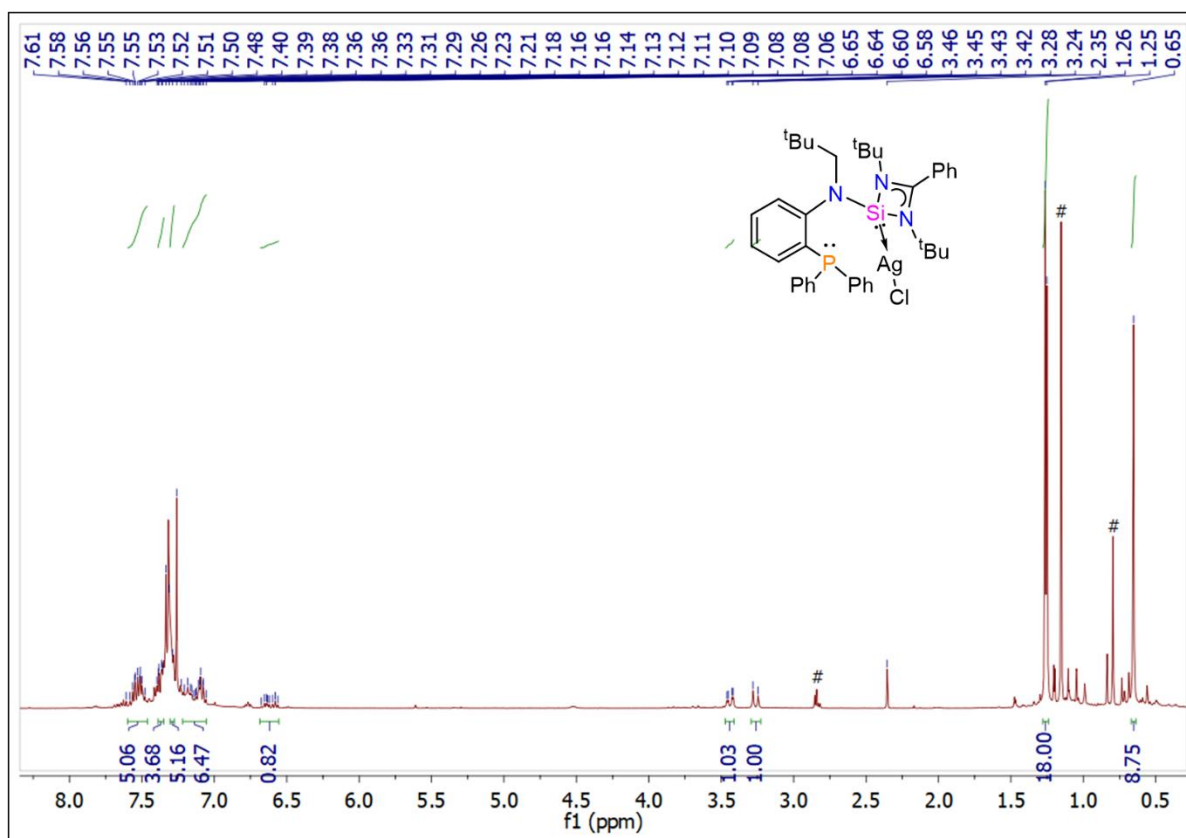


Figure 2B.A.27. ¹H NMR spectrum of **2B.6** (CDCl₃, 400 MHz, 298 K), #, impurity

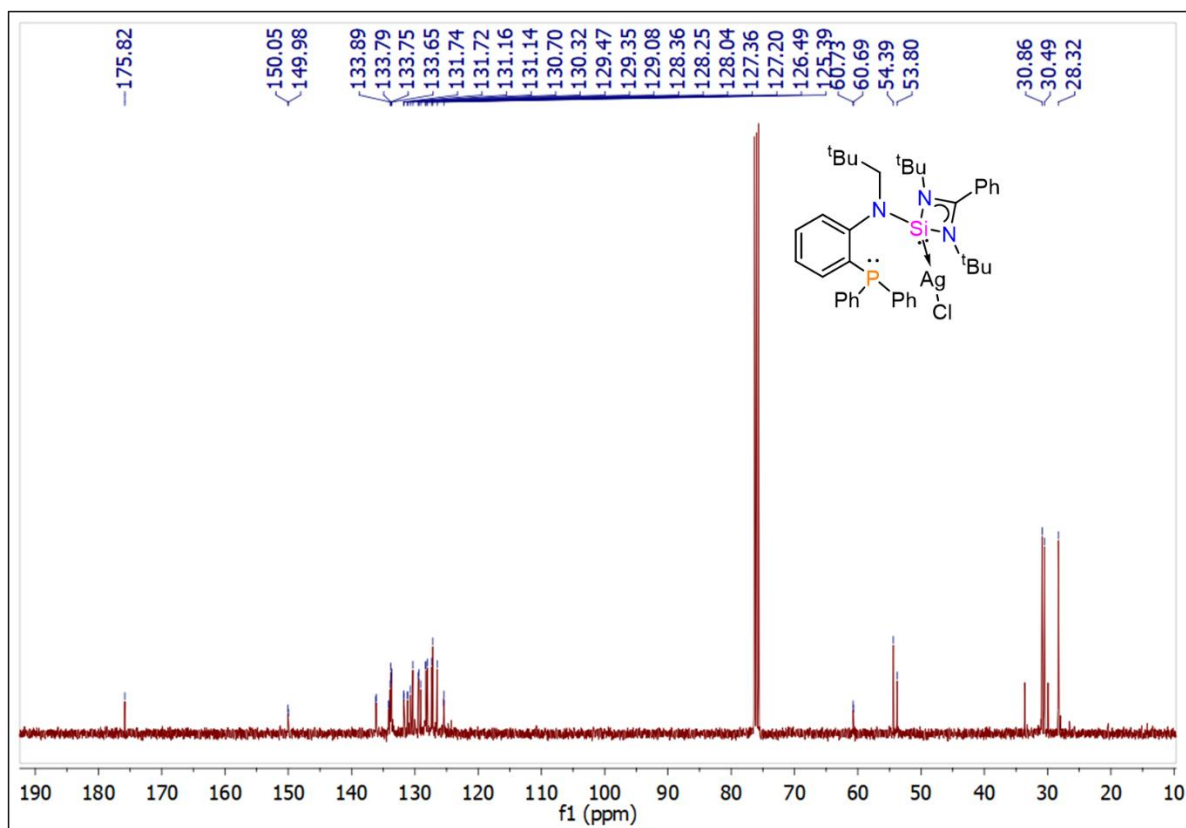


Figure 2B.A.28. ¹³C{¹H} NMR spectrum of **2B.6** (CDCl₃, 100.613 MHz, 298 K)

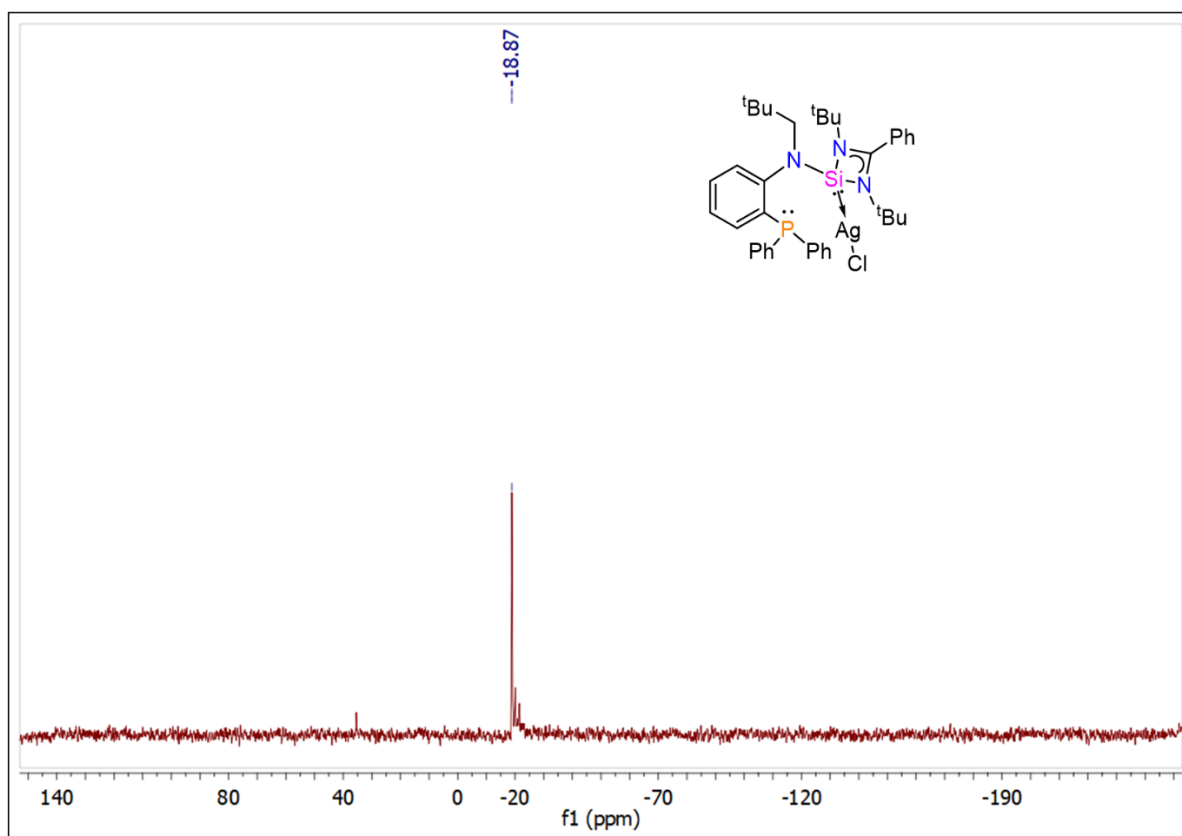


Figure 2B.A.29. $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2B.6** (CDCl_3 , 161.97 MHz, 298 K)

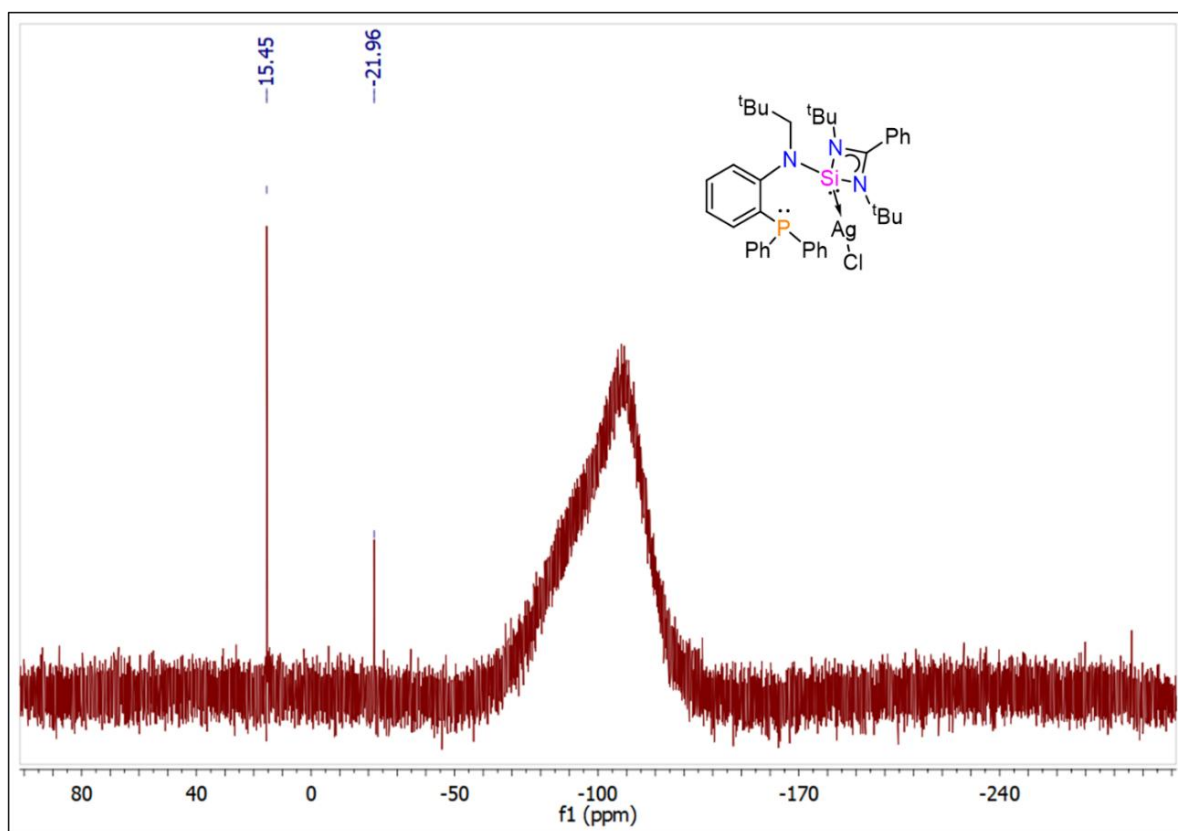


Figure 2B.A.30. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2B.6** (CDCl_3 , 79.49 MHz, 298 K)

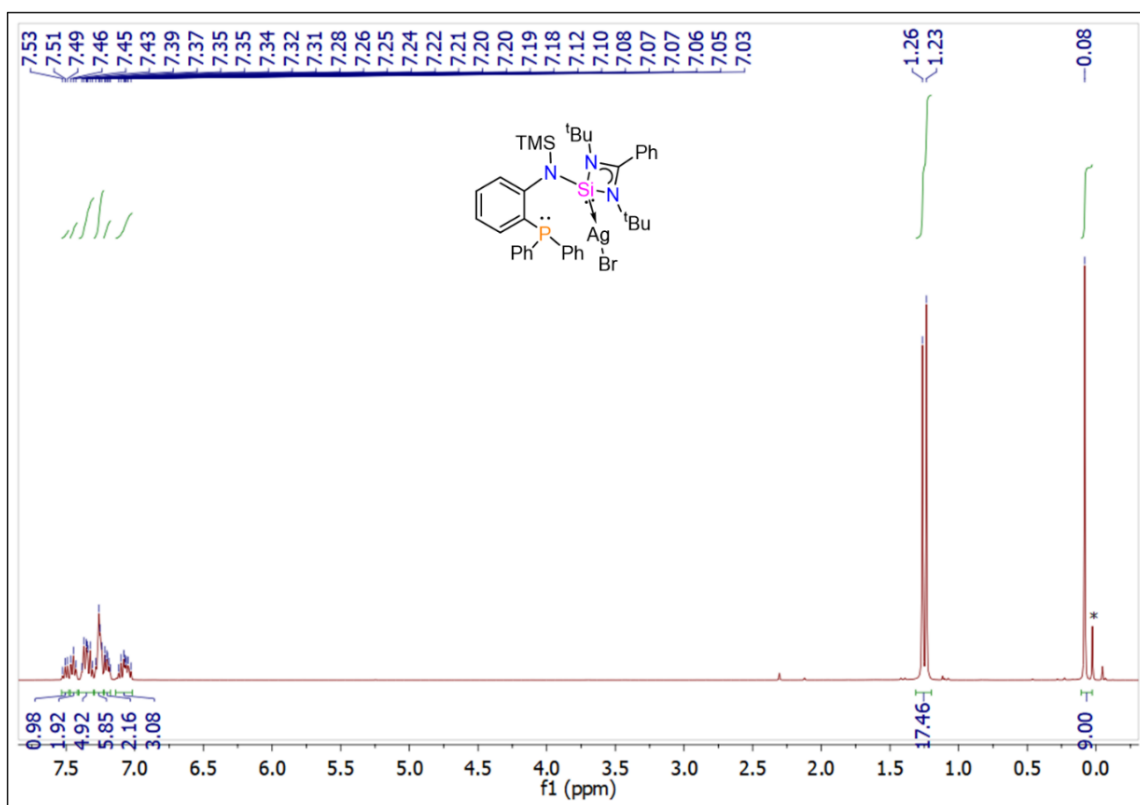


Figure 2B.A.31. ¹H NMR spectrum of **2B.7** (CDCl₃, 400 MHz, 298 K)

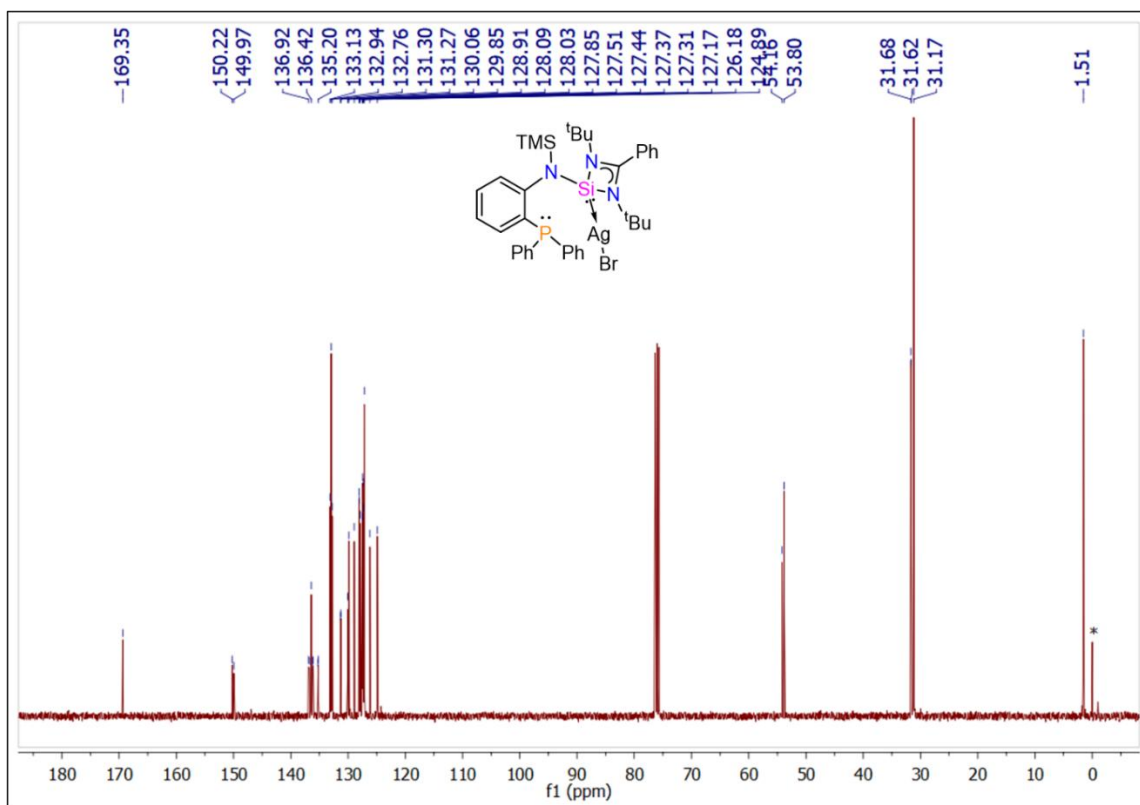


Figure 2B.A.32. ¹³C{¹H} NMR spectrum of **2B.7** (CDCl₃, 100.613 MHz, 298 K)

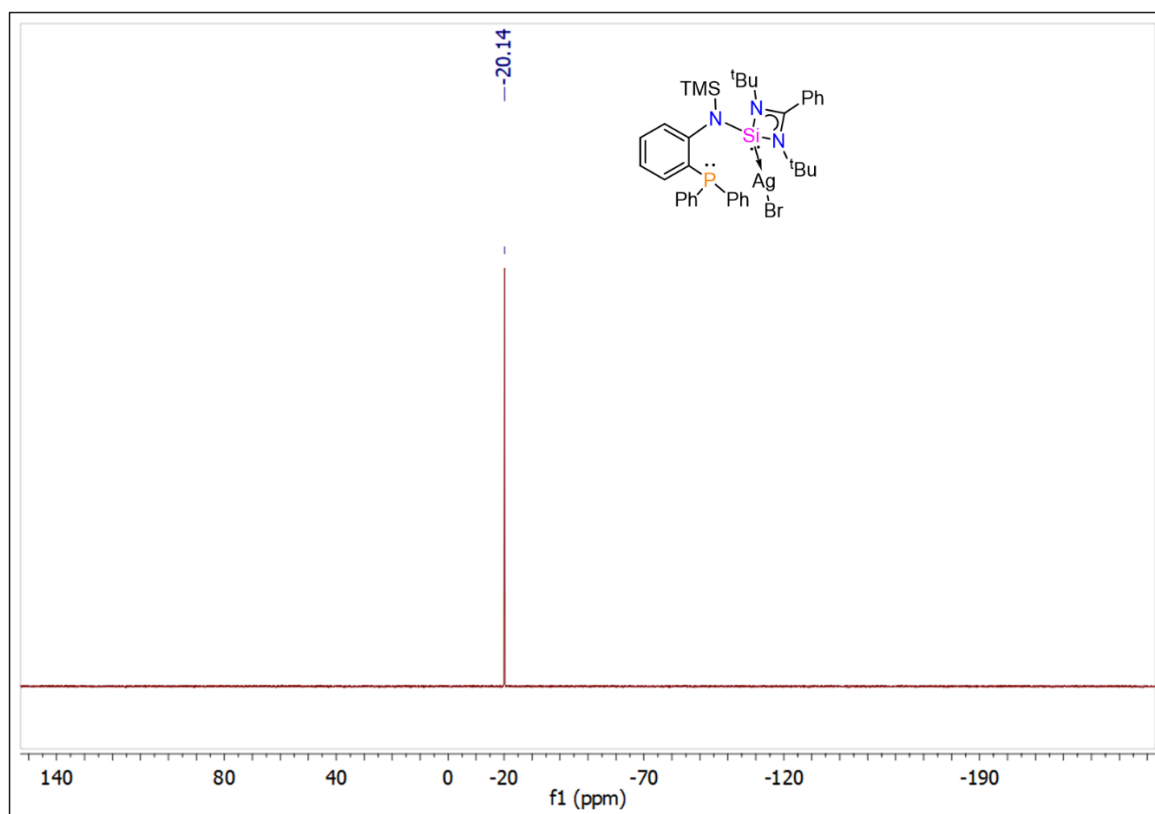


Figure 2B.A.33. $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2B.7** (CDCl_3 , 161.97 MHz, 298 K)

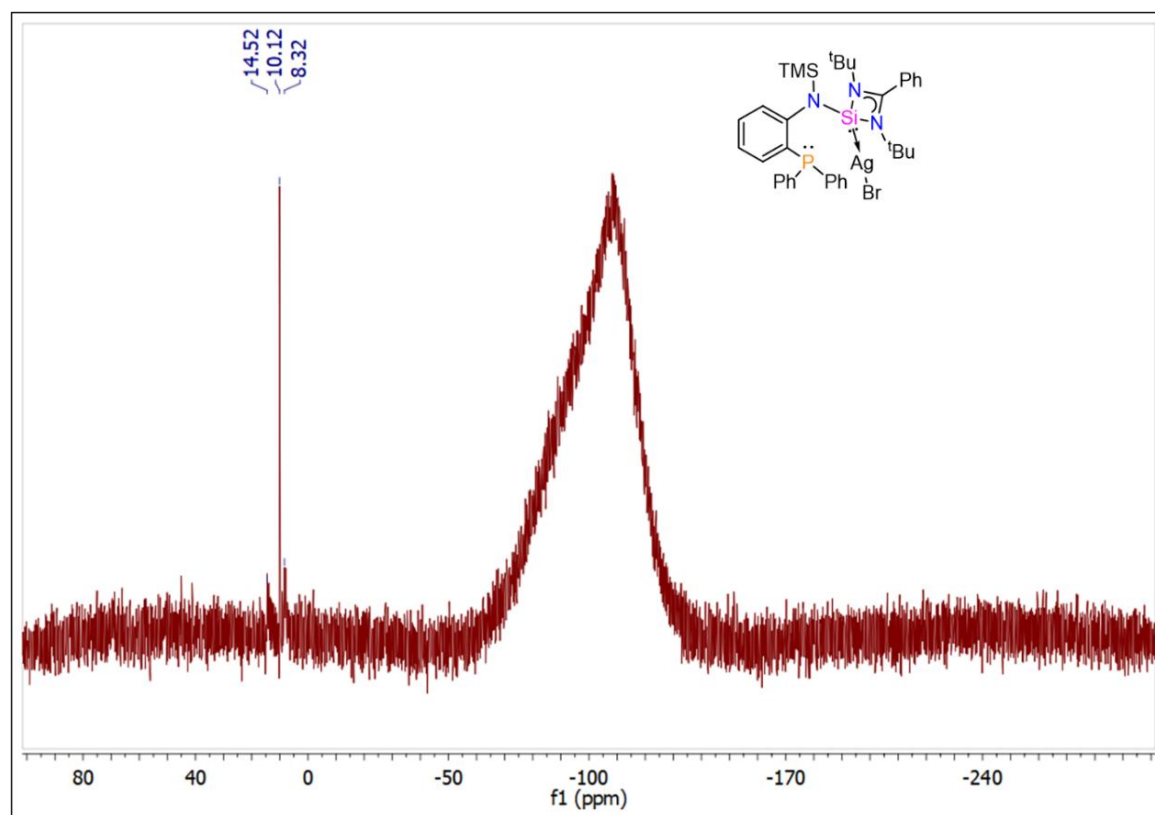


Figure 2B.A.34. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2B.7** (CDCl_3 , 79.49 MHz, 298 K)

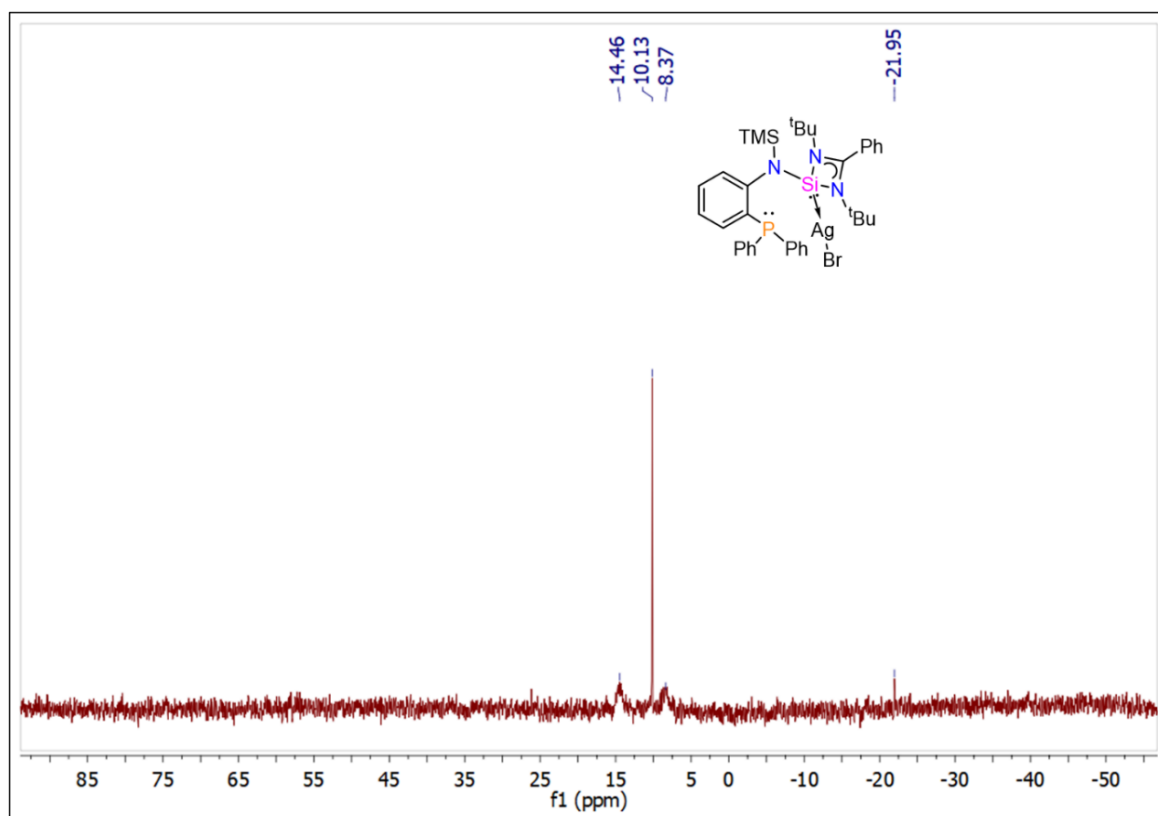


Figure 2B.A.35. $^{29}\text{Si}\{^1\text{H}\}$ zoomed NMR spectrum of **2B.7** (CDCl_3 , 79.49 MHz, 298 K)

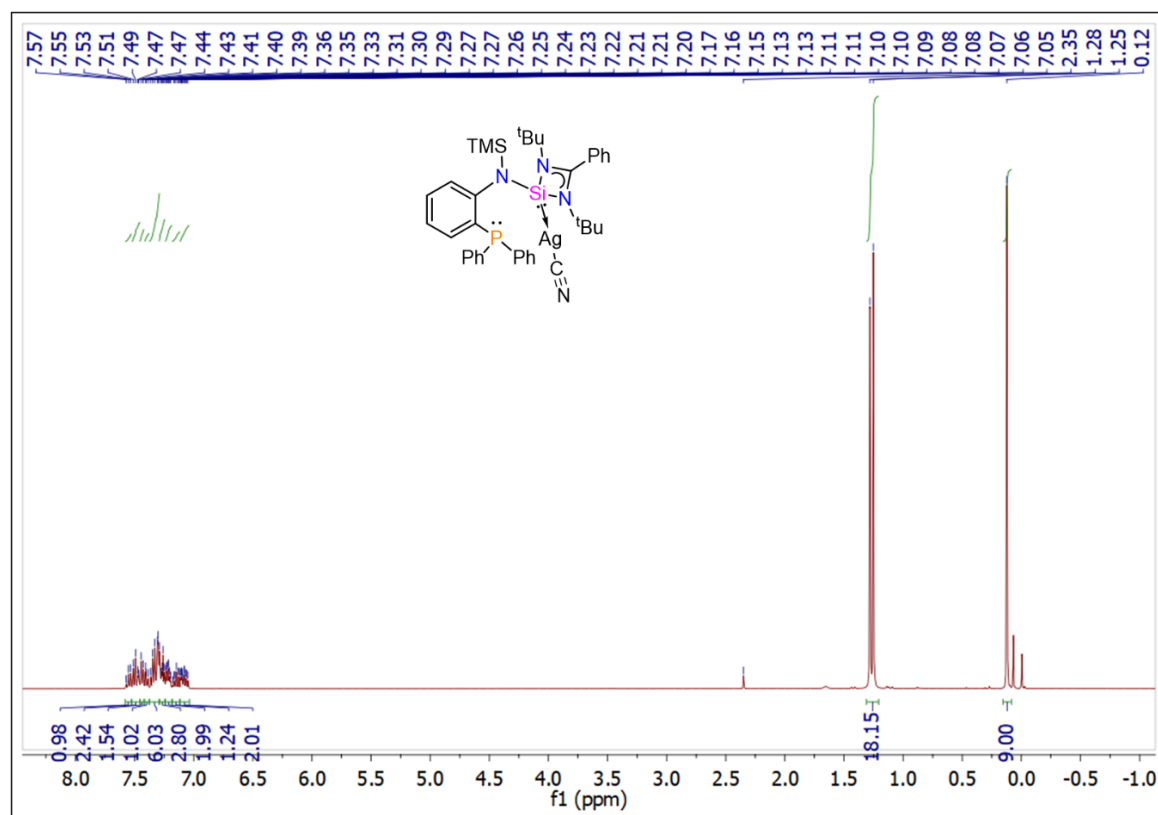


Figure 2B.A.36. ^1H NMR spectrum of **2B.8** (CDCl_3 , 400 MHz, 298 K)

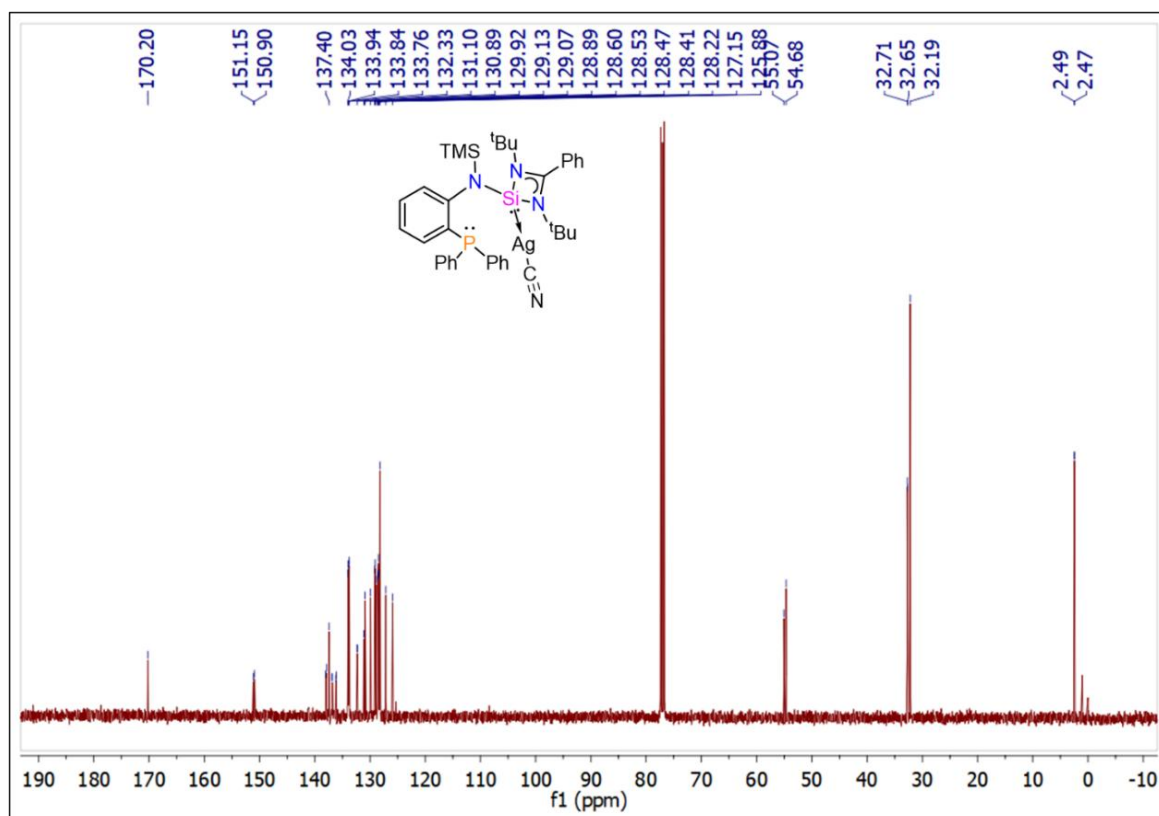


Figure 2B.A.37. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2B.8** (CDCl₃, 100.613 MHz, 298 K)

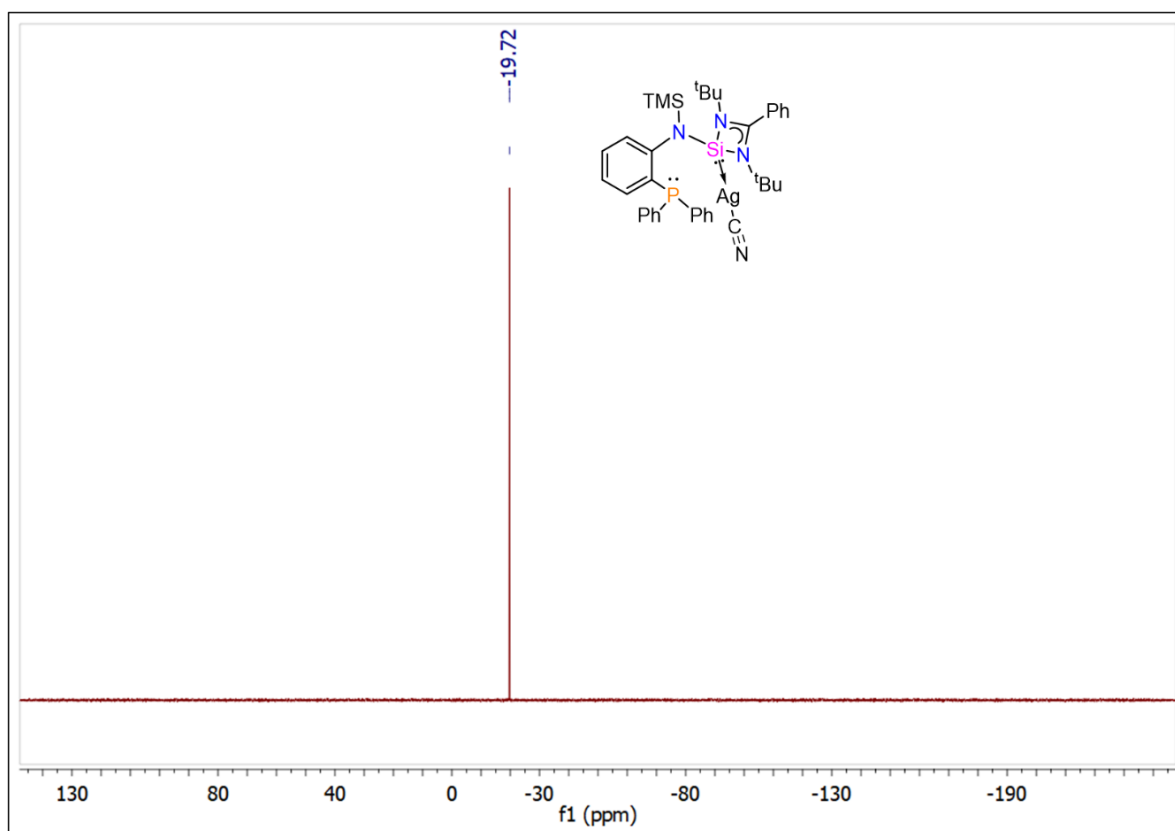


Figure 2B.A.38. $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2B.8** (CDCl₃, 161.97 MHz, 298 K)

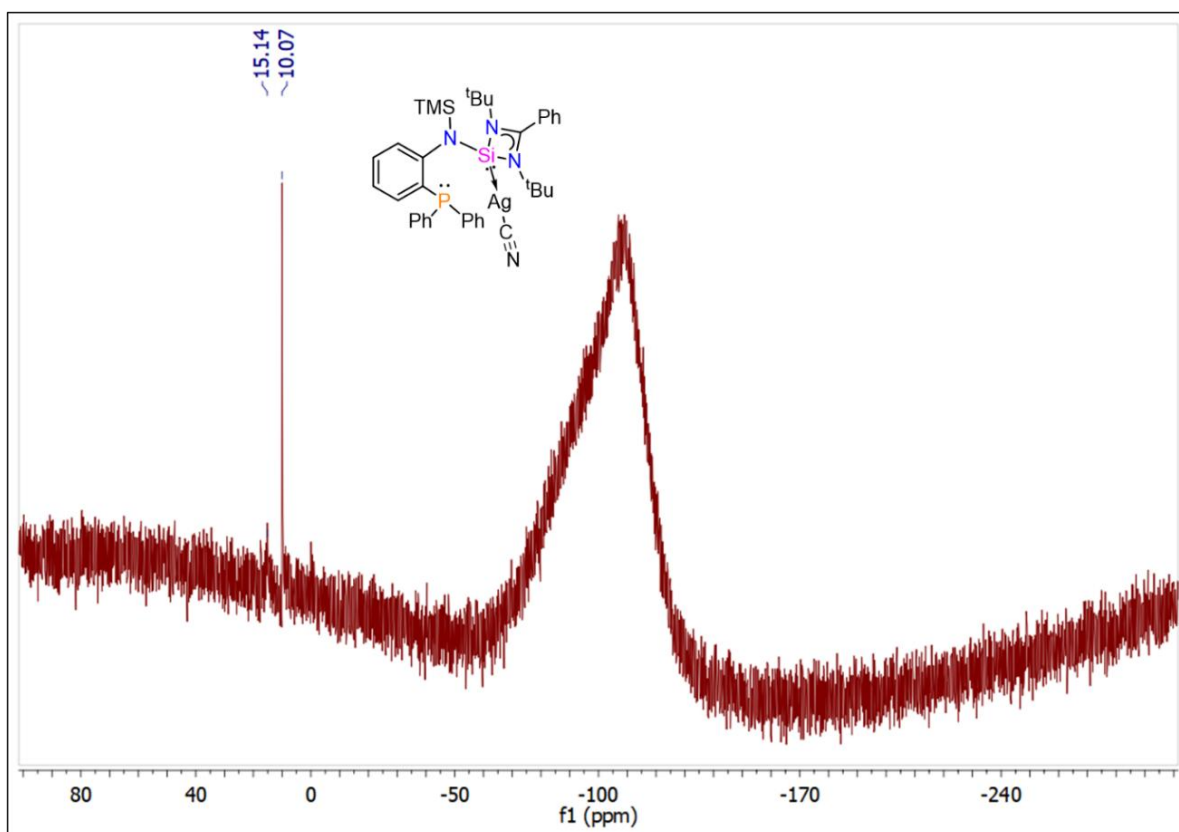


Figure 2B.A.39. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2B.8** (CDCl_3 , 79.49 MHz, 298 K)

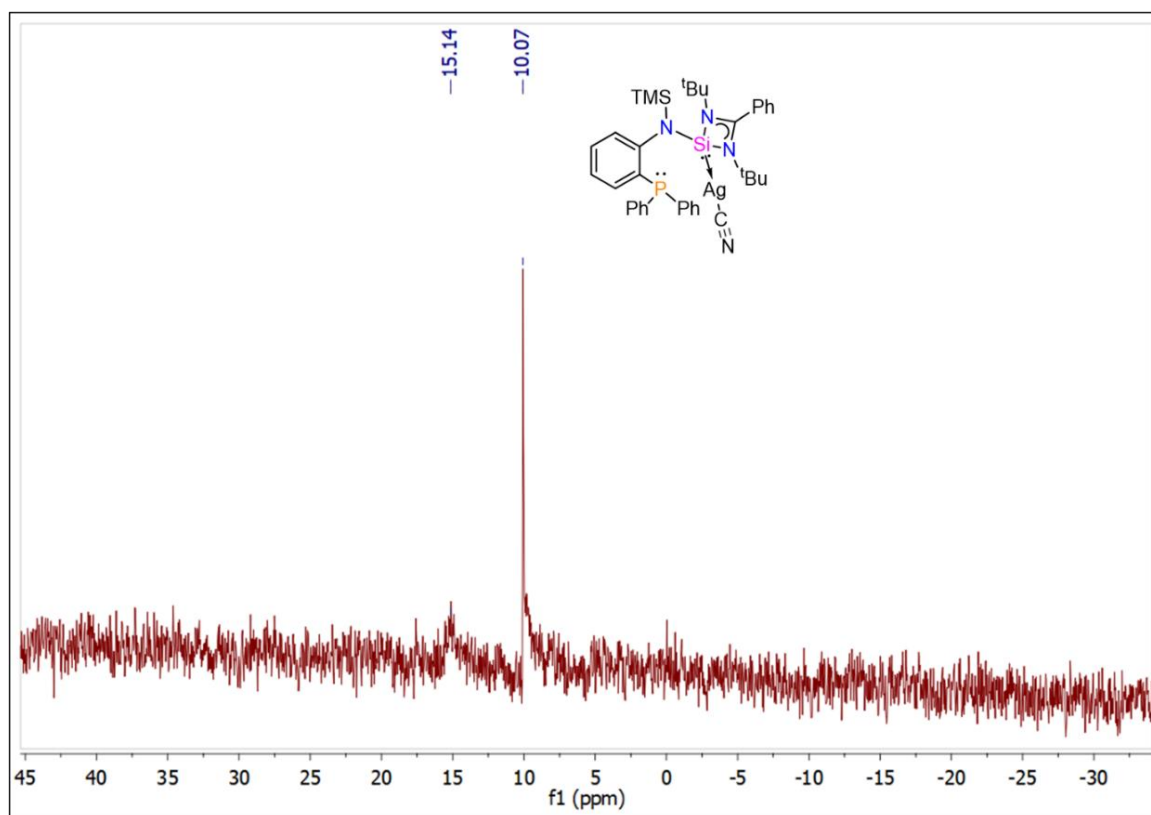


Figure 2B.A.40. $^{29}\text{Si}\{^1\text{H}\}$ zoomed NMR spectrum of **2B.8** (CDCl_3 , 79.49 MHz, 298 K)

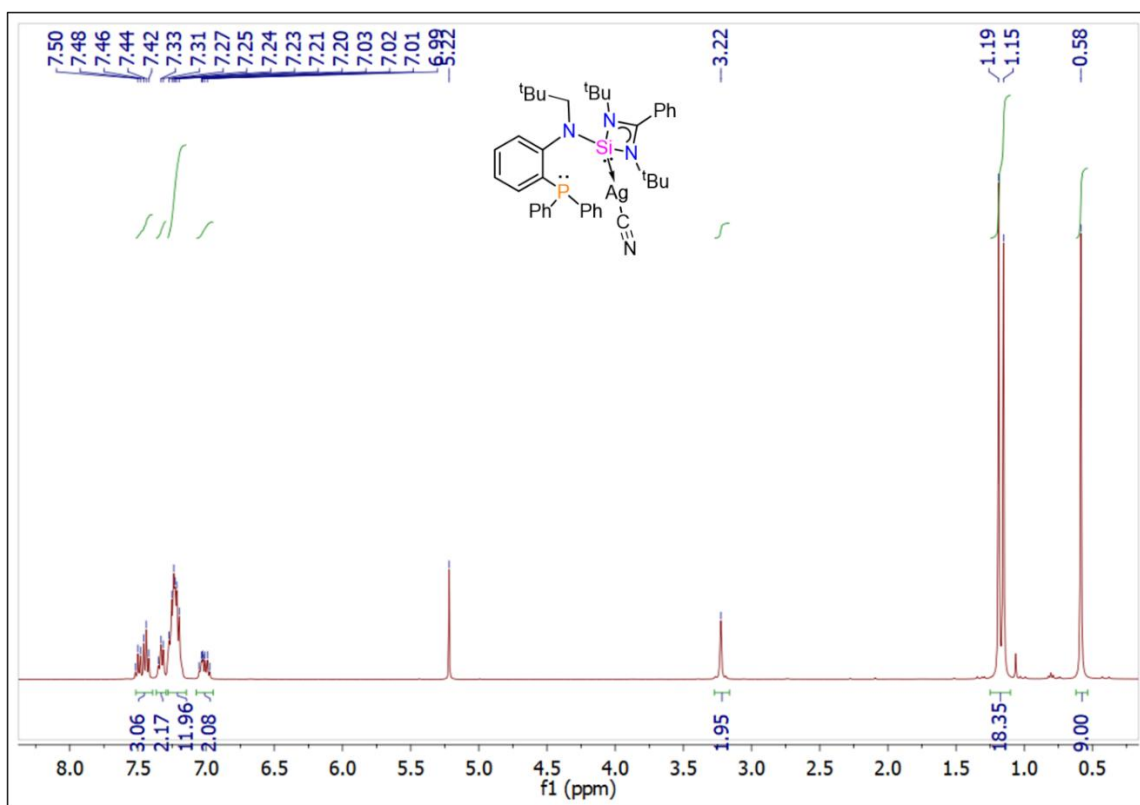


Figure 2B.A.41. ¹H NMR spectrum of **2B.9** (CDCl₃, 400 MHz, 298 K)

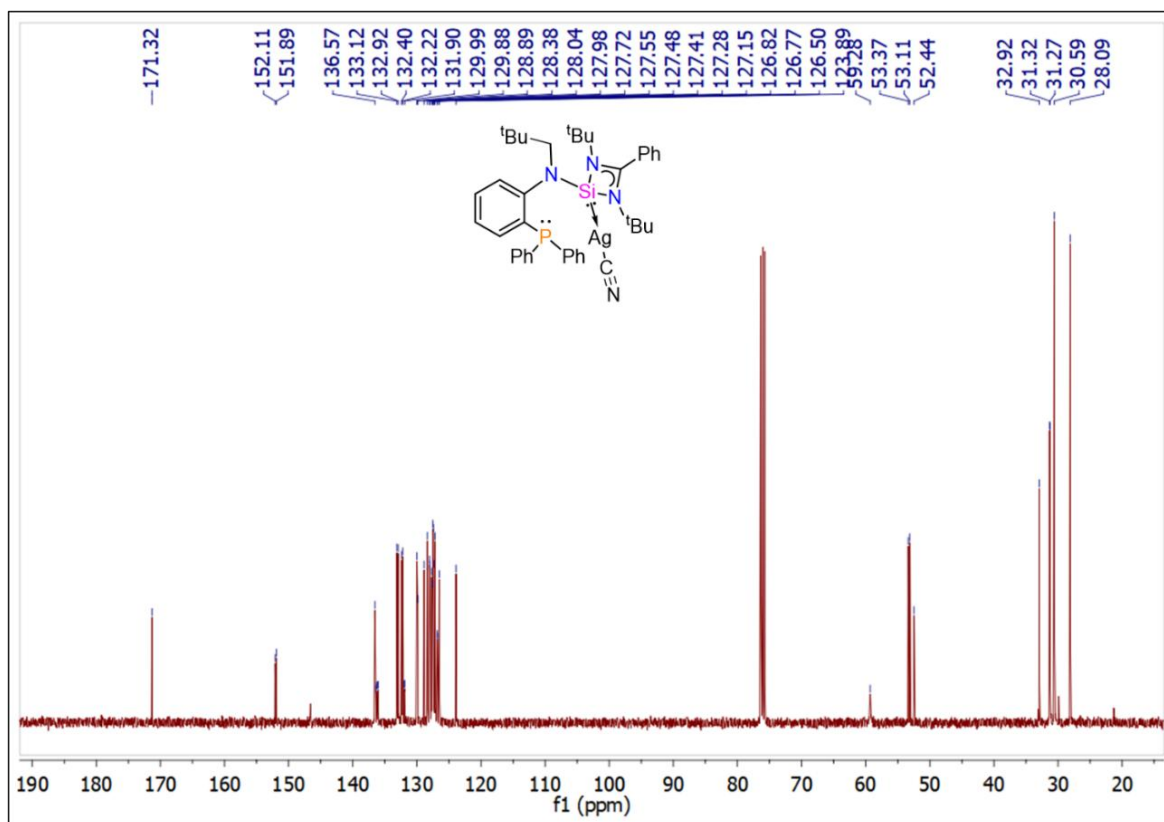


Figure 2B.A.42. ¹³C{¹H} NMR spectrum of **2B.9** (CDCl₃, 100.613 MHz, 298 K)

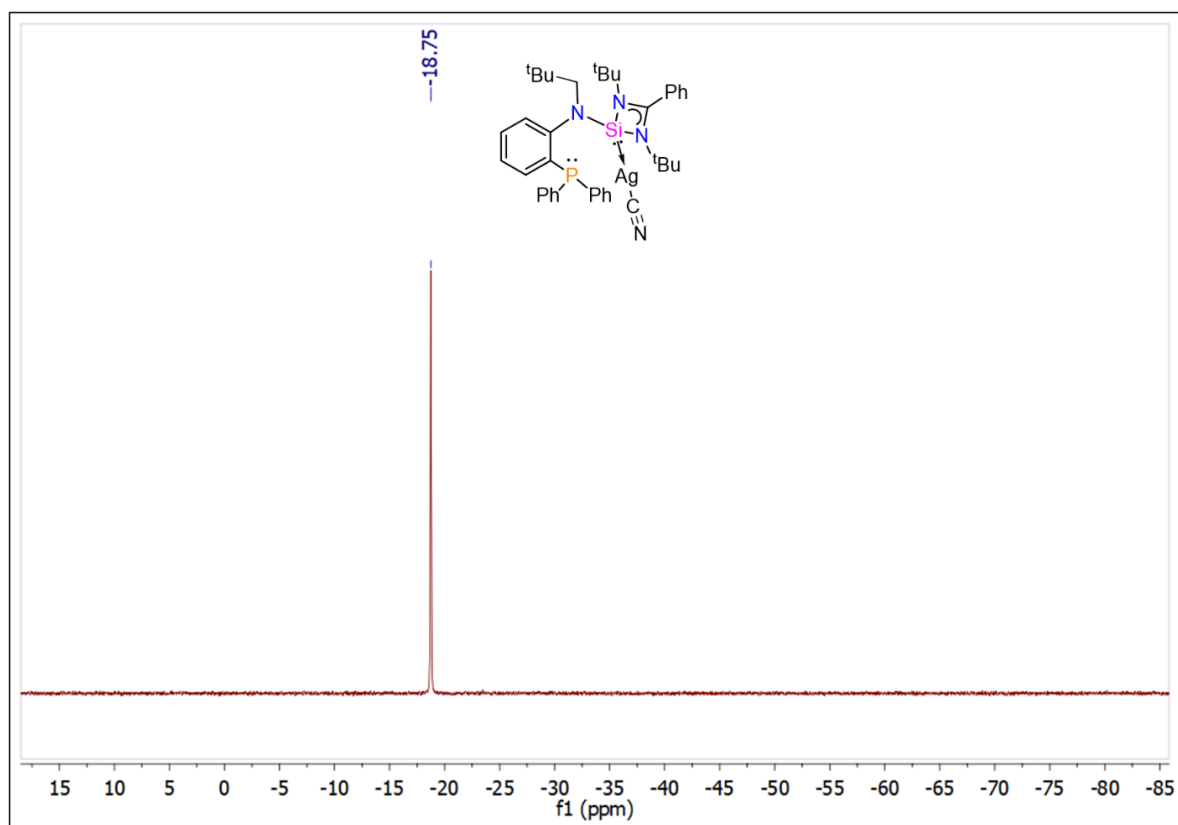


Figure 2B.A.43. $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2B.9** (CDCl_3 , 161.97 MHz, 298 K)

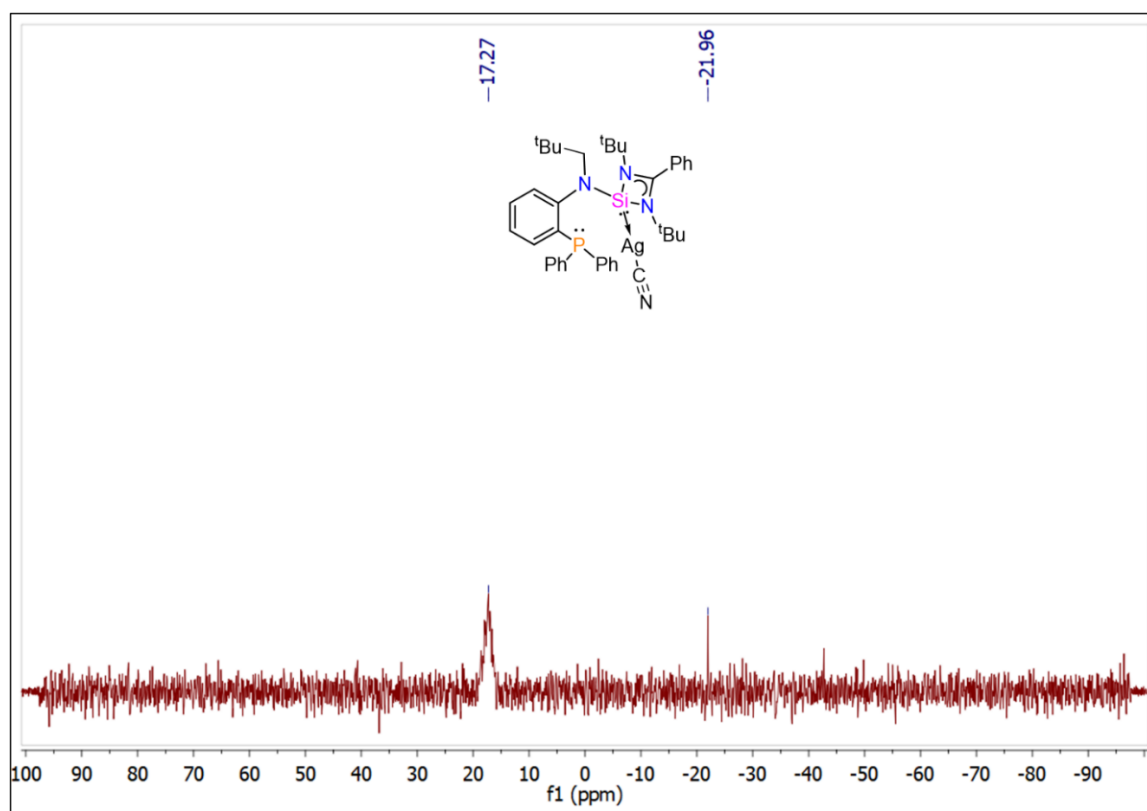


Figure 2B.A.44. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2B.9** (CDCl_3 , 79.49 MHz, 298 K)

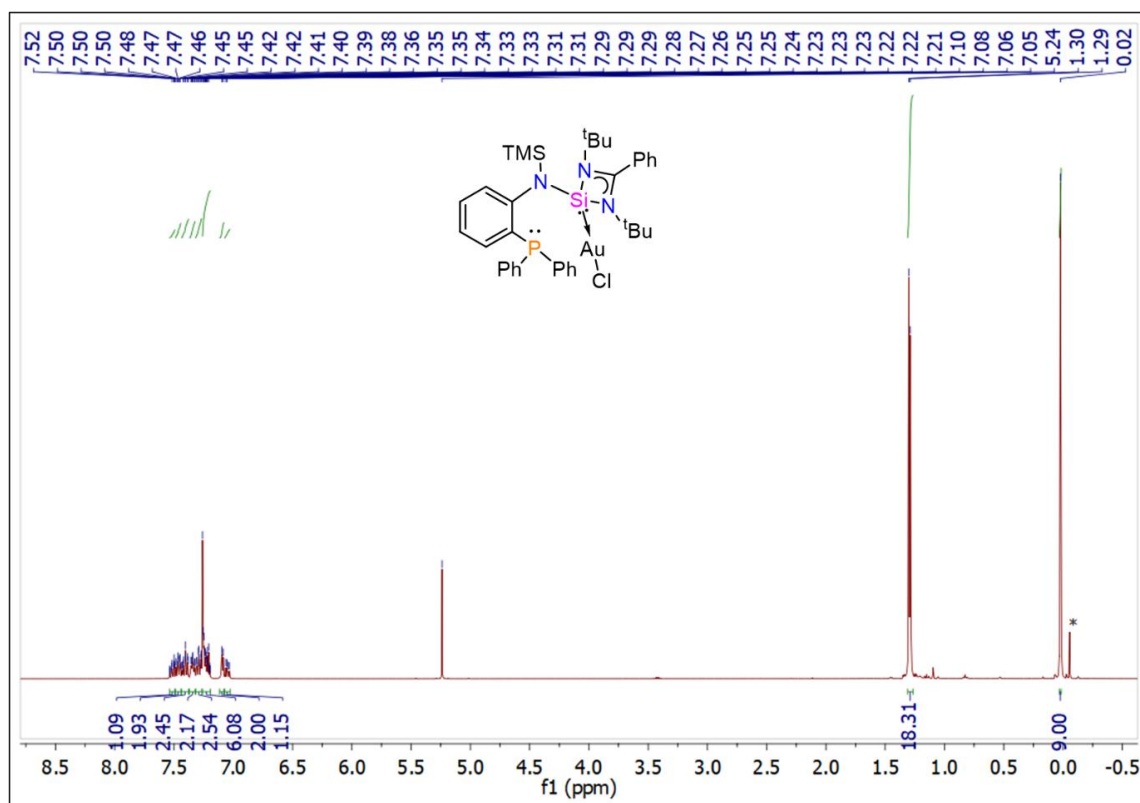


Figure 2B.A.45. ^1H NMR spectrum of **2B.10** (CDCl_3 , 400 MHz, 298 K)

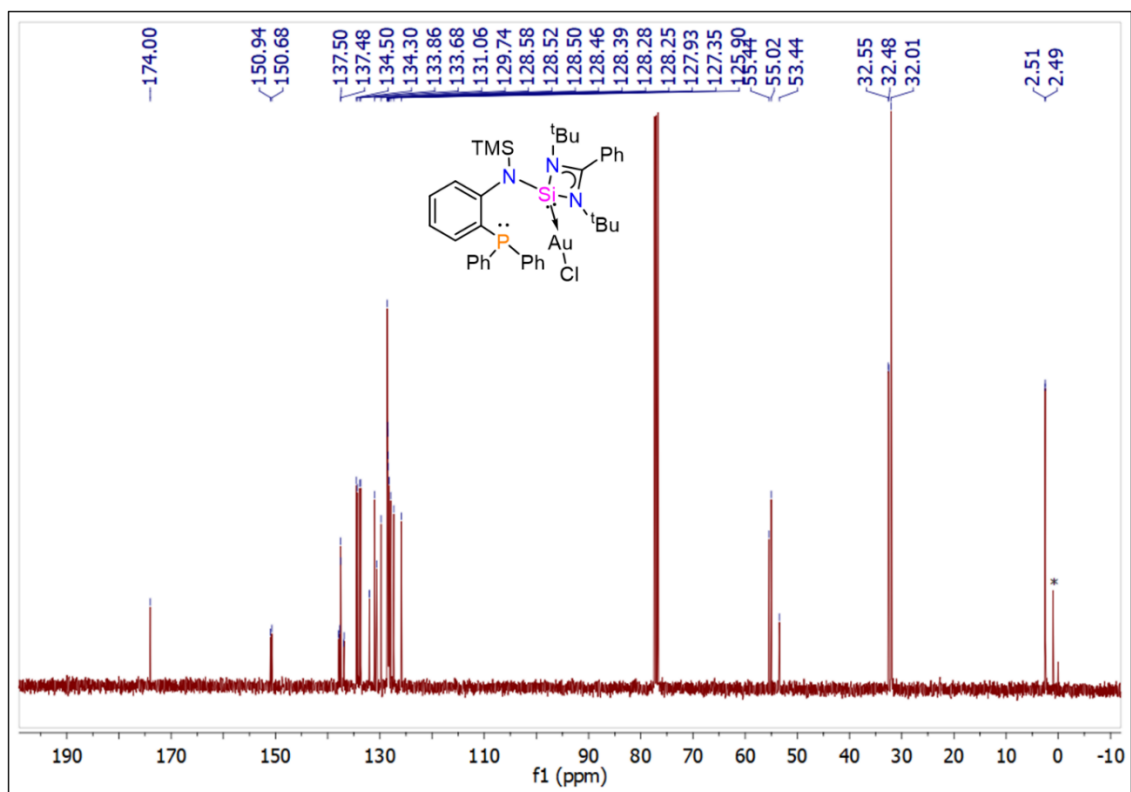


Figure 2B.A.46. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2B.10** (CDCl_3 , 100.613 MHz, 298 K)

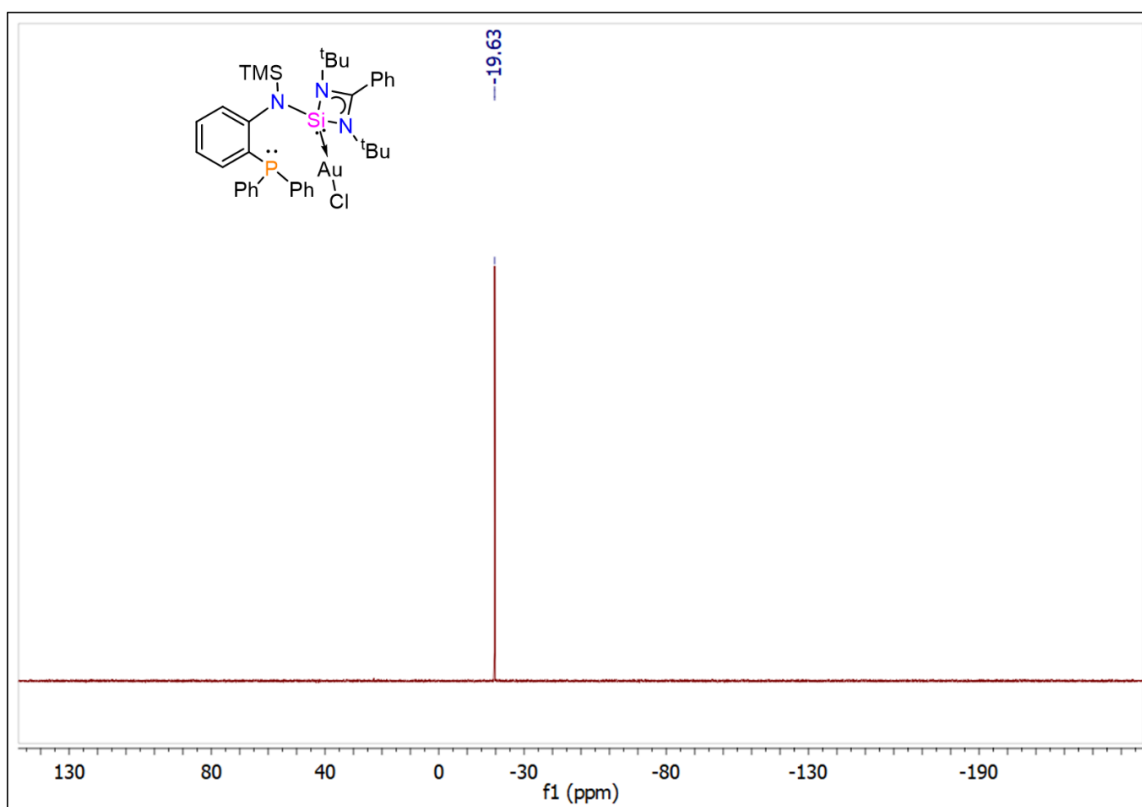


Figure 2B.A.47. $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2B.10** (CDCl₃, 161.97 MHz, 298 K)

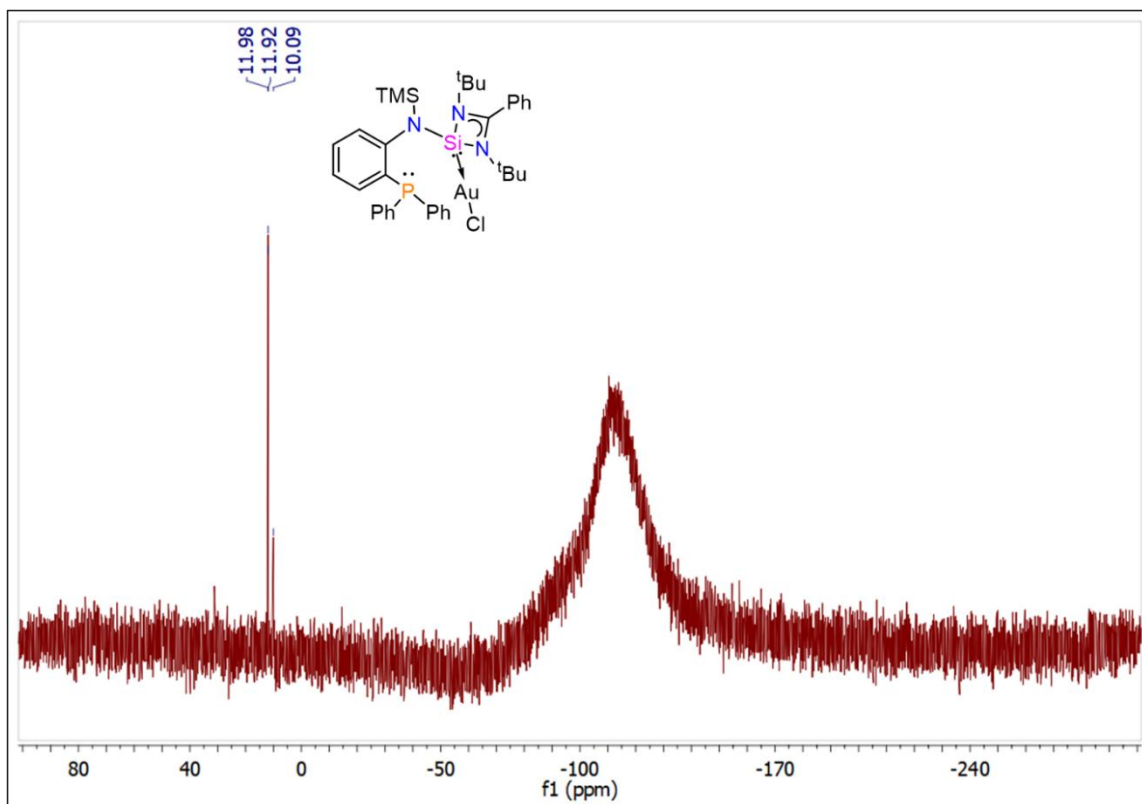


Figure 2B.A.48. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2B.10** (CDCl₃, 79.49 MHz, 298 K)

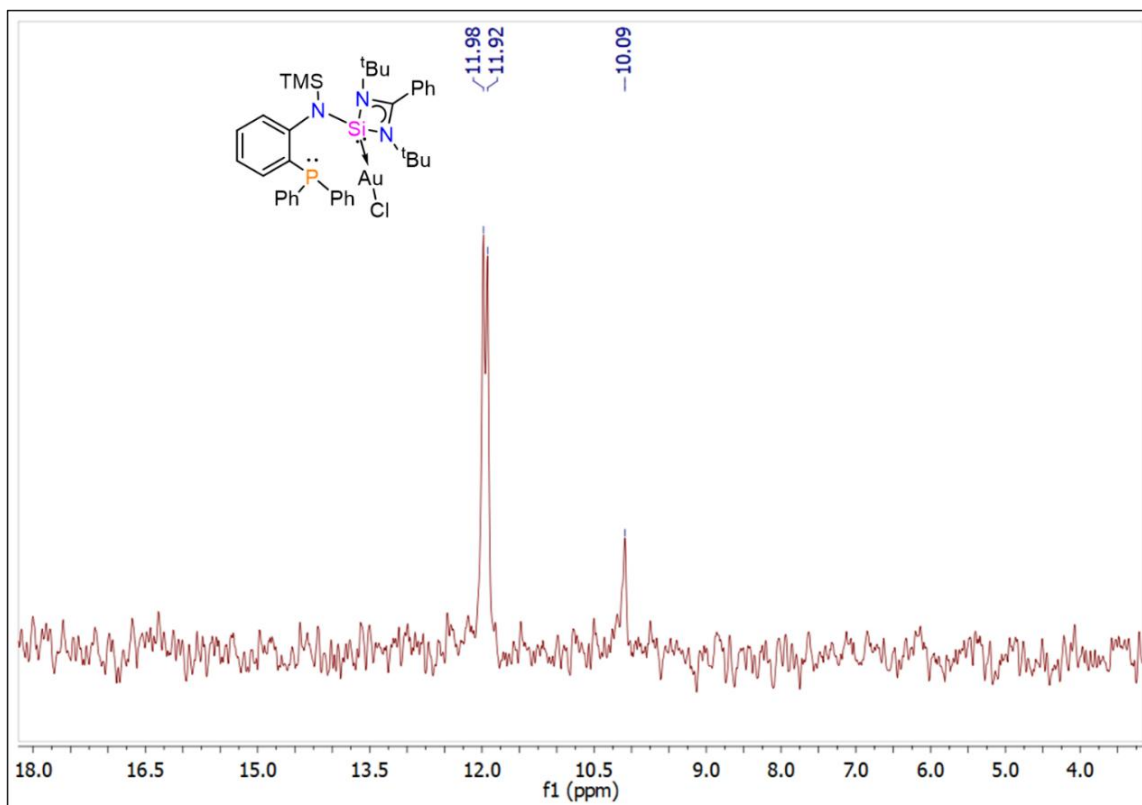


Figure 2B.A.49. $^{29}\text{Si}\{^1\text{H}\}$ zoomed NMR spectrum of **2B.10** (CDCl_3 , 79.49 MHz, 298 K)

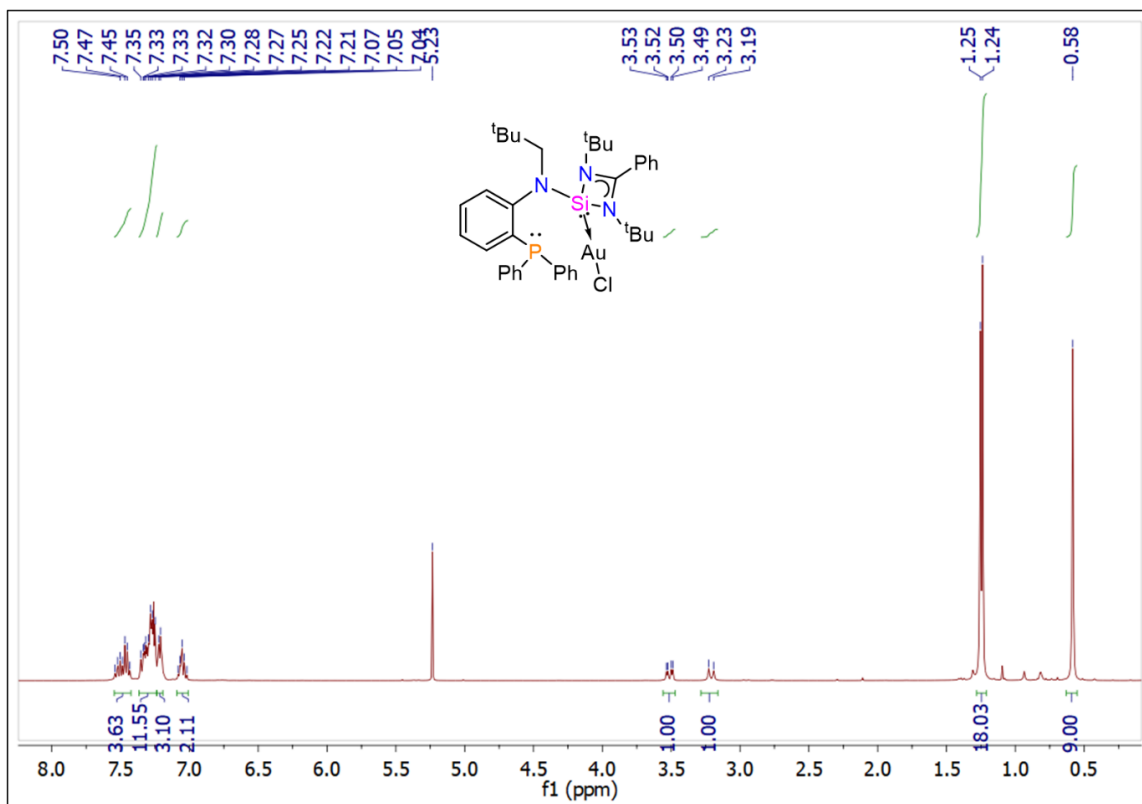


Figure 2B.A.50. ^1H NMR spectrum of **2B.11** (CDCl_3 , 400 MHz, 298 K)

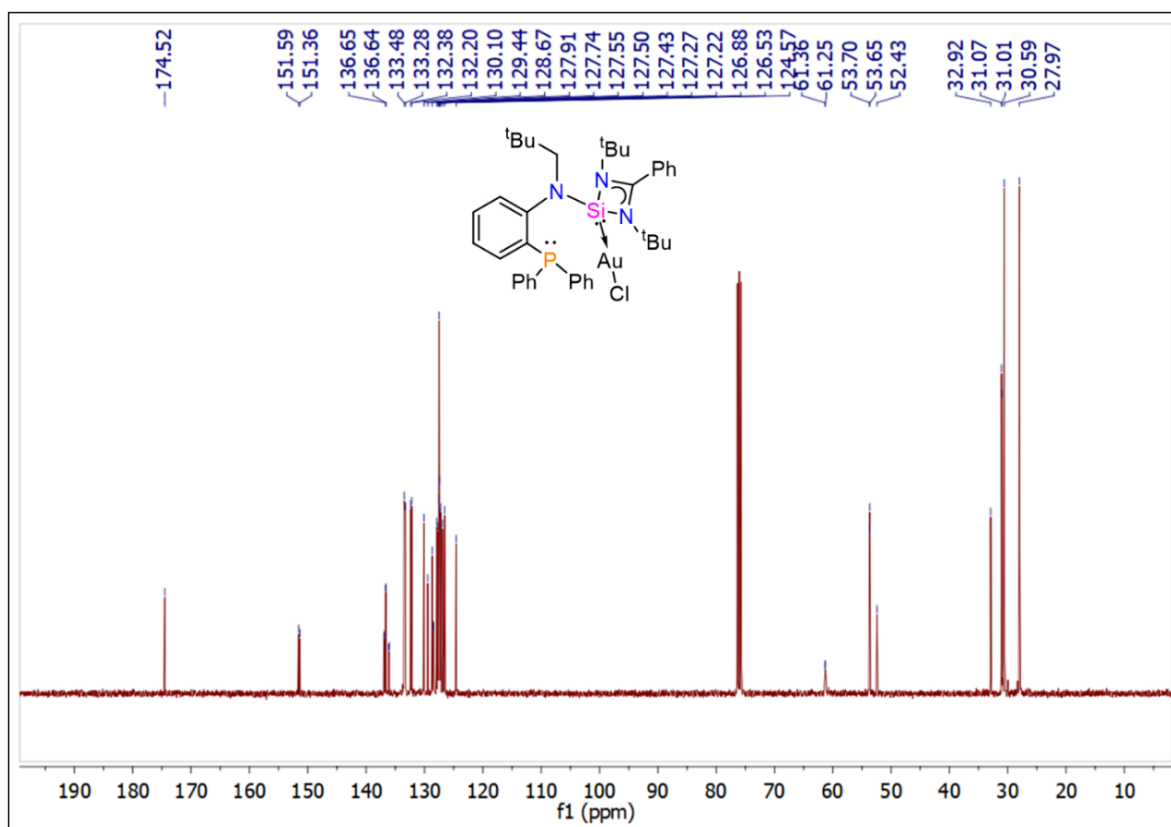


Figure 2B.A.51. ¹³C{¹H} NMR spectrum of **2B.11** (CDCl₃, 100.613 MHz, 298 K)

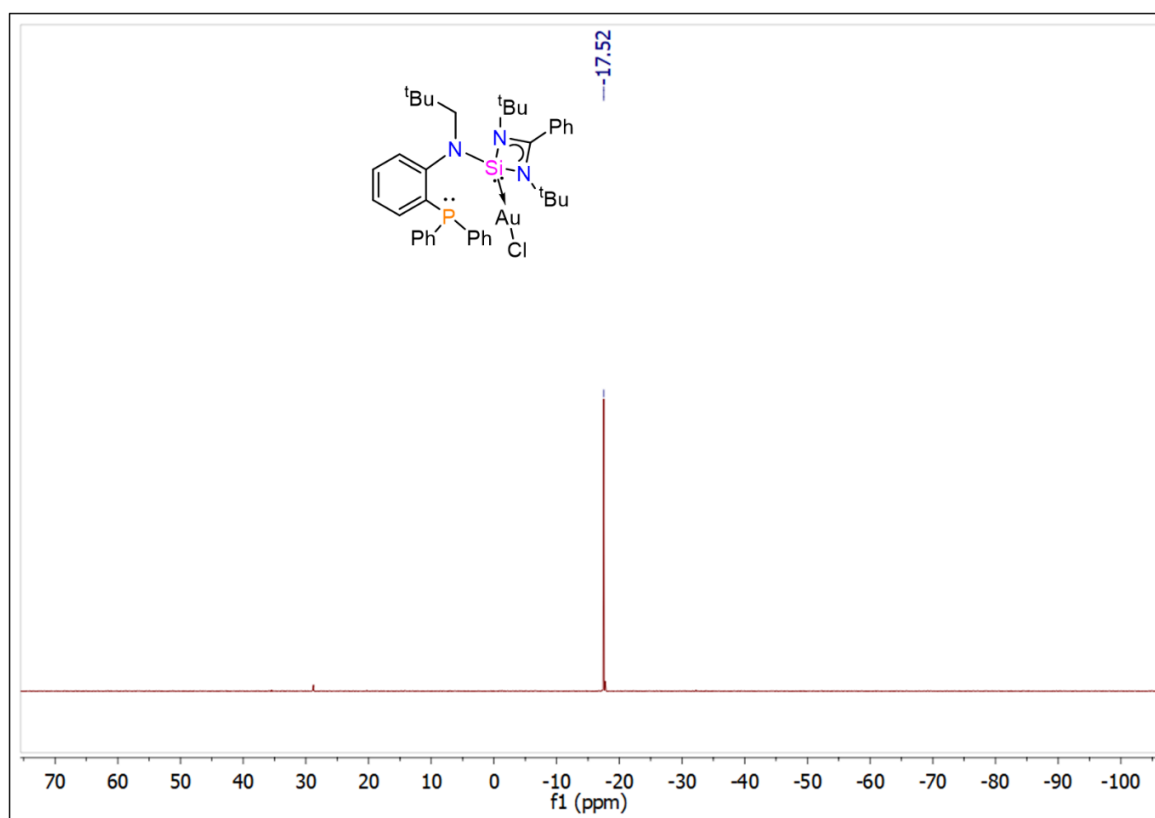


Figure 2B.A.52. ³¹P{¹H} spectrum of **2B.11** (CDCl₃, 161.97 MHz, 298 K)

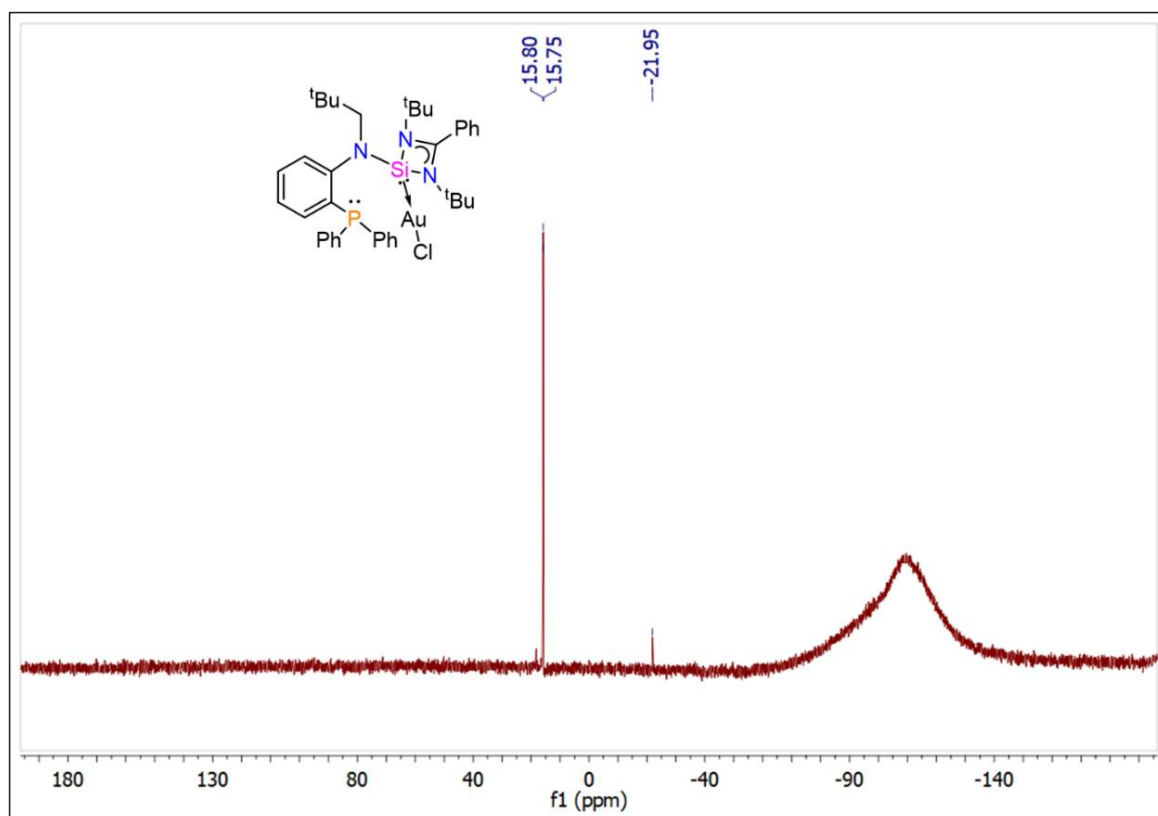


Figure 2B.A.53. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2B.11** (CDCl_3 , 79.49 MHz, 298 K)

3.A.1 Crystallographic data for complexes 3.1-3.8.

Table 3.A.1: Crystallographic data for complexes 3.1-3.4

Identification code	3.1	3.3	3.4
Empirical formula	C ₃₉ H ₅₅ N ₄ PSi ₃	C ₄₂ H ₆₀ N ₇ PSi ₂	C ₄₉ H ₆₅ N ₄ PSi
Formula weight	695.11	750.12	769.11
Temperature/K	150(2)	150.15	150.15
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P2 ₁ /n	P-1
a/Å	10.888(8)	12.093(2)	10.902(3)
b/Å	18.317(13)	14.640(3)	12.181(3)
c/Å	22.869(16)	24.012(5)	18.058(5)
α/°	67.761(16)	90	104.095(8)
β/°	77.114(18)	100.812(5)	103.516(8)
γ/°	87.811(19)	90	102.369(9)
Volume/Å ³	4110(5)	4175.3(13)	2166.1(10)
Z	4	4	2
ρ _{calc} /g/cm ³	1.123	1.193	1.179
μ/mm ⁻¹	0.185	0.162	0.129
F(000)	1496.0	1616.0	832.0
Crystal size/mm ³	0.178 × 0.163 × 0.136	0.165 × 0.152 × 0.131	0.227 × 0.214 × 0.184
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	2.466 to 49.998	4.118 to 50.168	4.012 to 50.426
Index ranges	-12 ≤ h ≤ 12, -21 ≤ k ≤ 21, -26 ≤ l ≤ 27	-14 ≤ h ≤ 14, -15 ≤ k ≤ 17, -28 ≤ l ≤ 28	-13 ≤ h ≤ 12, -14 ≤ k ≤ 14, -21 ≤ l ≤ 21
Reflections collected	54442	74836	65093
Independent reflections	14417 [R _{int} = 0.2346, R _{sigma} = 0.2644]	7422 [R _{int} = 0.3437, R _{sigma} = 0.1875]	7686 [R _{int} = 0.0885, R _{sigma} = 0.0471]
Data/restraints/parameters	14417/38/882	7422/0/482	7686/0/506
Goodness-of-fit on F ²	1.023	1.053	1.040
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0963, wR ₂ = 0.2149	R ₁ = 0.1007, wR ₂ = 0.1270	R ₁ = 0.0491, wR ₂ = 0.1221
Final R indexes [all data]	R ₁ = 0.2408, wR ₂ = 0.2908	R ₁ = 0.2022, wR ₂ = 0.1561	R ₁ = 0.0641, wR ₂ = 0.1322
Largest diff. peak/hole / e Å ⁻³	1.57/-0.44	0.43/-0.54	0.83/-0.48

Table 3.A.2: Crystallographic data for complexes **3.5-3.7**

Identification code	3.5	3.6	3.7
Empirical formula	C ₁₂₇ H ₂₀₄ N ₁₈ Si ₈	C ₃₀ H ₄₀ N ₄ Si ₂	C ₈₁ H ₉₂ N ₈ Si ₂
Formula weight	2207.79	512.84	1233.80
Temperature/K	150(2)	150.15	150.15
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P2 ₁ /n	P-1
a/Å	10.864(4)	10.156(2)	8.8583(7)
b/Å	16.735(5)	21.836(4)	10.4633(8)
c/Å	18.439(6)	13.847(3)	20.7501(16)
α/°	97.056(9)	90	79.270(2)
β/°	101.901(9)	104.991(6)	79.287(2)
γ/°	90.920(9)	90	69.176(2)
Volume/Å ³	3252.4(18)	2966.2(10)	1751.1(2)
Z	1	4	1
ρ _{calc} /cm ³	1.127	1.148	1.170
μ/mm ⁻¹	0.136	0.144	0.101
F(000)	1204.0	1104.0	662.0
Crystal size/mm ³	0.211 × 0.183 × 0.152	0.225 × 0.163 × 0.148	0.211 × 0.173 × 0.158
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.834 to 49.994	3.73 to 50.314	4.03 to 50.362
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 19, -21 ≤ l ≤ 21	-12 ≤ h ≤ 12, -26 ≤ k ≤ 26, -16 ≤ l ≤ 16	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -24 ≤ l ≤ 22
Reflections collected	55943	99118	27543
Independent reflections	11418 [R _{int} = 0.1001, R _{sigma} = 0.0819]	5302 [R _{int} = 0.0488, R _{sigma} = 0.0164]	6273 [R _{int} = 0.0377, R _{sigma} = 0.0306]
Data/restraints/parameters	11418/37/730	5302/0/335	6273/42/437
Goodness-of-fit on F ²	1.018	1.052	1.046
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0640, wR ₂ = 0.1308	R ₁ = 0.0411, wR ₂ = 0.1014	R ₁ = 0.0499, wR ₂ = 0.1219
Final R indexes [all data]	R ₁ = 0.1112, wR ₂ = 0.1560	R ₁ = 0.0465, wR ₂ = 0.1054	R ₁ = 0.0625, wR ₂ = 0.1296
Largest diff. peak/hole / e Å ⁻³	0.41/-0.40	0.28/-0.26	0.59/-0.35

Table 3.A.3: Crystallographic data for complexes **3.8**

Identification code	3.8
Empirical formula	C ₂₂ H ₅₁ N ₅ Si ₅
Formula weight	526.12
Temperature/K	150.15
Crystal system	Triclinic
Space group	P-1
a/Å	9.1447(6)
b/Å	10.5791(6)
c/Å	16.9334(10)
α /°	95.117(2)
β /°	99.529(2)
γ /°	106.312(2)
Volume/Å ³	1534.53(16)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.139
μ/mm^{-1}	0.252
F(000)	576.0
Crystal size/mm ³	0.271 × 0.266 × 0.247
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.054 to 50.312
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -20 ≤ l ≤ 20
Reflections collected	56690
Independent reflections	5467 [R _{int} = 0.0592, R _{sigma} = 0.0265]
Data/restraints/parameters	5467/12/306
Goodness-of-fit on F ²	1.041
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0316, wR ₂ = 0.0814
Final R indexes [all data]	R ₁ = 0.0344, wR ₂ = 0.0840
Largest diff. peak/hole / e Å ⁻³	0.34/-0.4

3.A.2 NMR spectrum for 3.1-3.8.

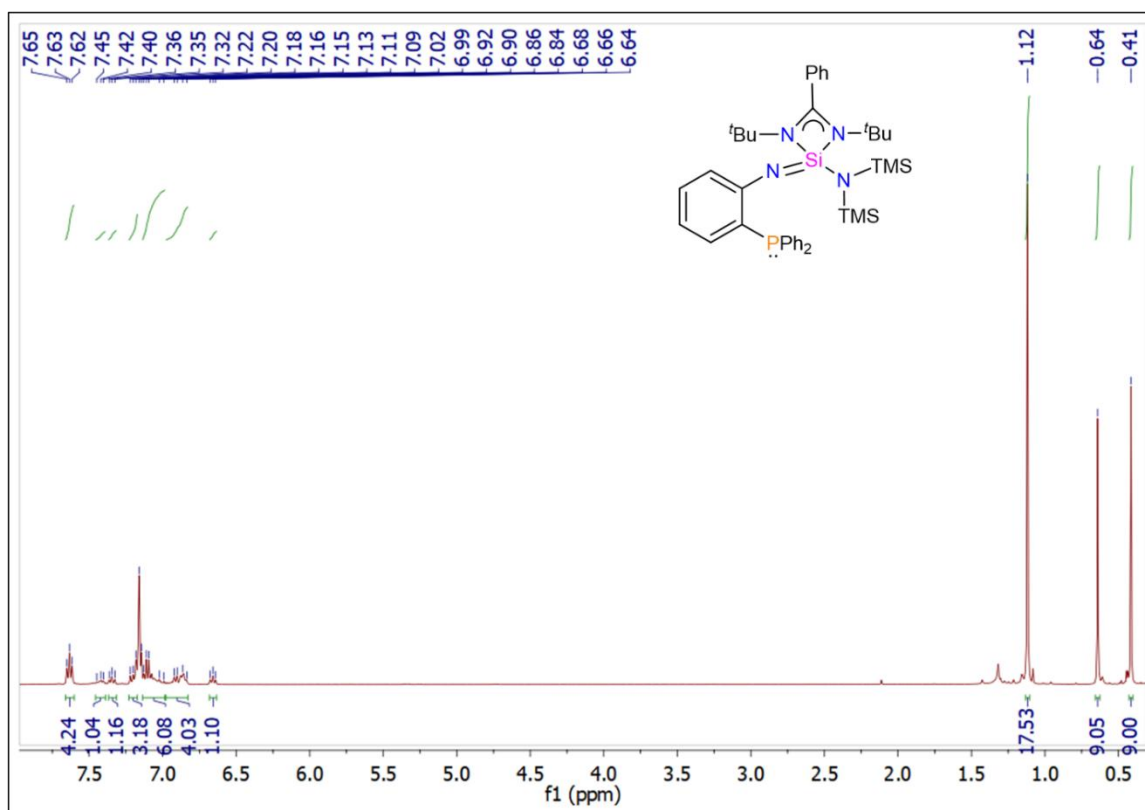


Figure 3.A.1. ¹H NMR spectrum of **3.1** (C₆D₆, 400 MHz, 298 K)

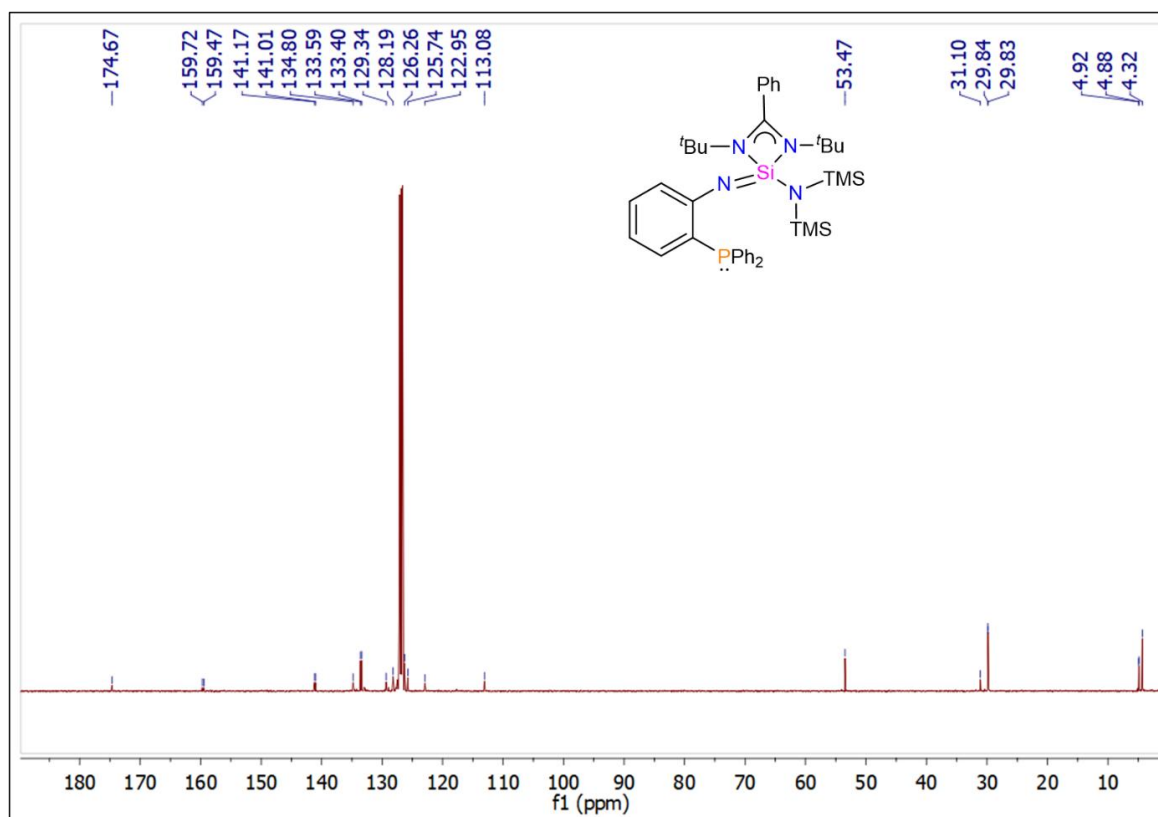


Figure 3.A.2. ¹³C{¹H} NMR spectrum of **3.1** (100.613 MHz, C₆D₆, 298 K)

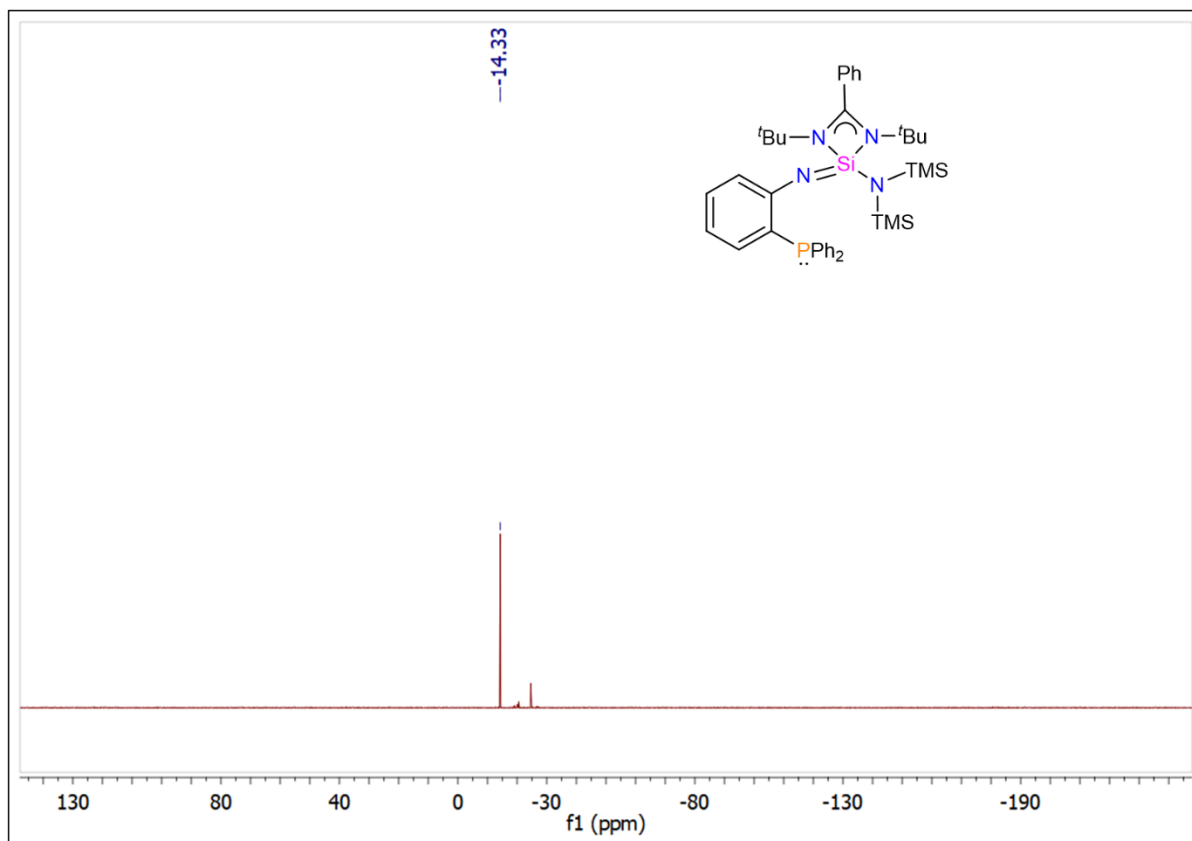


Figure 3.A.3. $^{31}\text{P}\{^1\text{H}\}$ full NMR spectrum of **3.1** (C_6D_6 , 161.97 MHz, 298 K)

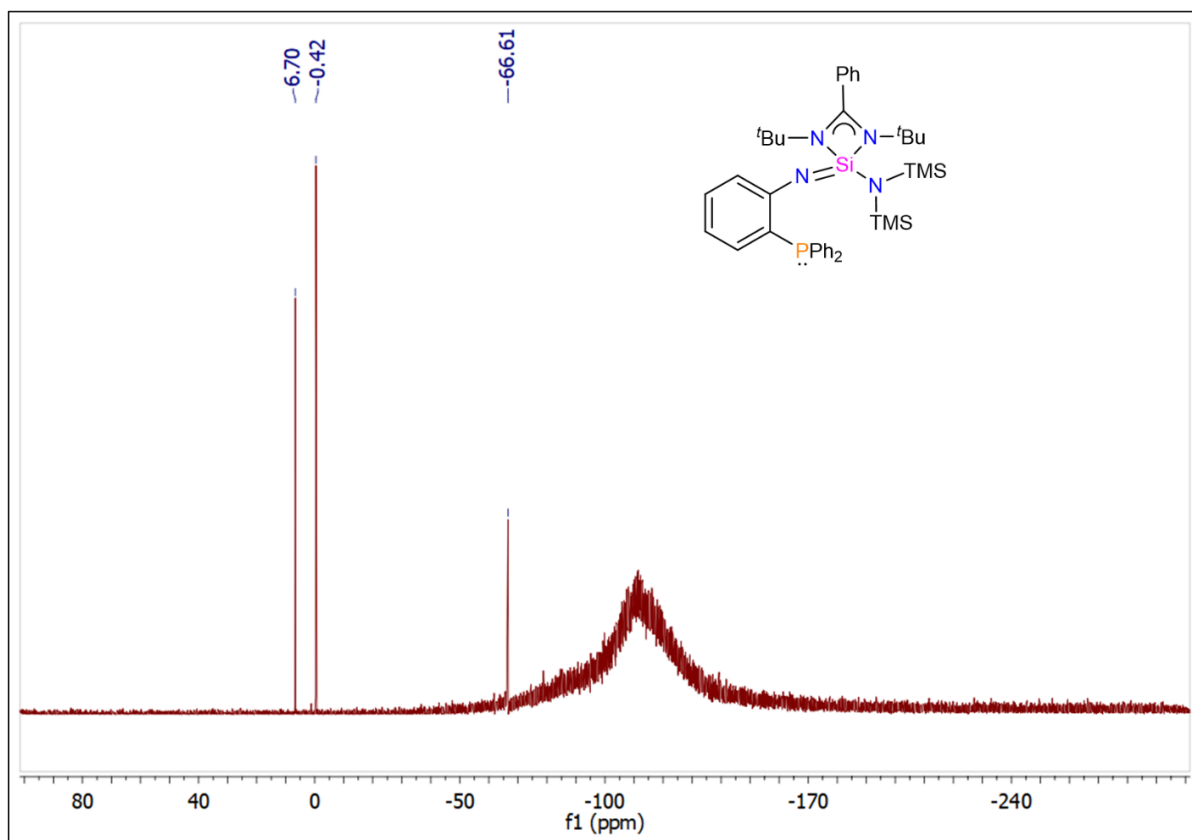


Figure 3.A.4. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3.1** (C_6D_6 , 79.49 MHz, 298 K)

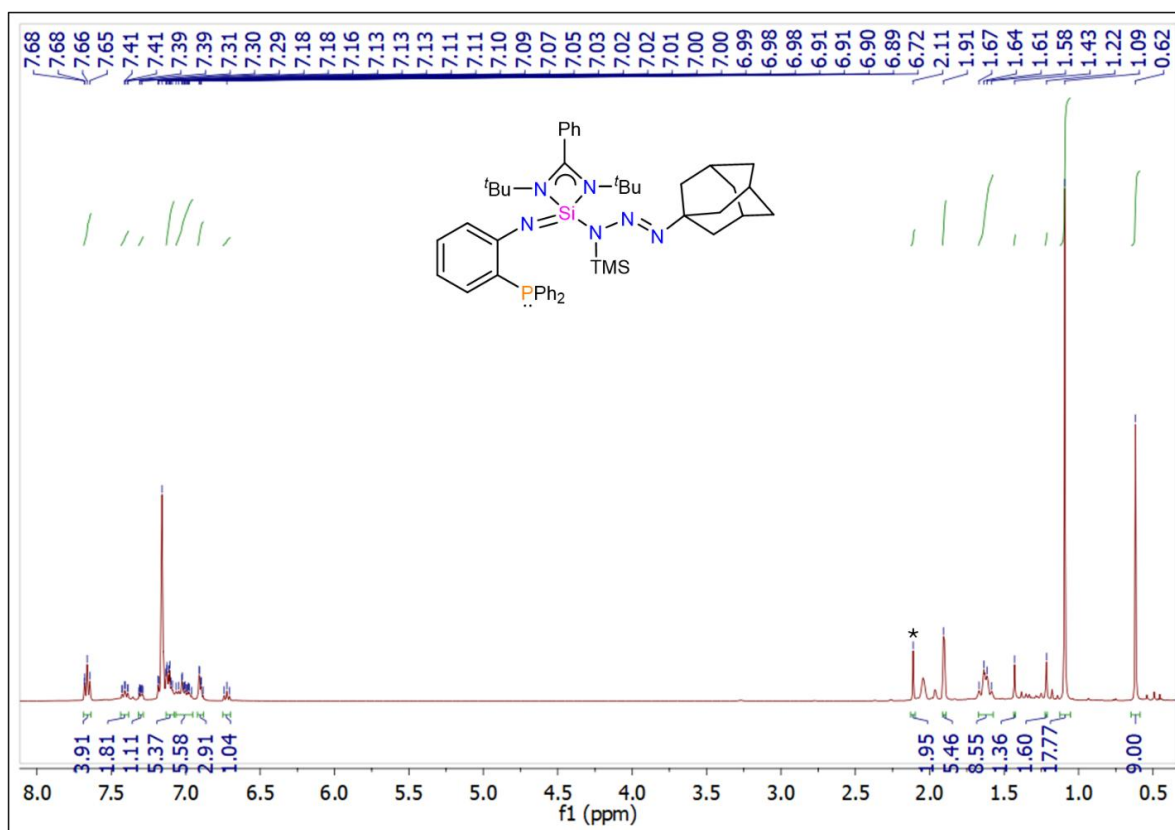


Figure 3.A.5. ¹H NMR spectrum of **3.2** (C₆D₆, 400 MHz, 298 K), * Grease

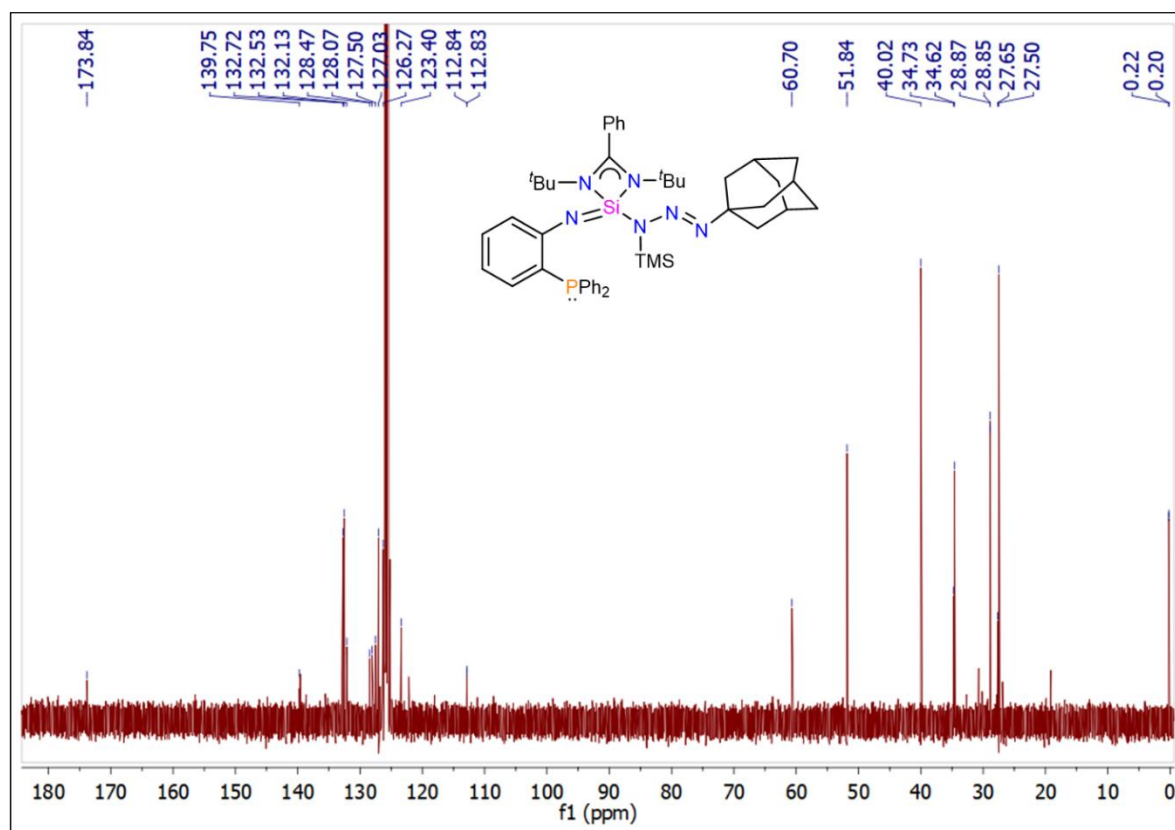


Figure 3.A.6. ¹³C{¹H} NMR spectrum of **3.2** (100.613 MHz, C₆D₆, 298 K)

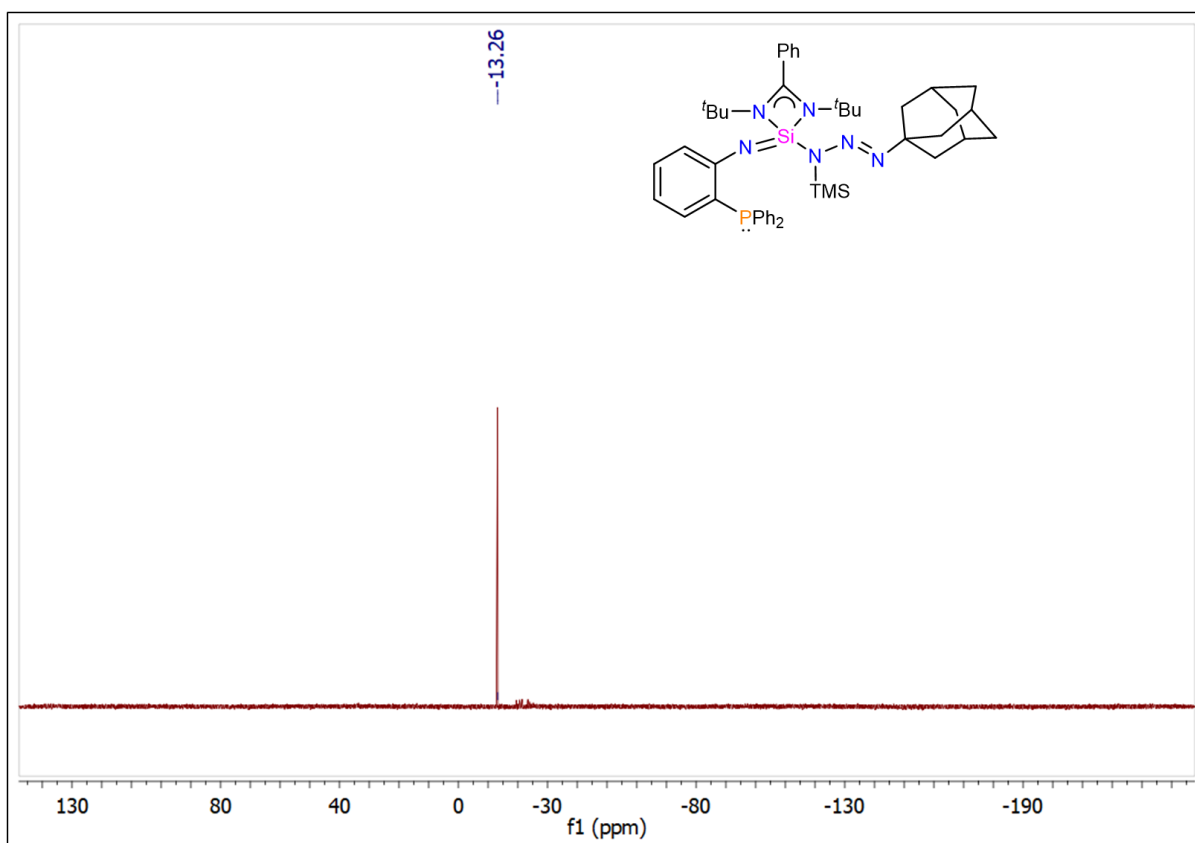


Figure 3.A.7. $^{31}\text{P}\{^1\text{H}\}$ full NMR spectrum of **3.2** (C_6D_6 , 161.97 MHz, 298 K)

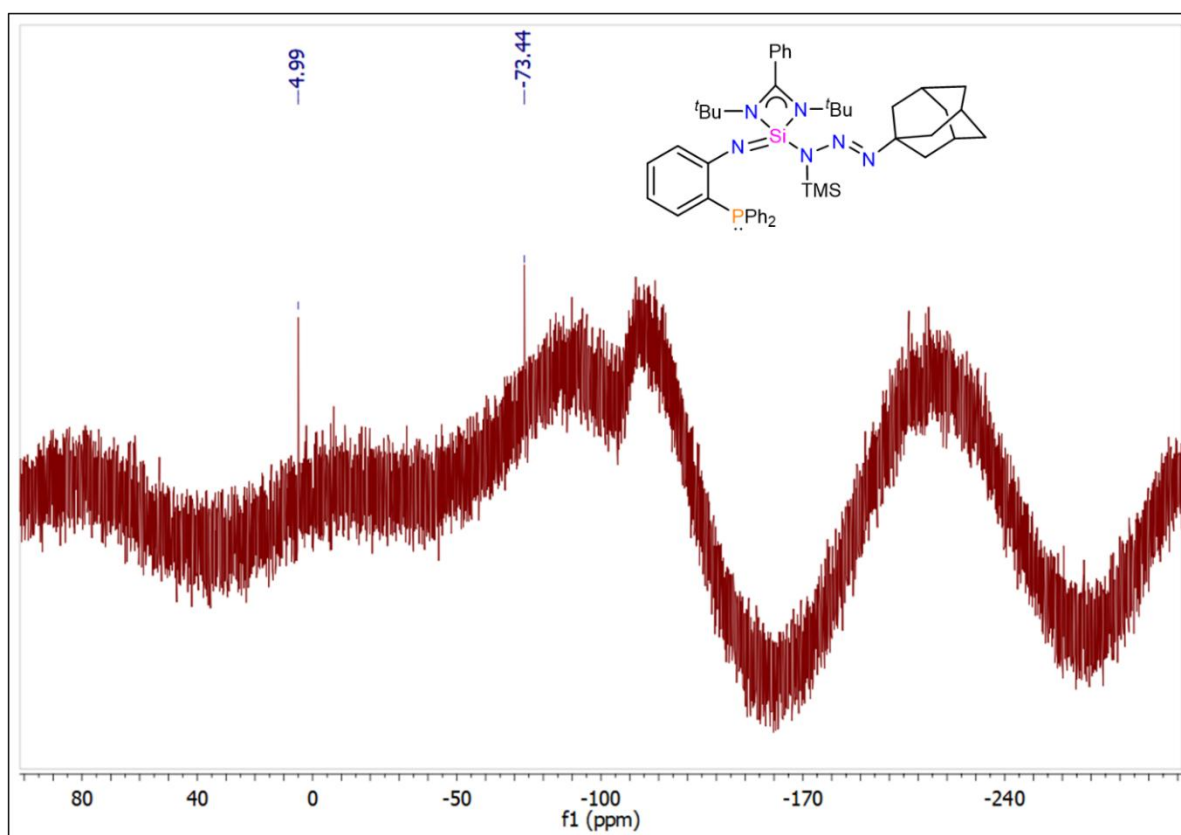


Figure 3.A.8. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3.2** (C_6D_6 , 79.49 MHz, 298 K)

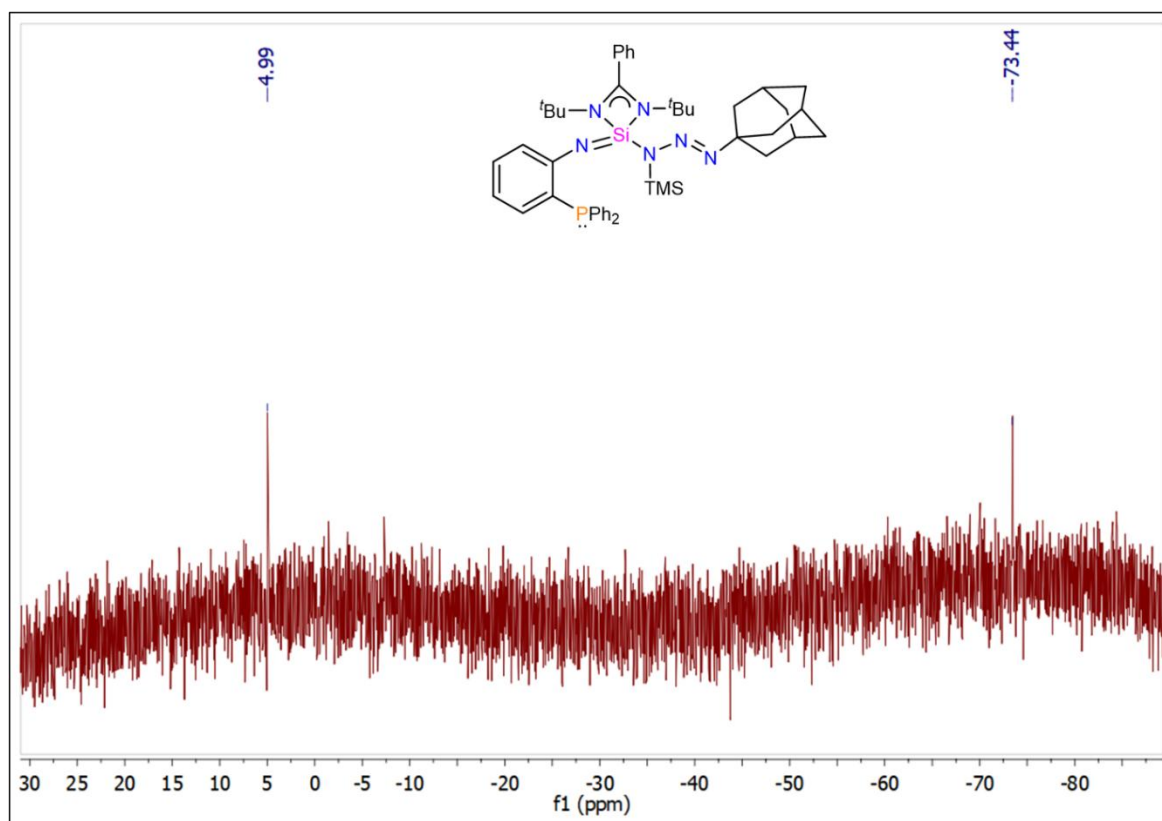


Figure 3.A.9. Zoomed $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3.2** (C_6D_6 , 79.49 MHz, 298 K)

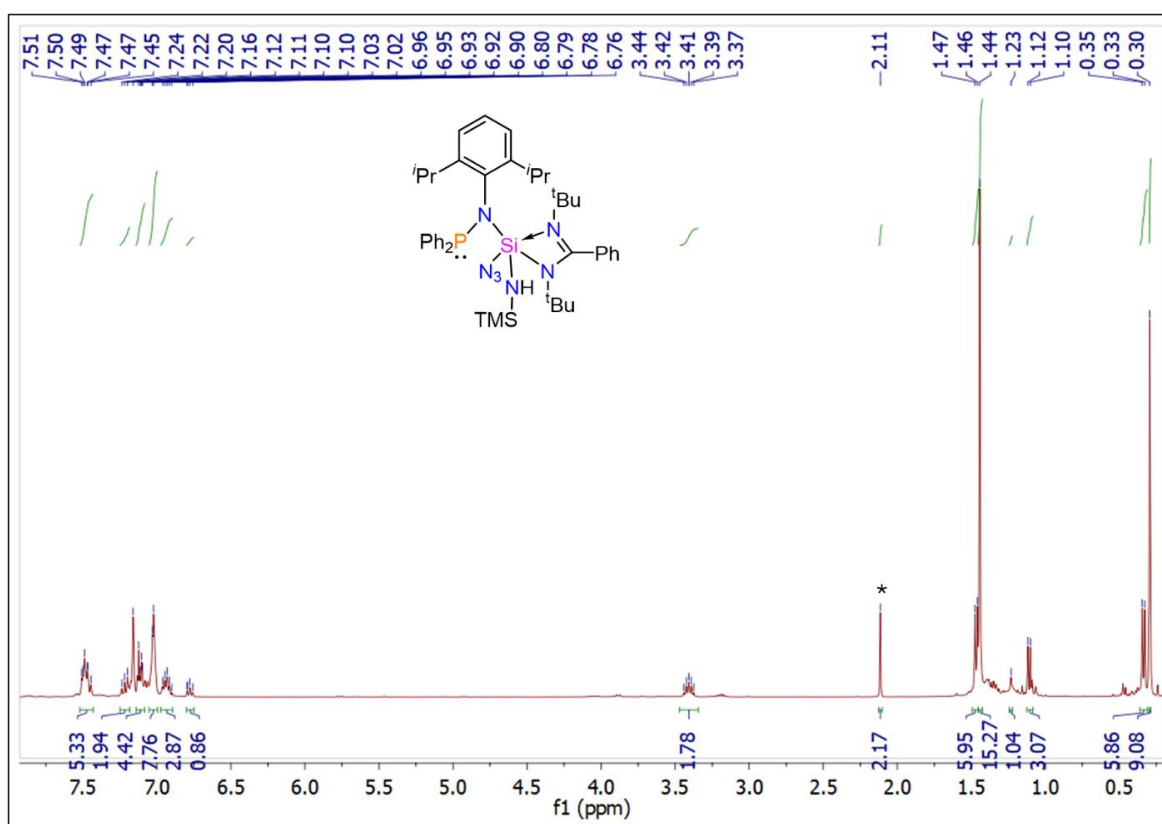


Figure 3.A.10. ^1H NMR spectrum of **3.3** (C_6D_6 , 400 MHz, 298 K), *Toluene

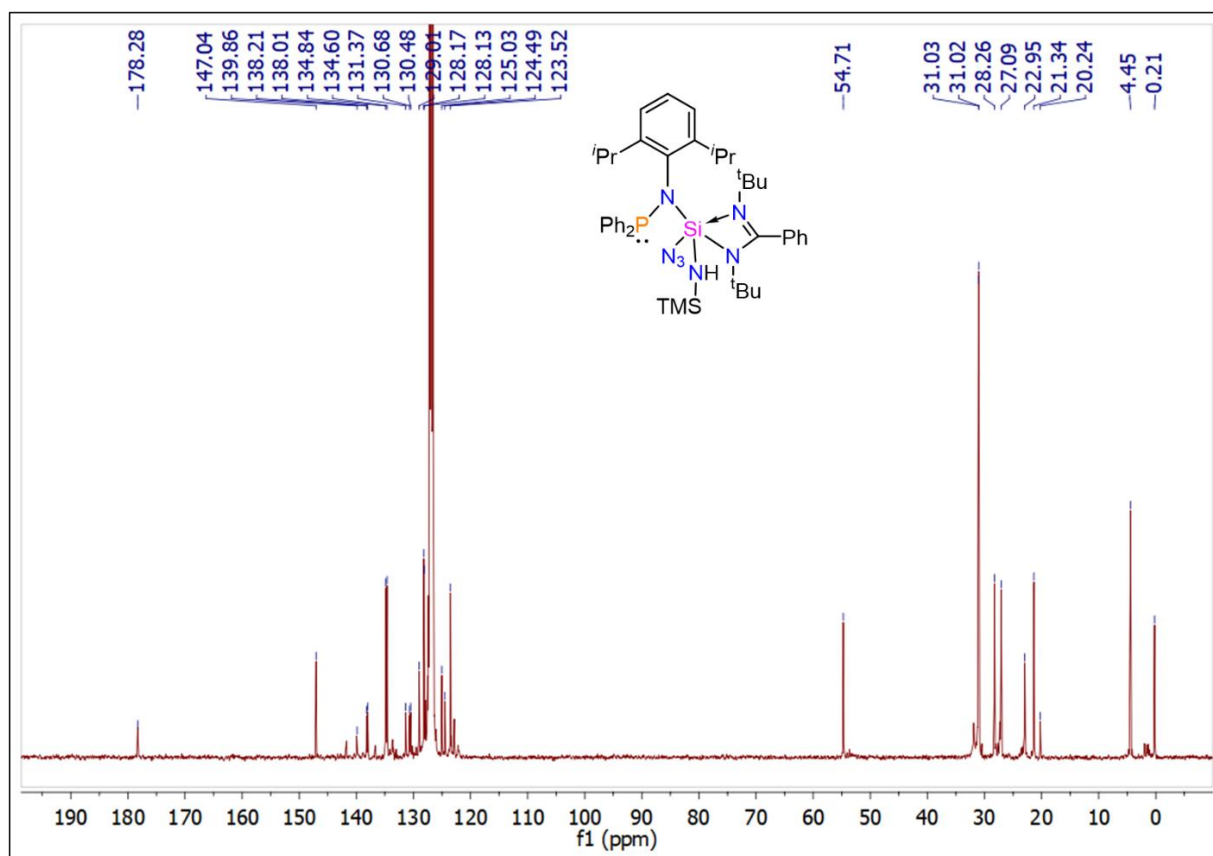


Figure 3.A.11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3.3** (100.613 MHz, C_6D_6 , 298 K)

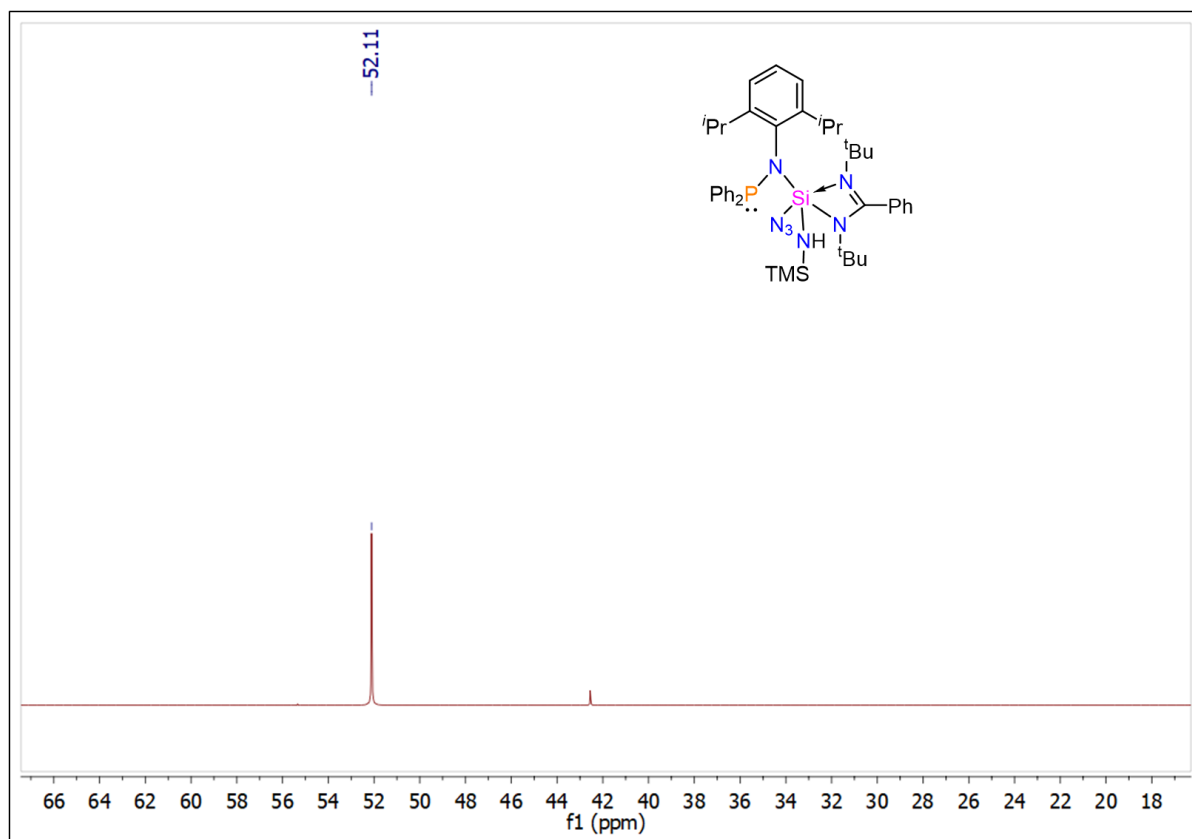


Figure 3.A.12. $^{31}\text{P}\{^1\text{H}\}$ full NMR spectrum of **3.3** (C_6D_6 , 161.97 MHz, 298 K)

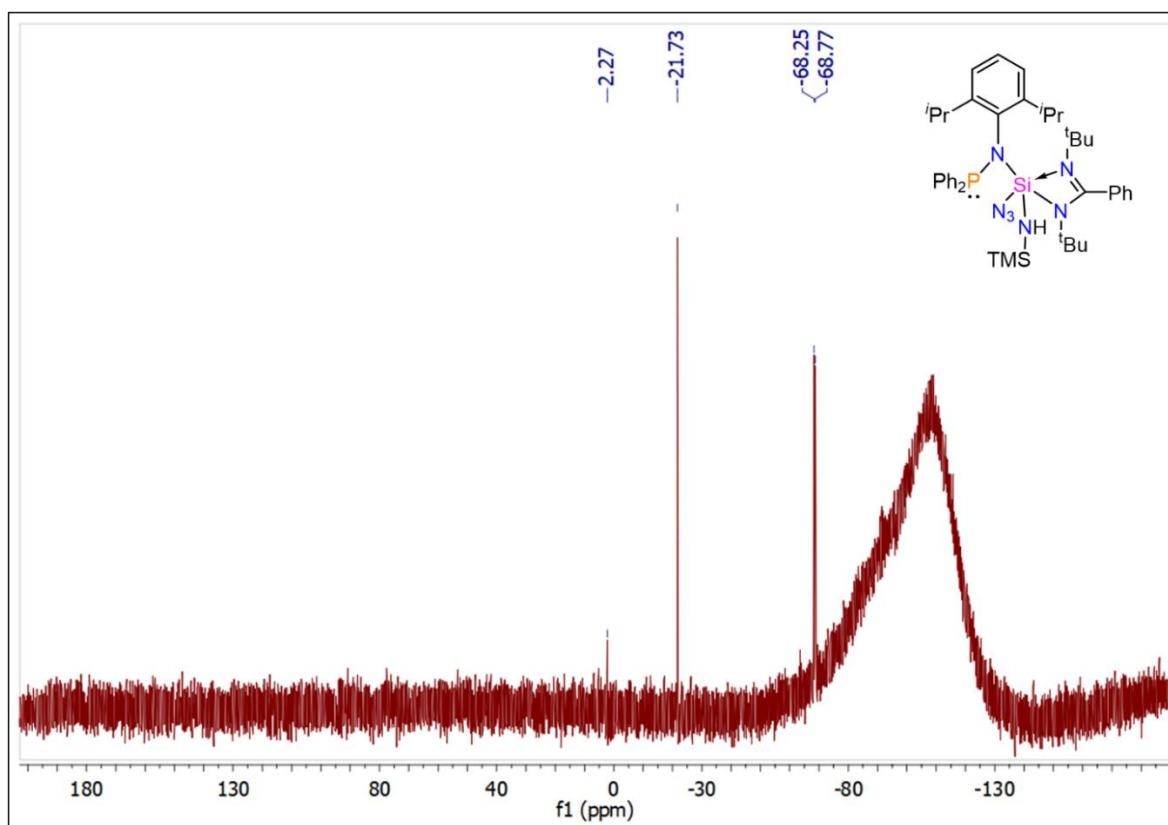


Figure 3.A.13. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3.3** (C_6D_6 , 79.49 MHz, 298 K)

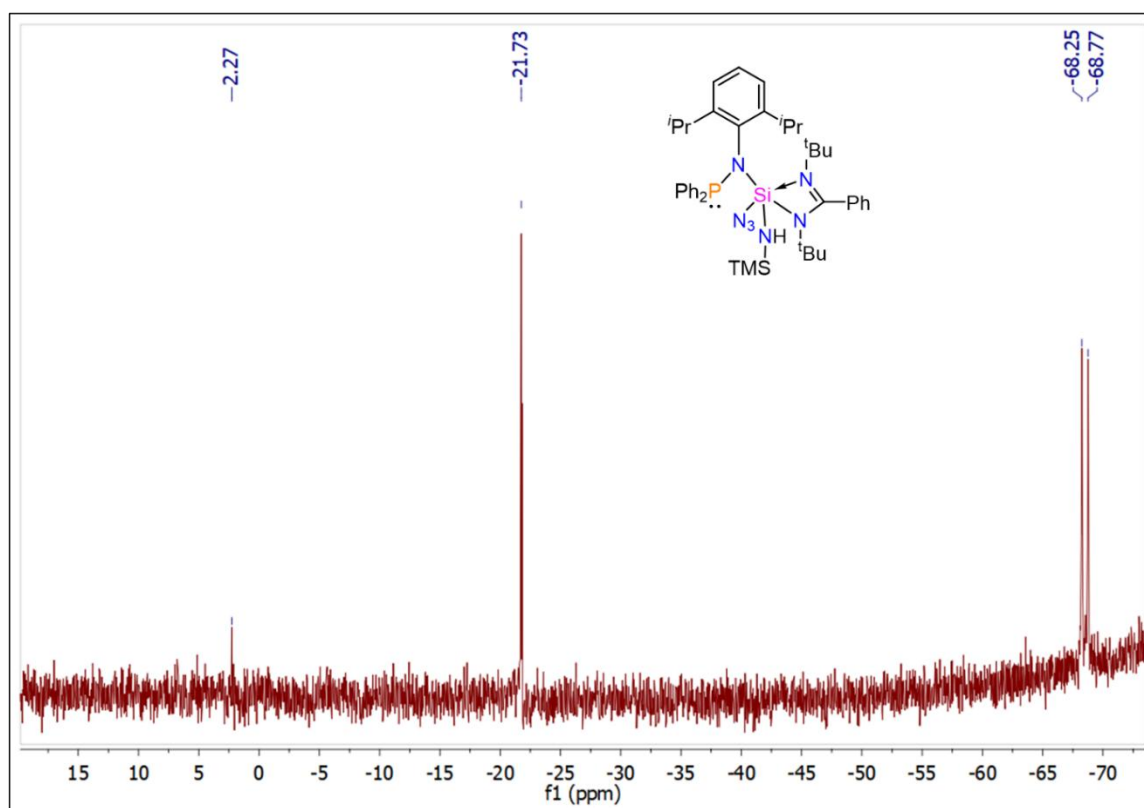


Figure 3.A.14. Zoomed $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3.3** (C_6D_6 , 79.49 MHz, 298 K)

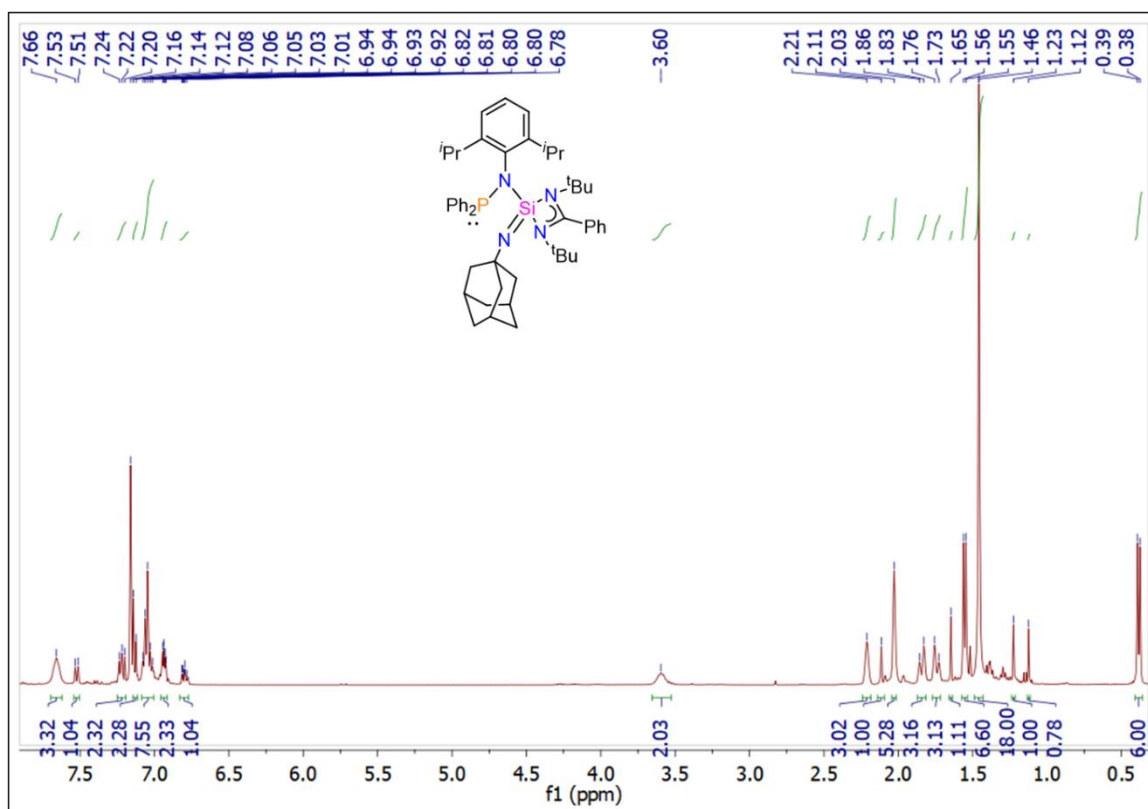


Figure 3.A.15. ¹H NMR spectrum of **3.4** (C₆D₆, 400 MHz, 298 K)

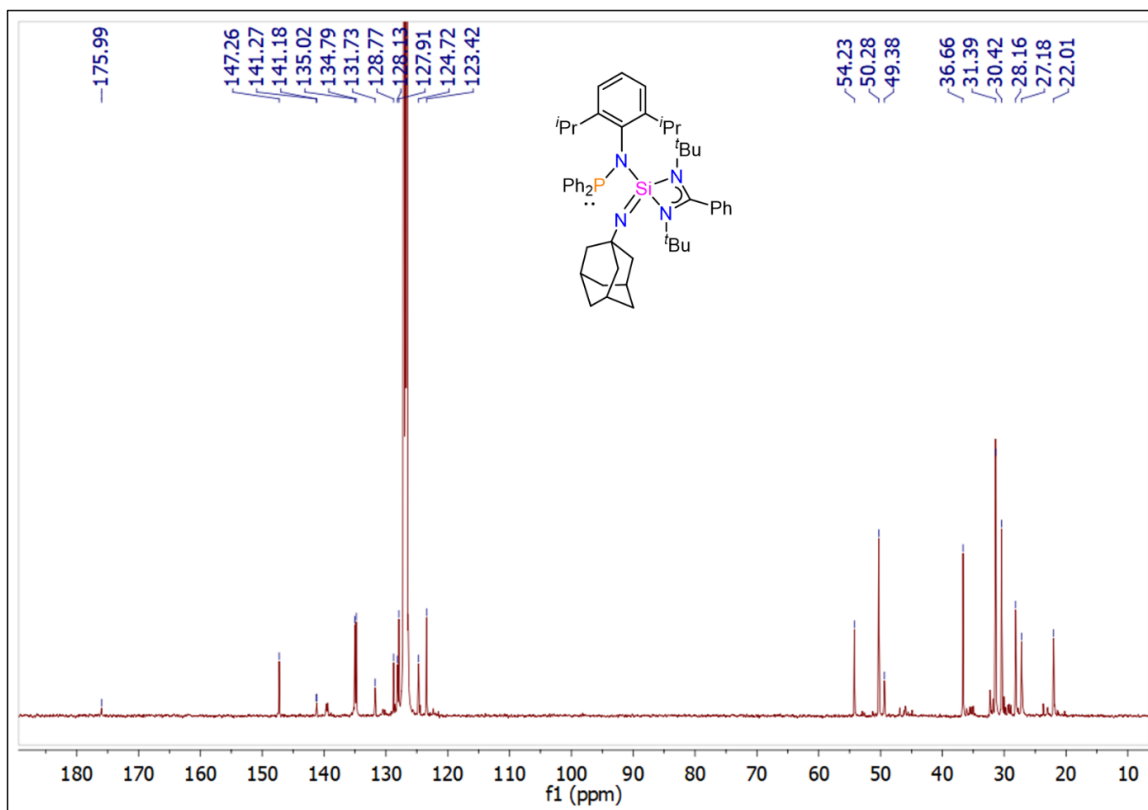


Figure 3.A.16. ¹³C{¹H} NMR spectrum of **3.4** (100.613 MHz, C₆D₆, 298 K)

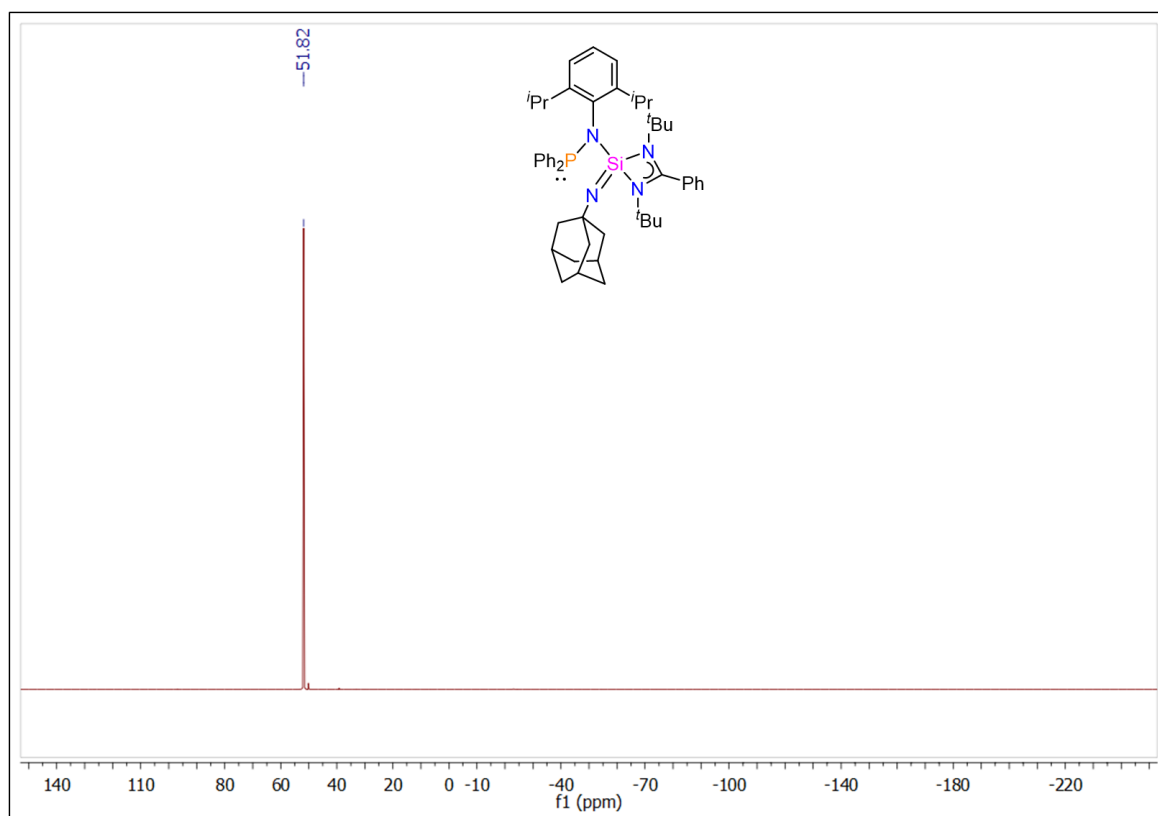


Figure 3.A.17. $^{31}\text{P}\{^1\text{H}\}$ full NMR spectrum of **3.4** (C_6D_6 , 161.97 MHz, 298 K)

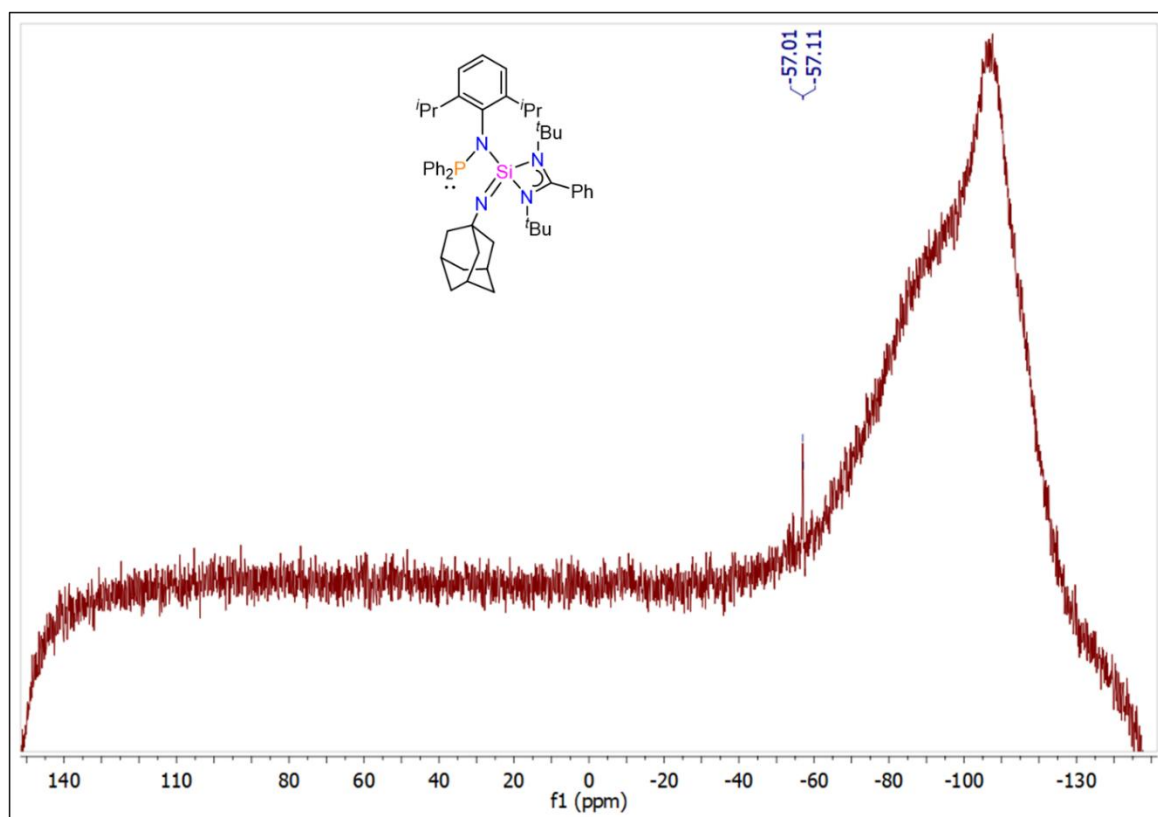


Figure 3.A.18. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3.4** (C_6D_6 , 79.49 MHz, 298 K)

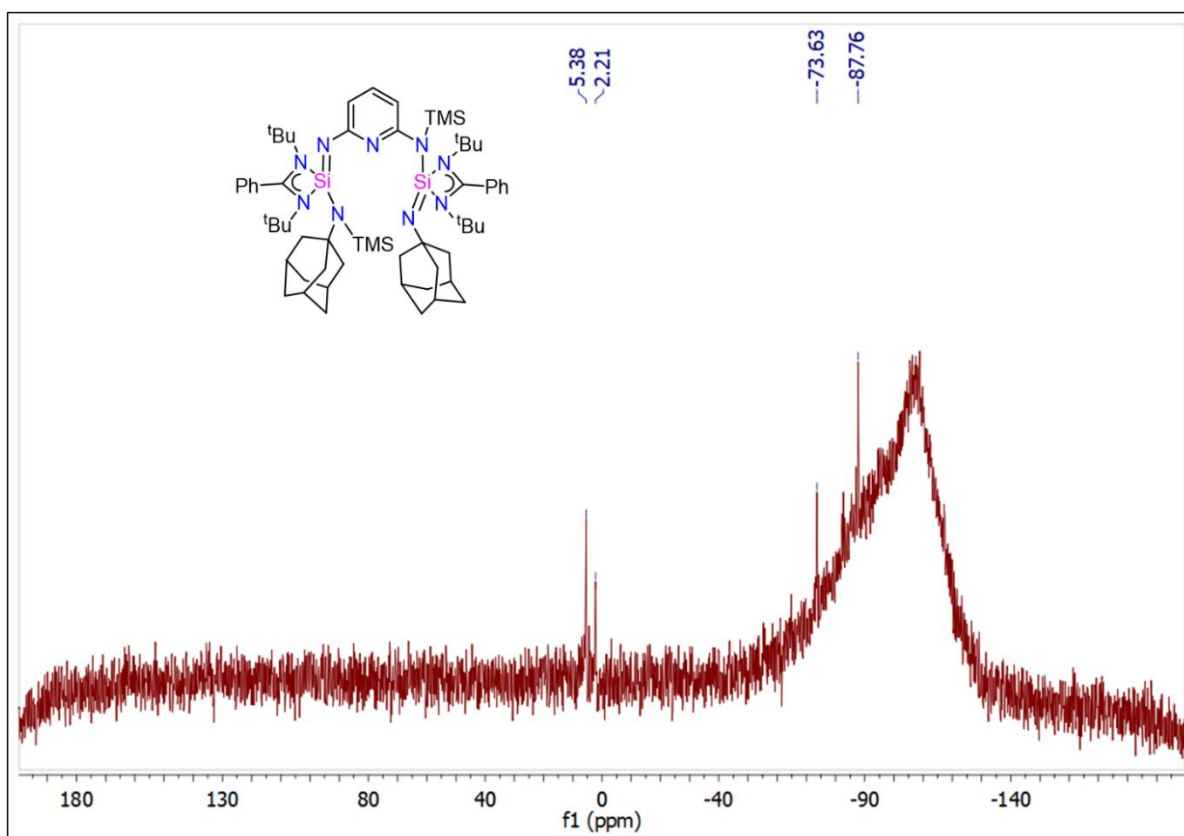


Figure 3.A.19. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3.5** (C_6D_6 , 79.49 MHz, 298 K)

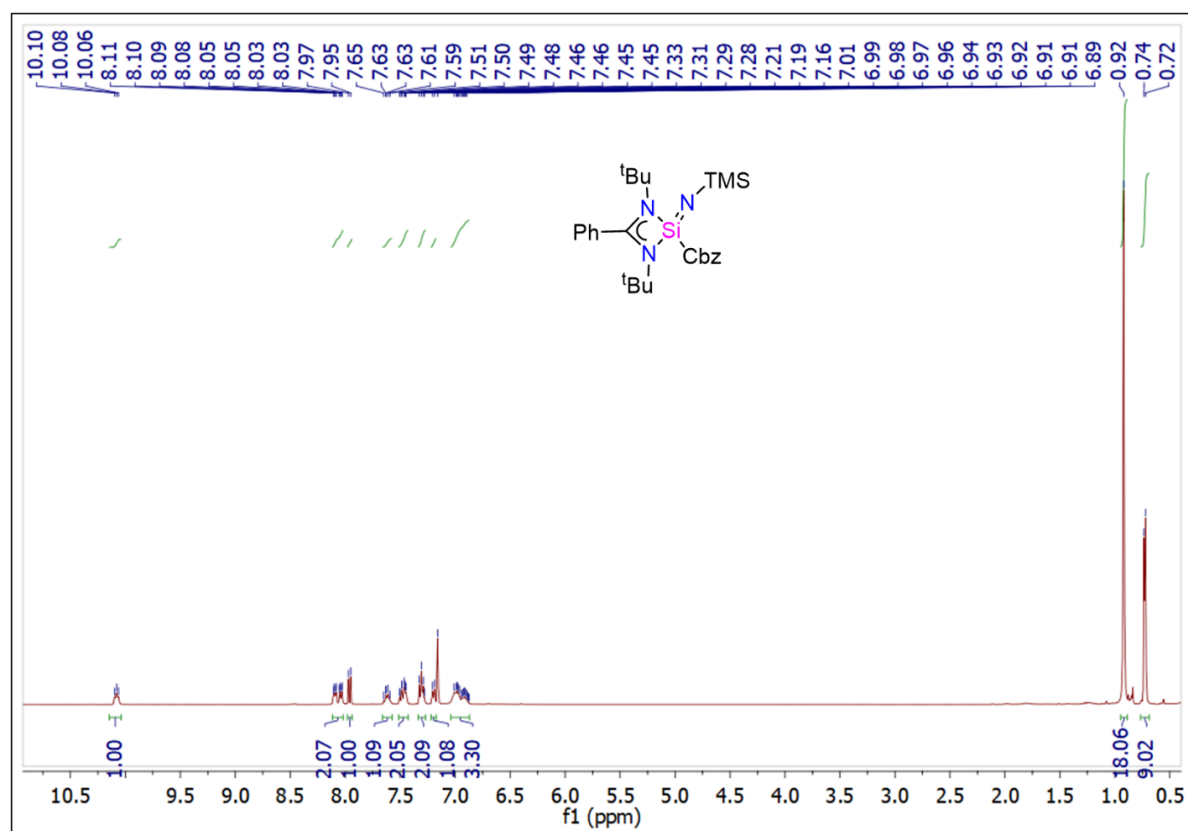


Figure 3.A.20. ^1H NMR spectrum of **3.6** (C_6D_6 , 400 MHz, 298 K)

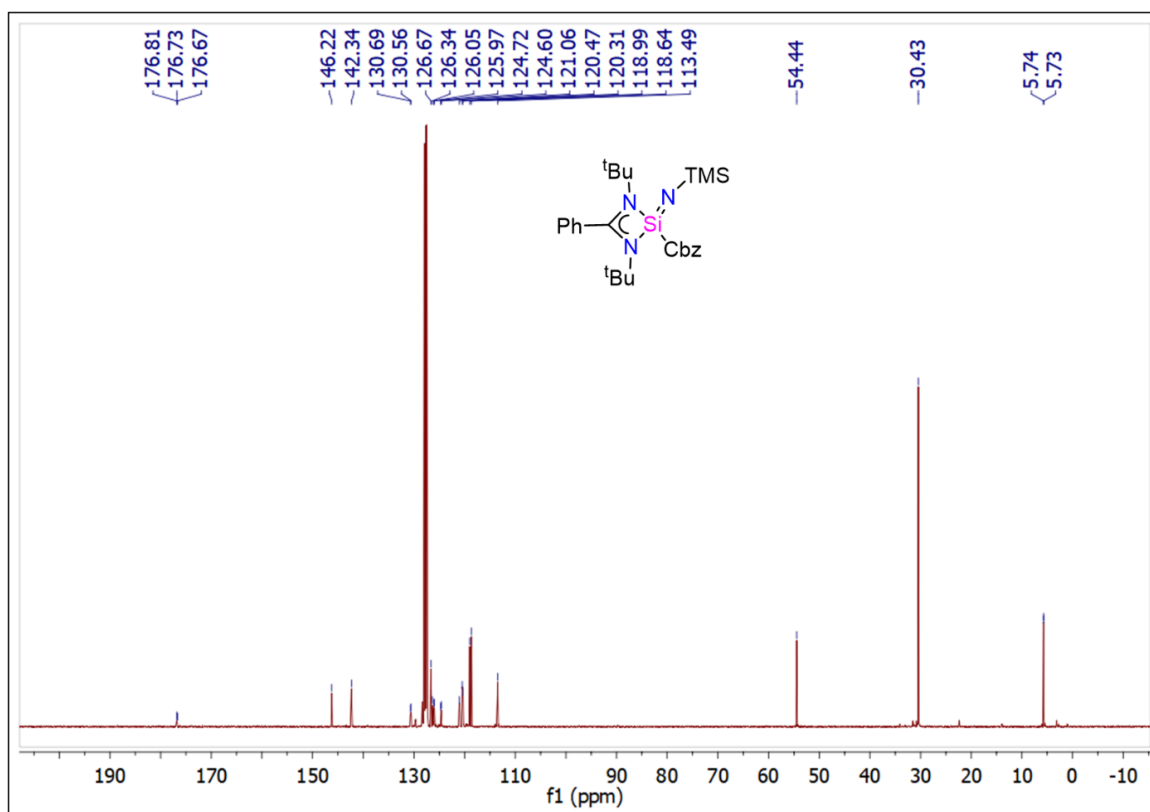


Figure 3.A.21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3.6** (100.613 MHz, C_6D_6 , 298 K)

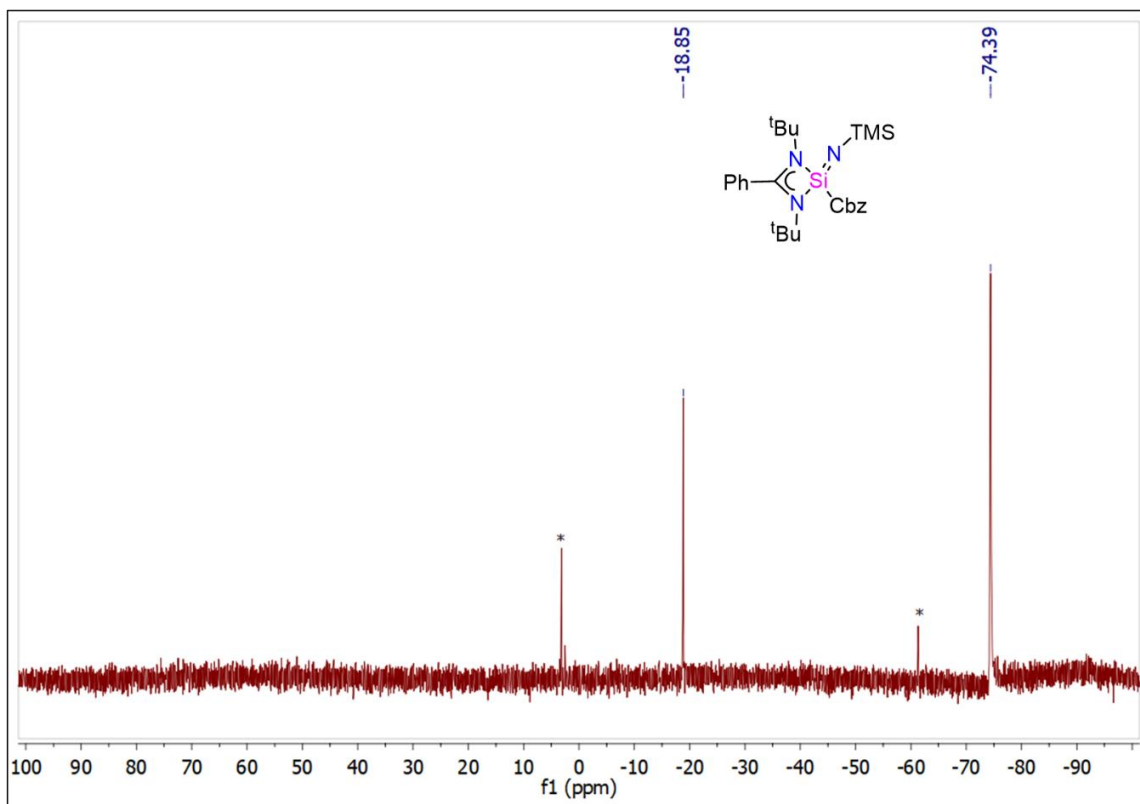


Figure 3.A.22. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3.1** (C_6D_6 , 79.49 MHz, 298 K), * Unidentified peak

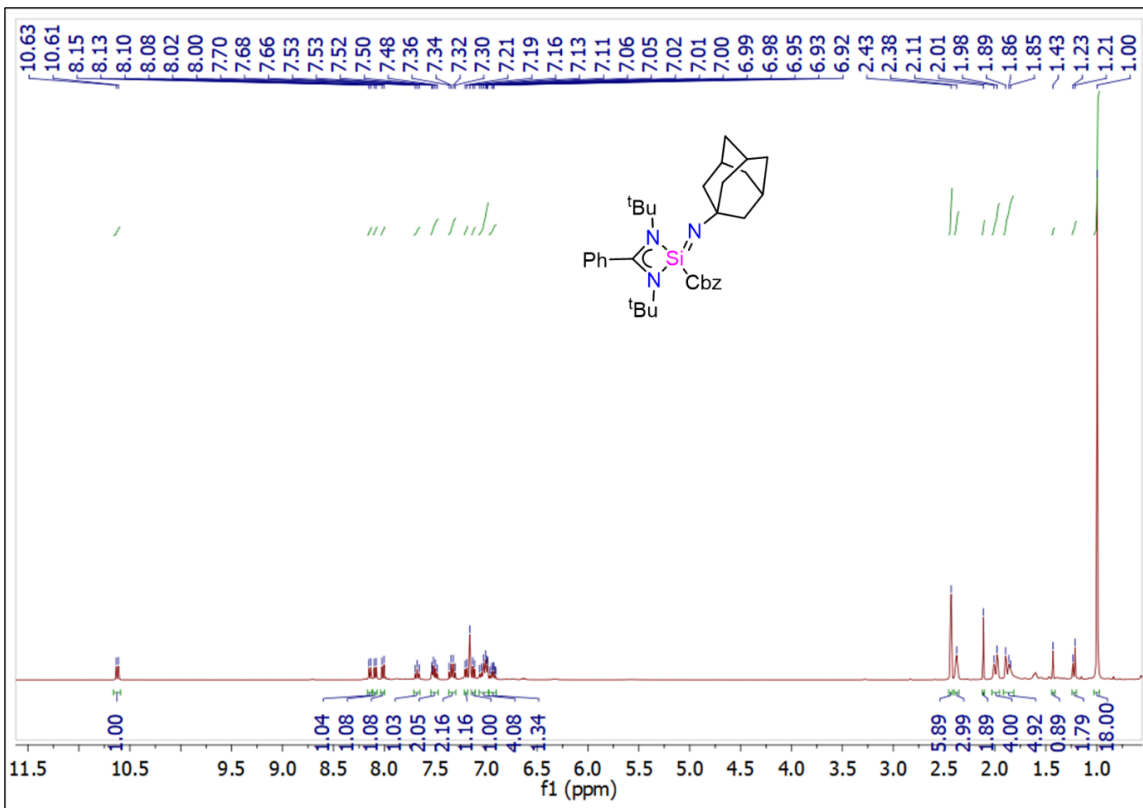


Figure 3.A.23. ^1H NMR spectrum of **3.7** (C_6D_6 , 400 MHz, 298 K)

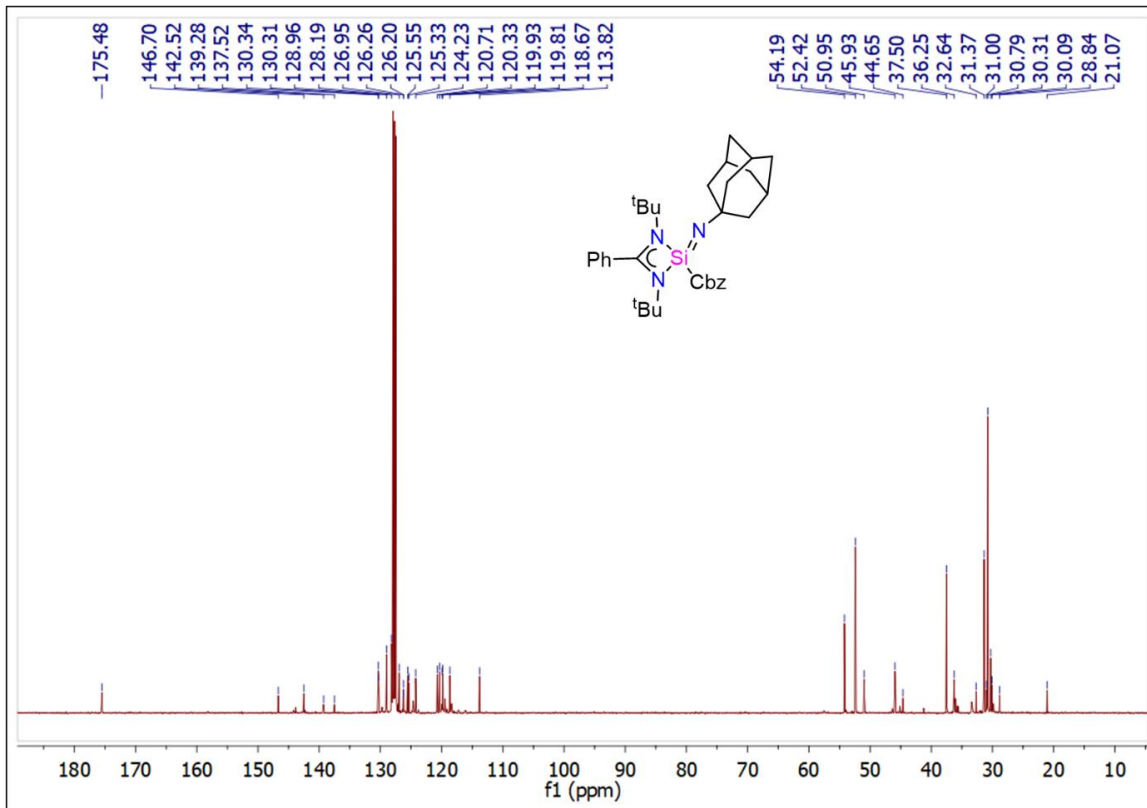


Figure 3.A.24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3.7** (100.613 MHz, C_6D_6 , 298 K)

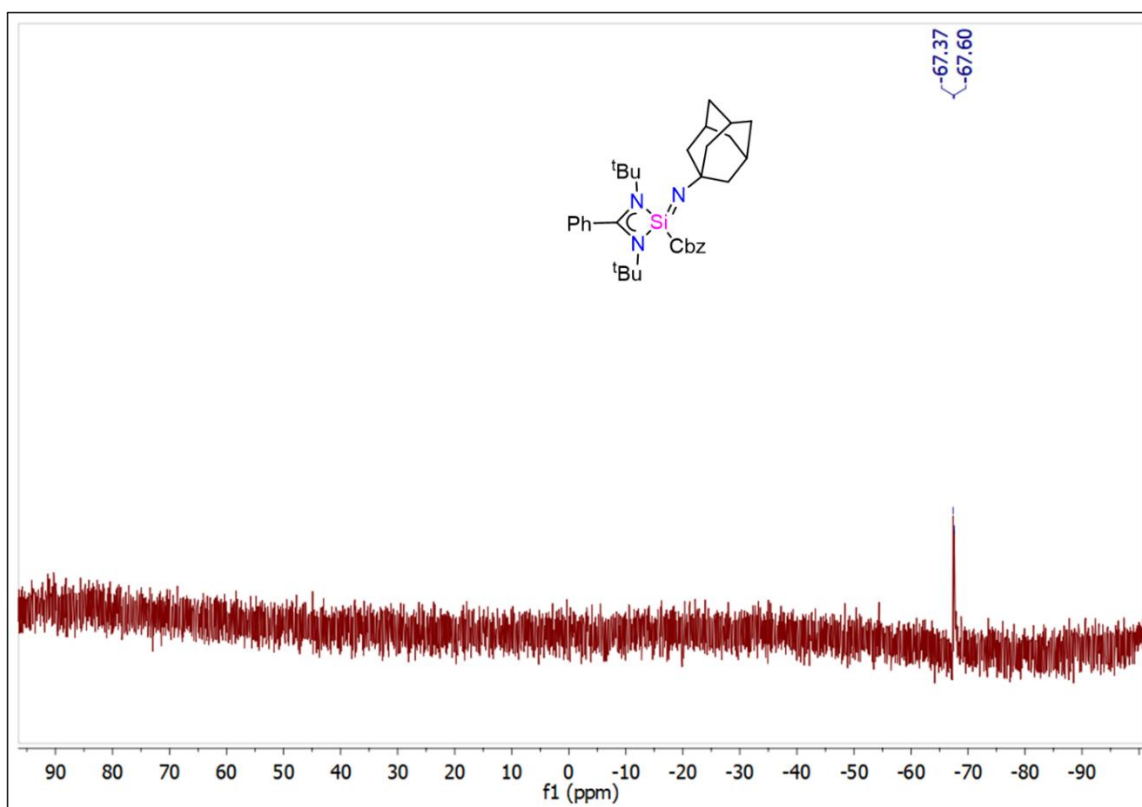


Figure 3.A.25. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3.7** (C_6D_6 , 79.49 MHz, 298 K)

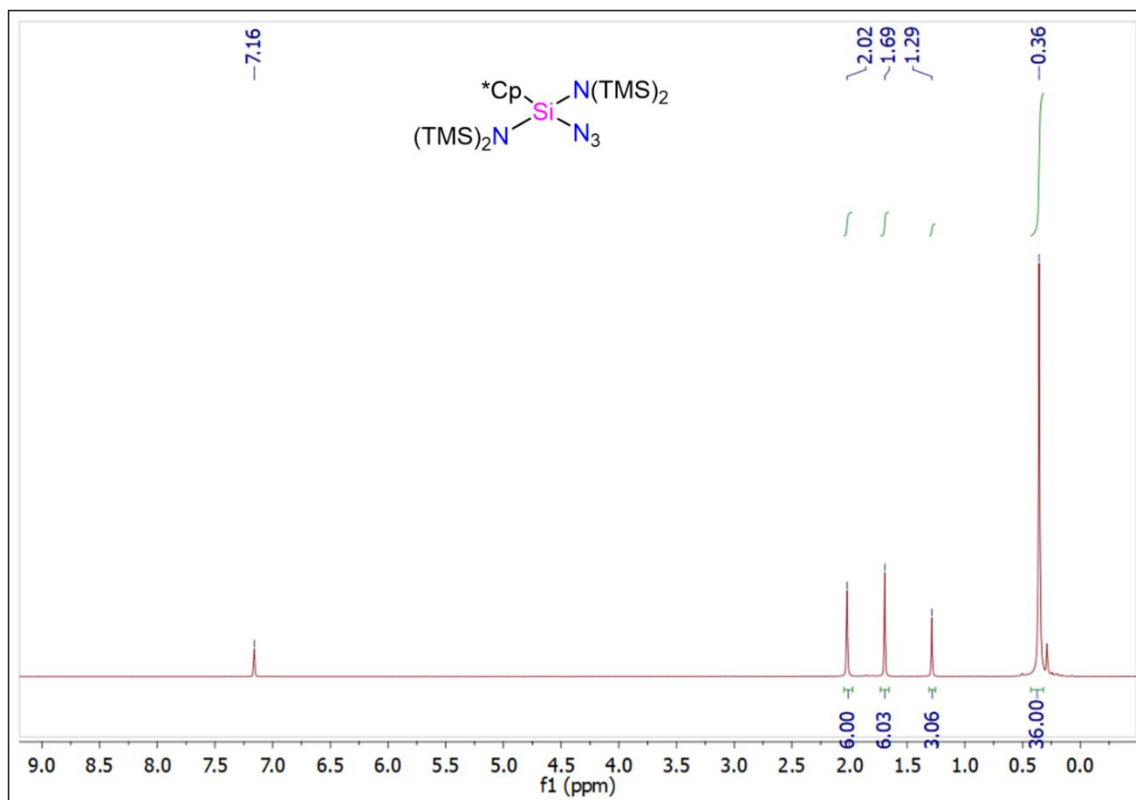


Figure 3.A.26. ^1H NMR spectrum of **3.8** (C_6D_6 , 400 MHz, 298 K)

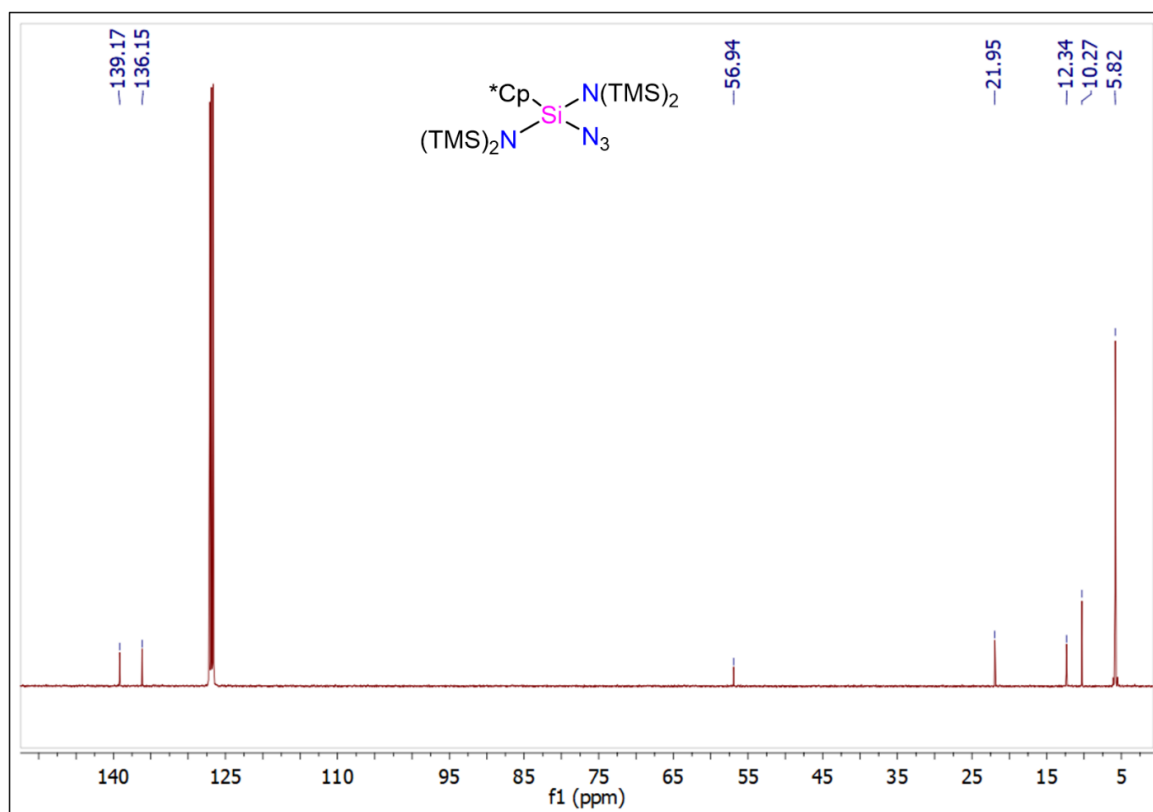


Figure 3.A.27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3.8** (100.613 MHz, C_6D_6 , 298 K)

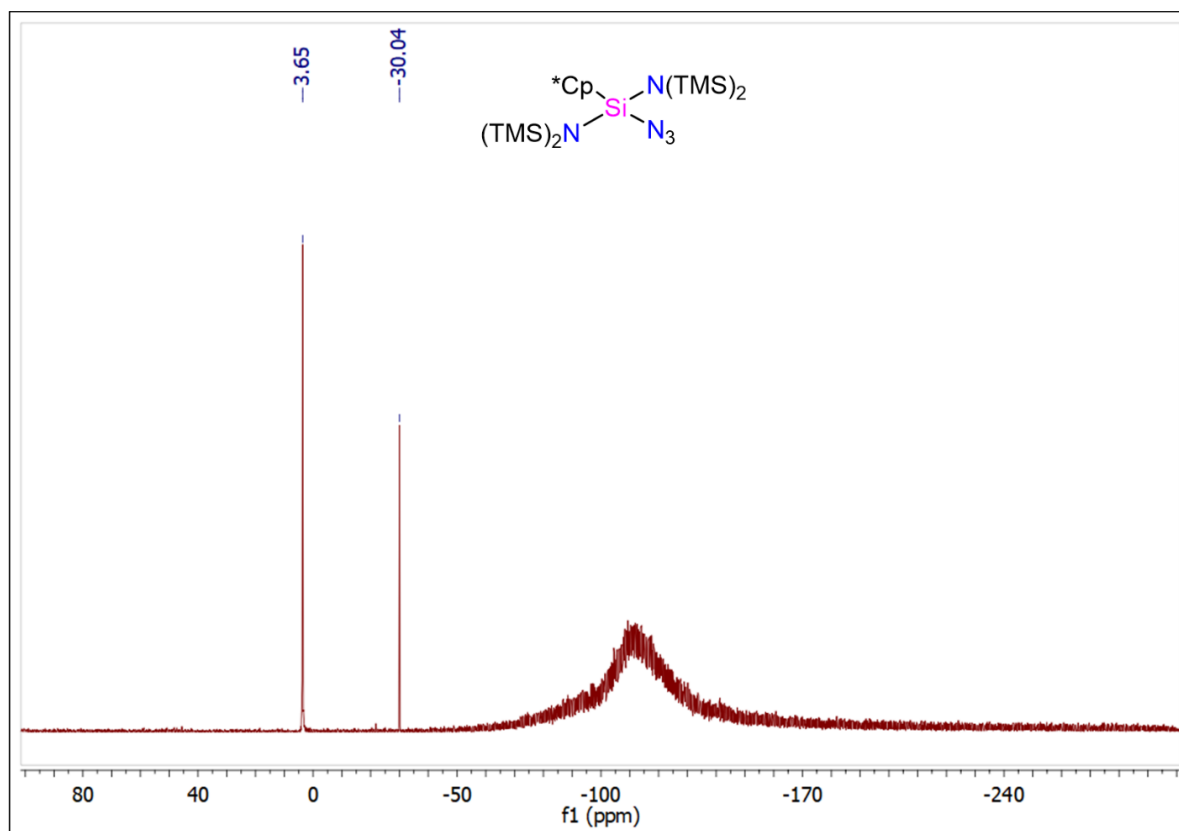


Figure 3.A.28. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3.8** (C_6D_6 , 79.49 MHz, 298 K)

4A.A.1 Crystallographic data for complexes 4A.5-4A.9.

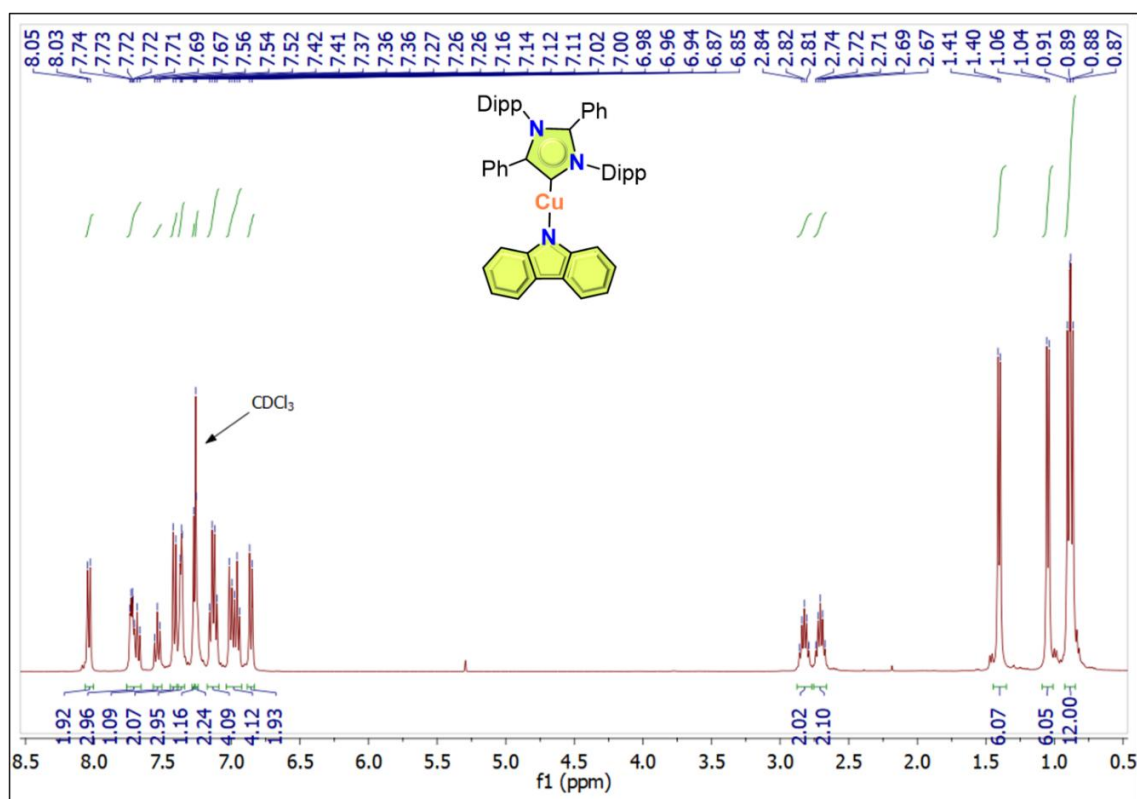
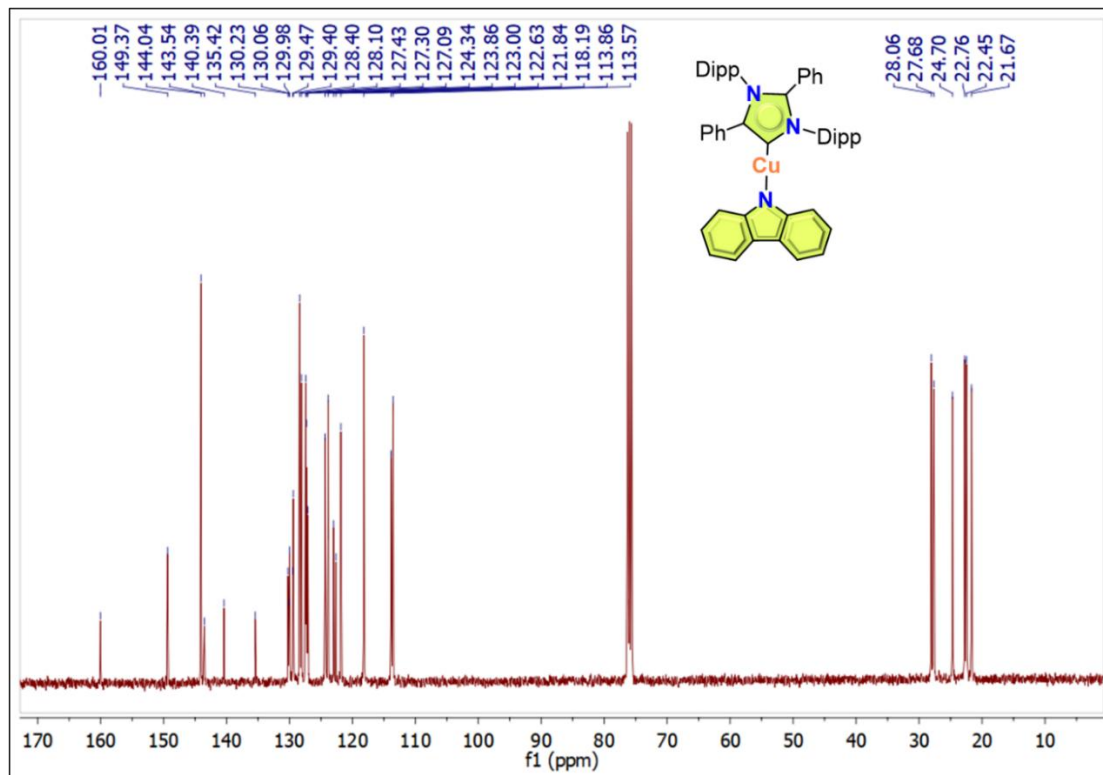
Table 4A.A.1: Crystallographic data for complexes 4A.5-4A.7

Identification code	4A.5	4A.6	4A.7
Empirical formula	C ₅₁ H ₅₂ CuN ₃	C ₅₁ H ₅₂ AgN ₃	C ₅₁ H ₅₂ AuN ₃
Formula weight	770.49	814.82	903.92
Temperature/K	150.15	150.15	150.15
Crystal system	Triclinic	Triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	11.4045(15)	11.2881(13)	11.427(7)
<i>b</i> /Å	13.4322(16)	13.3351(14)	13.502(9)
<i>c</i> /Å	15.483(2)	15.8465(18)	15.800(9)
α /°	108.918(3)	108.529(3)	108.469(18)
β /°	105.824(3)	107.001(3)	106.600(17)
γ /°	100.838(3)	99.858(3)	100.262(19)
Volume/Å ³	2056.7(5)	2069.1(4)	2117(2)
<i>Z</i>	2	2	2
ρ_{calc} /cm ³	1.244	1.308	1.418
μ /mm ⁻¹	0.570	0.526	3.513
<i>F</i> (000)	816.0	852.0	916.0
Crystal size/mm ³	0.215 × 0.182 × 0.158	0.211 × 0.193 × 0.158	0.429 × 0.085 × 0.08
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.896 to 50	3.94 to 50.236	3.894 to 50.24
Index ranges	-13 ≤ <i>h</i> ≤ 13, -15 ≤ <i>k</i> ≤ 15, -18 ≤ <i>l</i> ≤ 18	-13 ≤ <i>h</i> ≤ 13, -15 ≤ <i>k</i> ≤ 15, -18 ≤ <i>l</i> ≤ 18	-13 ≤ <i>h</i> ≤ 13, -16 ≤ <i>k</i> ≤ 16, -18 ≤ <i>l</i> ≤ 18
Reflections collected	36992	72931	47576
Independent reflections	7240 [<i>R</i> _{int} = 0.1194, <i>R</i> _{sigma} = 0.0975]	7368 [<i>R</i> _{int} = 0.0871, <i>R</i> _{sigma} = 0.0456]	7486 [<i>R</i> _{int} = 0.1711, <i>R</i> _{sigma} = 0.1105]
Data/restraints/parameters	7240/0/504	7368/0/504	7486/24/504
Goodness-of-fit on <i>F</i> ²	1.062	1.025	1.035
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0580, <i>wR</i> ₂ = 0.0958	<i>R</i> ₁ = 0.0345, <i>wR</i> ₂ = 0.0626	<i>R</i> ₁ = 0.0728, <i>wR</i> ₂ = 0.1516
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1047, <i>wR</i> ₂ = 0.1116	<i>R</i> ₁ = 0.0496, <i>wR</i> ₂ = 0.0671	<i>R</i> ₁ = 0.1114, <i>wR</i> ₂ = 0.1729
Largest diff. peak/hole / e Å ⁻³	0.40/-0.53	0.45/-0.56	3.36/-2.00

Table 4A.A.2: Crystallographic data for complexes **4A.8-4A.9**

Identification code	4A.8	4A.9
Empirical formula	C _{69.5} H ₇₇ CuN ₃	C ₇₃ H ₈₄ AgN ₃
Formula weight	1017.88	1111.30
Temperature/K	150.15	273.15
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	20.275(3)	20.556(6)
<i>b</i> /Å	23.540(3)	23.402(6)
<i>c</i> /Å	11.8842(16)	11.728(3)
α /°	90	90
β /°	90	90
γ /°	90	90
Volume/Å ³	5671.9(13)	5642(3)
<i>Z</i>	4	4
ρ_{calc} /cm ³	1.192	1.308
μ /mm ⁻¹	0.867	0.405
<i>F</i> (000)	2176.0	2360.0
Crystal size/mm ³	0.211 × 0.188 × 0.152	0.543 × 0.251 × 0.239
Radiation	CuK α (λ = 1.54178)	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.752 to 153.526	2.636 to 50
Index ranges	-25 ≤ <i>h</i> ≤ 25, -29 ≤ <i>k</i> ≤ 29, -14 ≤ <i>l</i> ≤ 14	-24 ≤ <i>h</i> ≤ 24, -27 ≤ <i>k</i> ≤ 27, -13 ≤ <i>l</i> ≤ 13
Reflections collected	139265	159362
Independent reflections	11569 [<i>R</i> _{int} = 0.1096, <i>R</i> _{sigma} = 0.0443]	9925 [<i>R</i> _{int} = 0.1563, <i>R</i> _{sigma} = 0.0818]
Data/restraints/parameters	11569/957/818	9925/409/511
Goodness-of-fit on <i>F</i> ²	1.990	1.069
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1662, <i>wR</i> ₂ = 0.4167	<i>R</i> ₁ = 0.1355, <i>wR</i> ₂ = 0.3250
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1750, <i>wR</i> ₂ = 0.4296	<i>R</i> ₁ = 0.1528, <i>wR</i> ₂ = 0.3393
Largest diff. peak/hole / e Å ⁻³	1.43/-0.72	2.39/-2.12
Flack Parameter	0.49(10)	0.37(11)

4A.A.2 NMR spectrum for 4A.5-4A.10.

Figure 4A.A.1. ¹H NMR spectrum of 4A.5 (CDCl₃, 400 MHz, 298 K)Figure 4A.A.2. ¹³C {¹H} NMR spectrum of 4A.5 (CDCl₃, 100.613 MHz, 298 K)

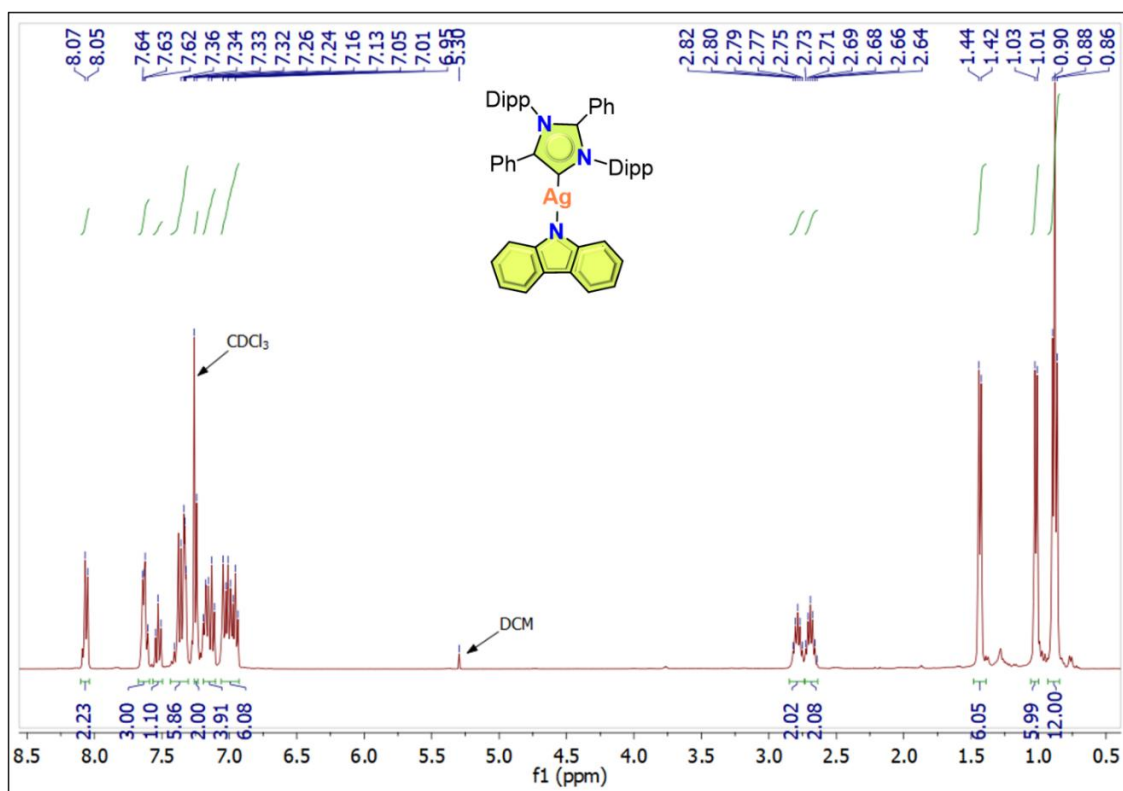


Figure 4A.A.3. ^1H NMR spectrum of 6 (CDCl_3 , 400 MHz, 298 K)

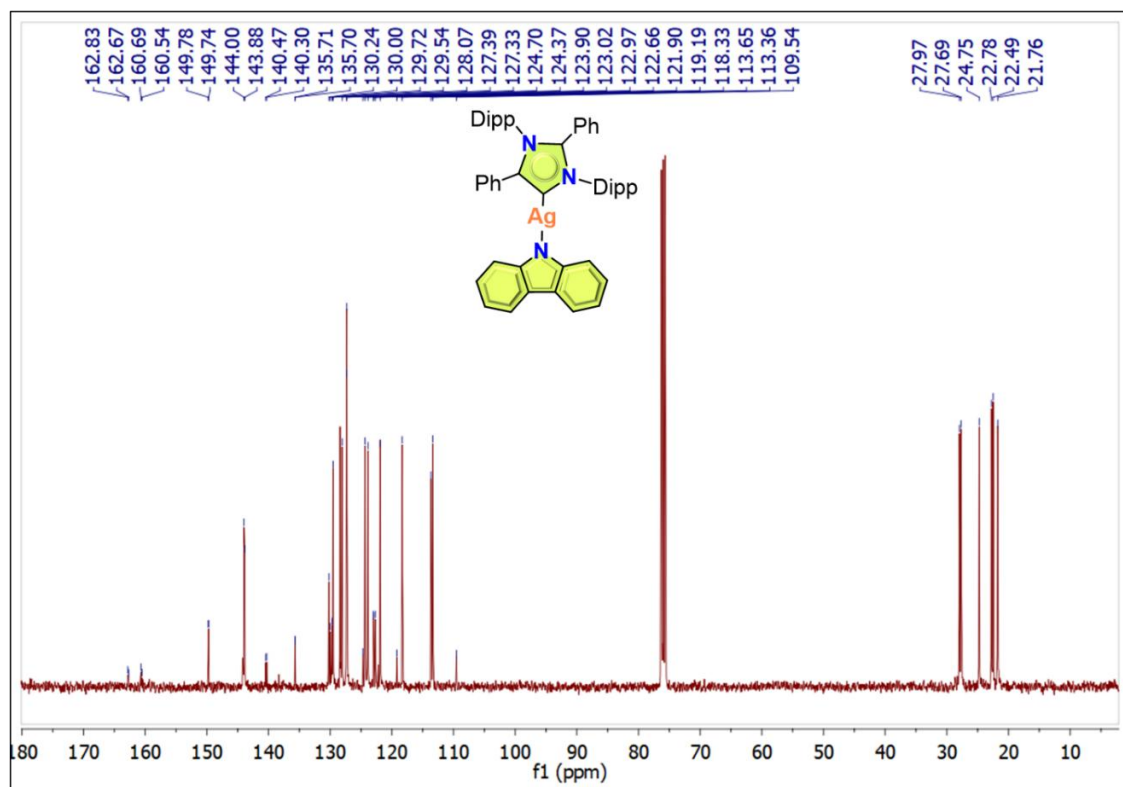


Figure 4A.A.4. ^{13}C $\{^1\text{H}\}$ NMR spectrum of 4A.6 (CDCl_3 , 100.613 MHz, 298 K)

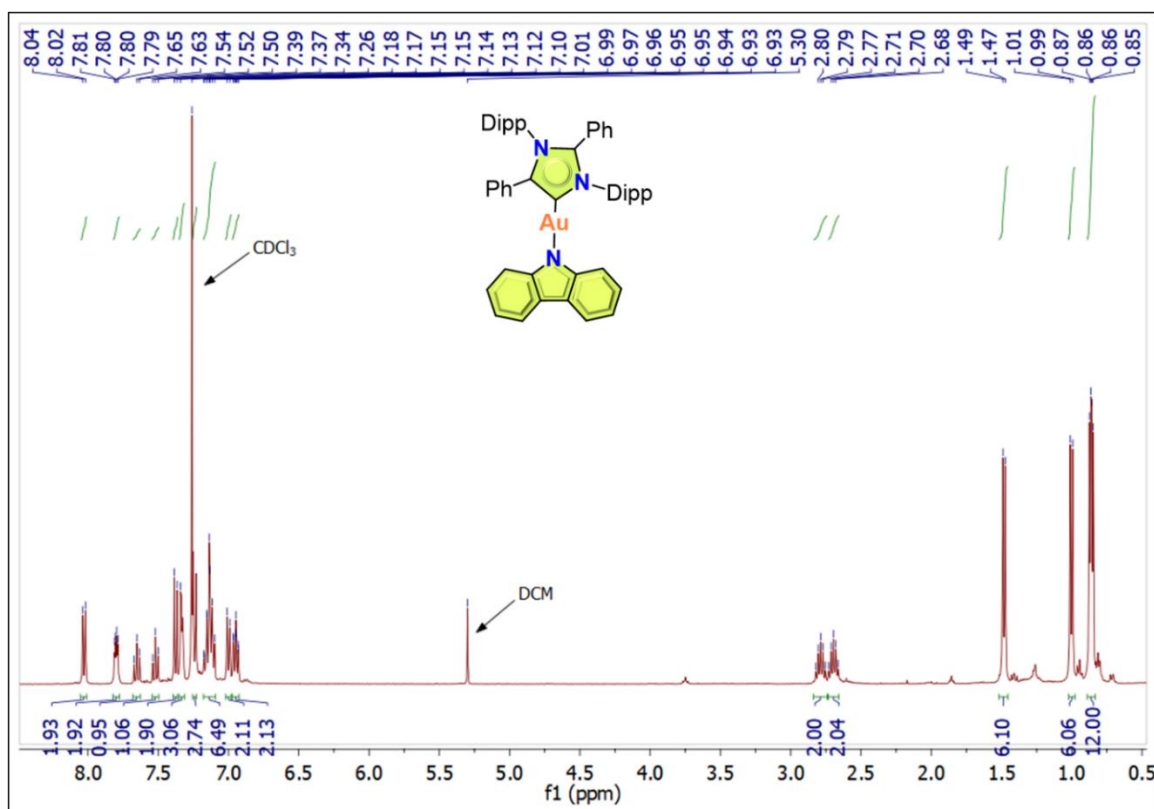


Figure 4A.A.5. ¹H NMR spectrum of 4A.7 (CDCl₃, 400 MHz, 298 K)

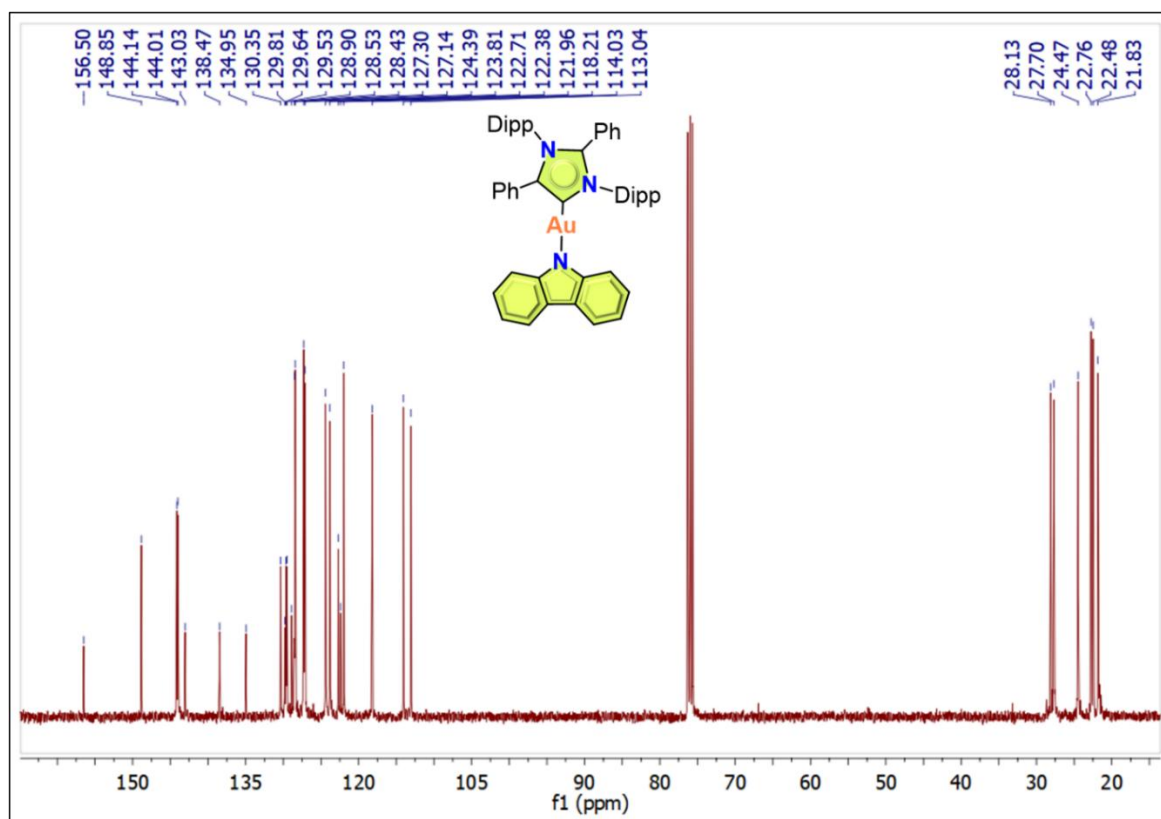


Figure 4A.A.6. ¹³C{¹H} NMR spectrum of 4A.7 (CDCl₃, 100.613 MHz, 298 K)

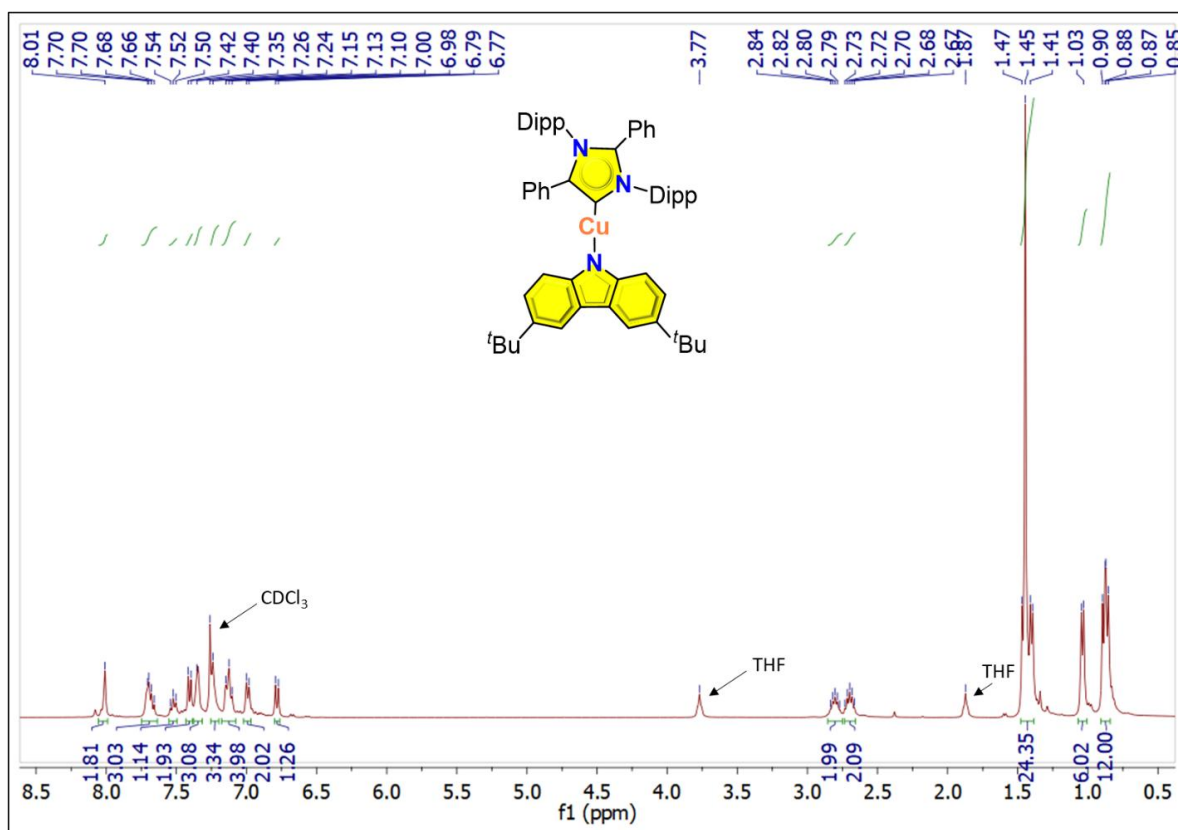


Figure 4A.A.7. ¹H NMR spectrum of **4A.8** (CDCl₃, 400 MHz, 298 K)

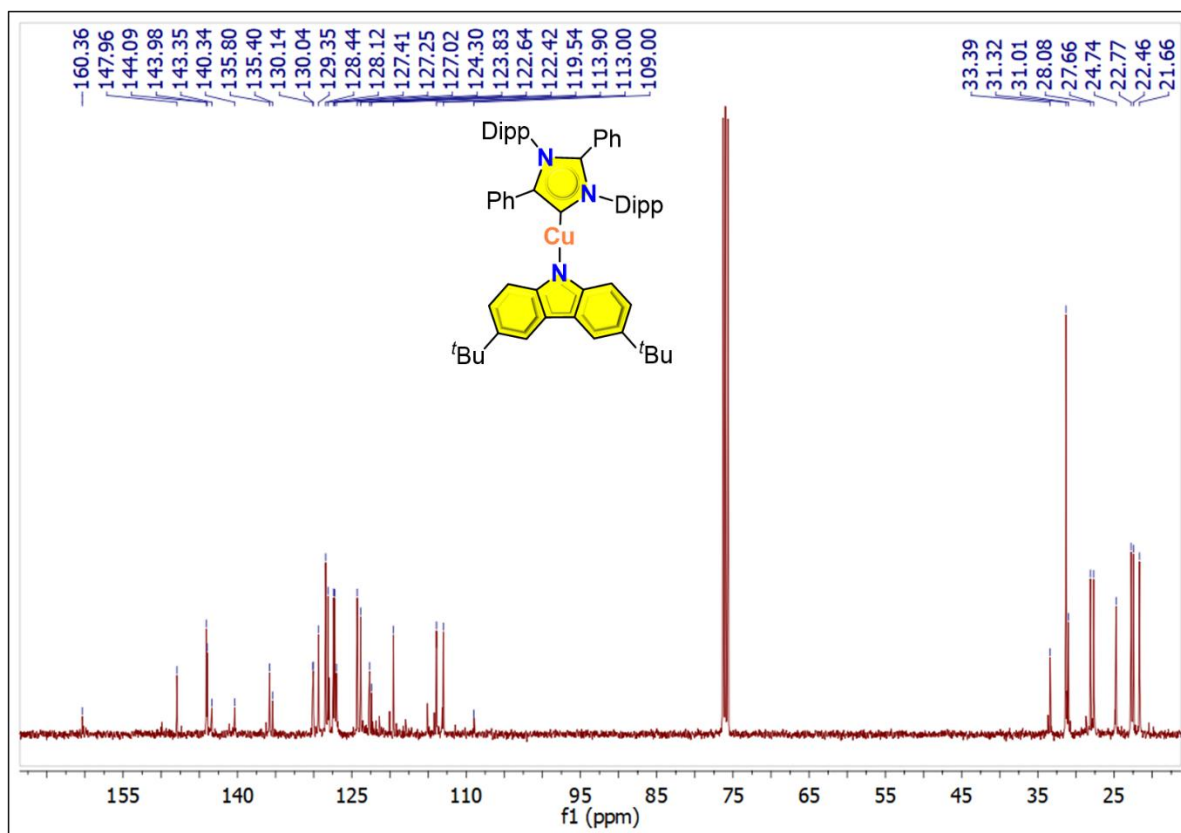


Figure 4A.A.8. ¹³C{¹H} NMR spectrum of **4A.8** (CDCl₃, 400 MHz, 298 K)

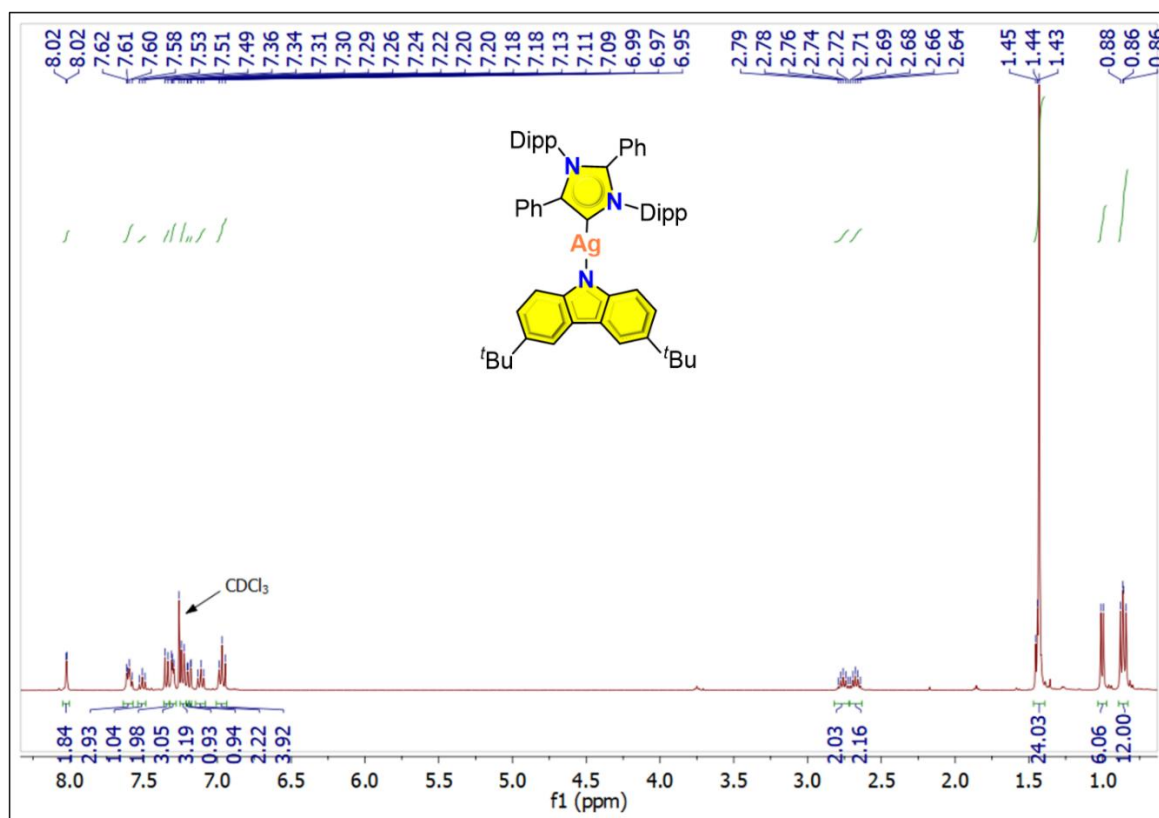


Figure 4A.A.9. ¹H NMR spectrum of **4A.9** (CDCl₃, 400 MHz, 298 K)

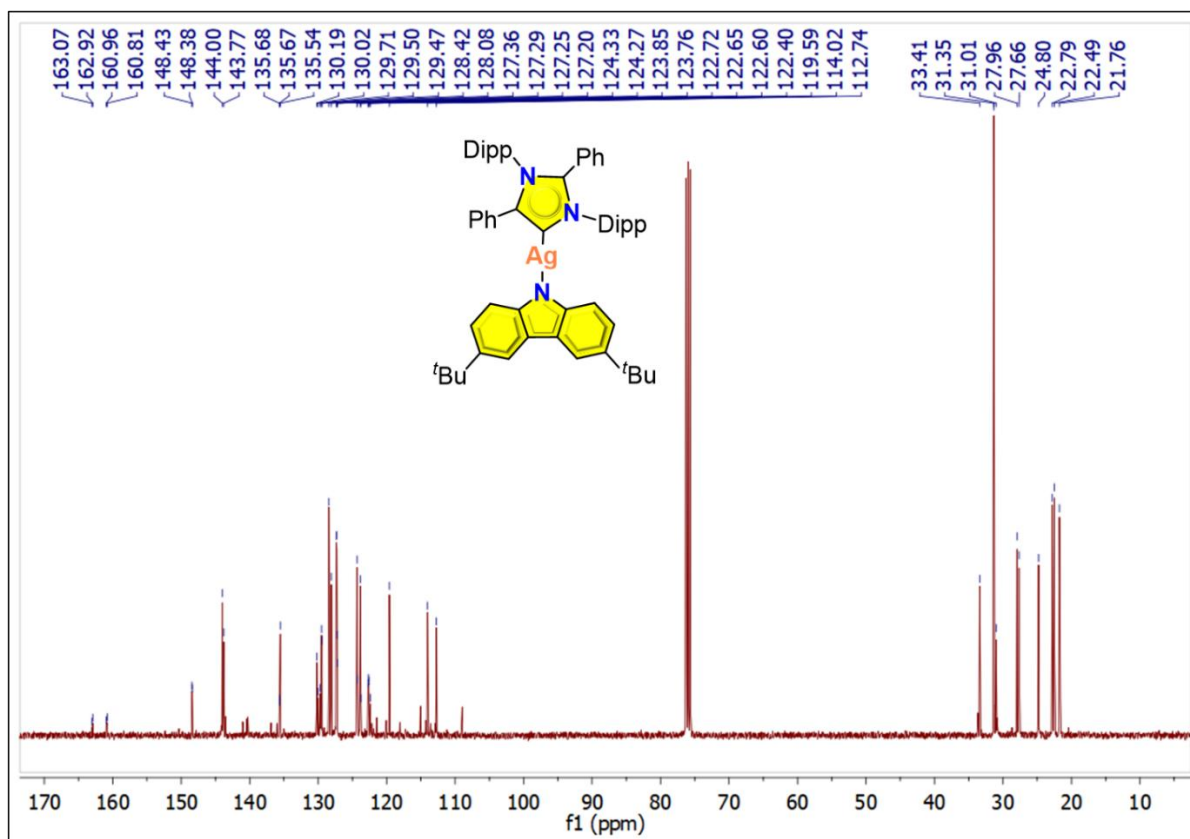


Figure 4A.A.10. ¹³C{¹H} NMR spectrum of **4A.9** (CDCl₃, 100.613 MHz, 298 K)

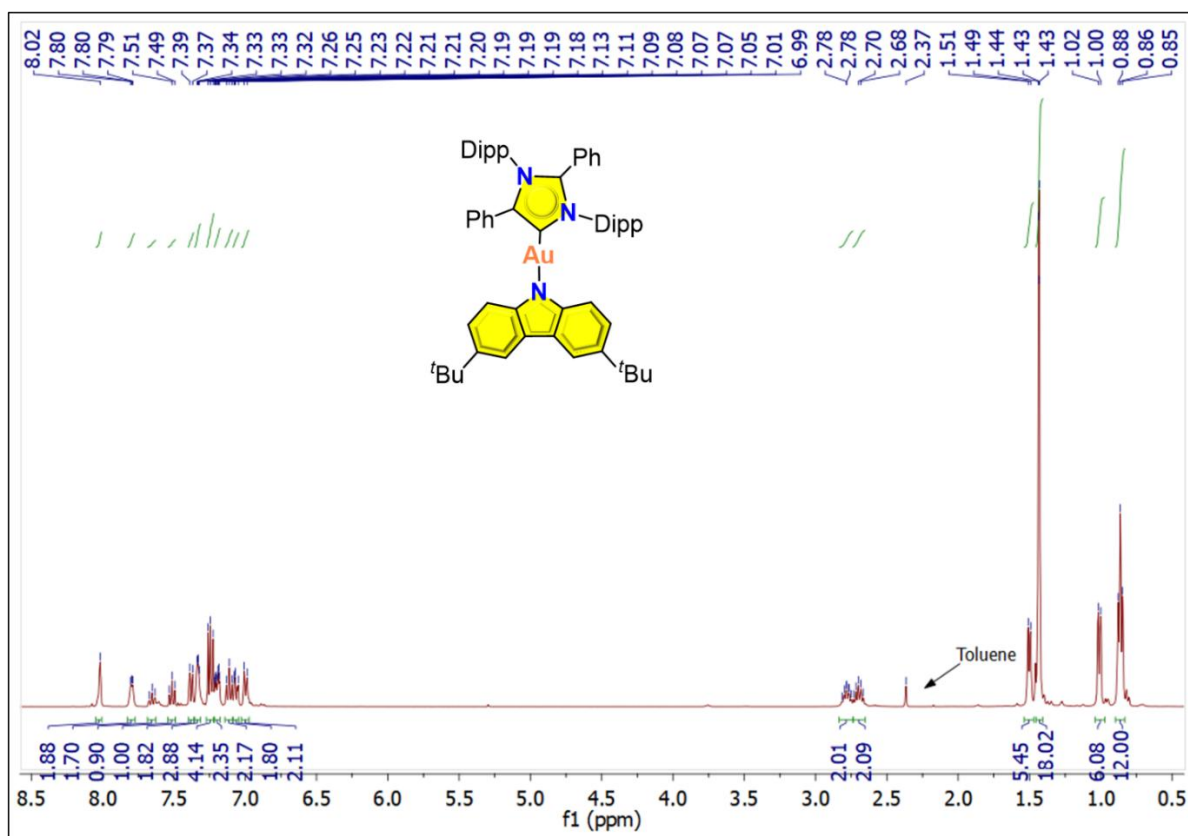


Figure 4A.A.11. ¹H NMR spectrum of 4A.10 (CDCl₃, 400 MHz, 298 K)

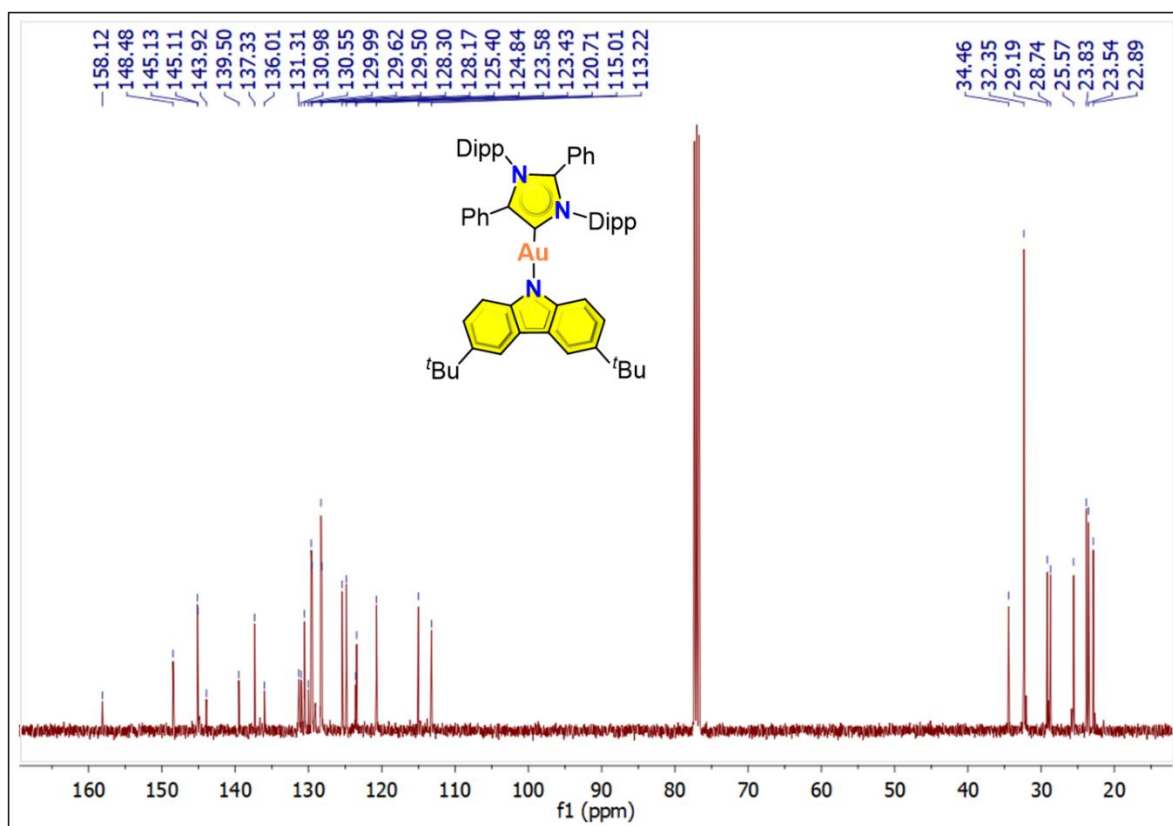


Figure 4A.A.12. ¹³C{¹H} NMR spectrum of 4A.10 (CDCl₃, 100.613 MHz, 298 K)

4A.A.3. Crystal structure of Complex 4A.10

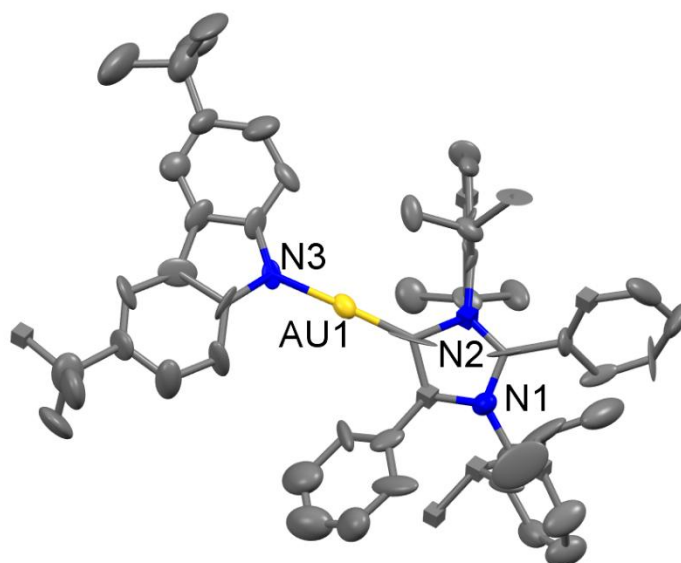


Figure 4A.A.13. Molecular structure of **4A.10** with anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms are not shown for clarity. Space group P212121 Cell parameter $a = 11.5227(13)$, $b = 21.202(3)$, $c = 21.874(3)$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, Volume 5343.89.

4A.A.4. α and β planes of complex 4A.5-4A.10.

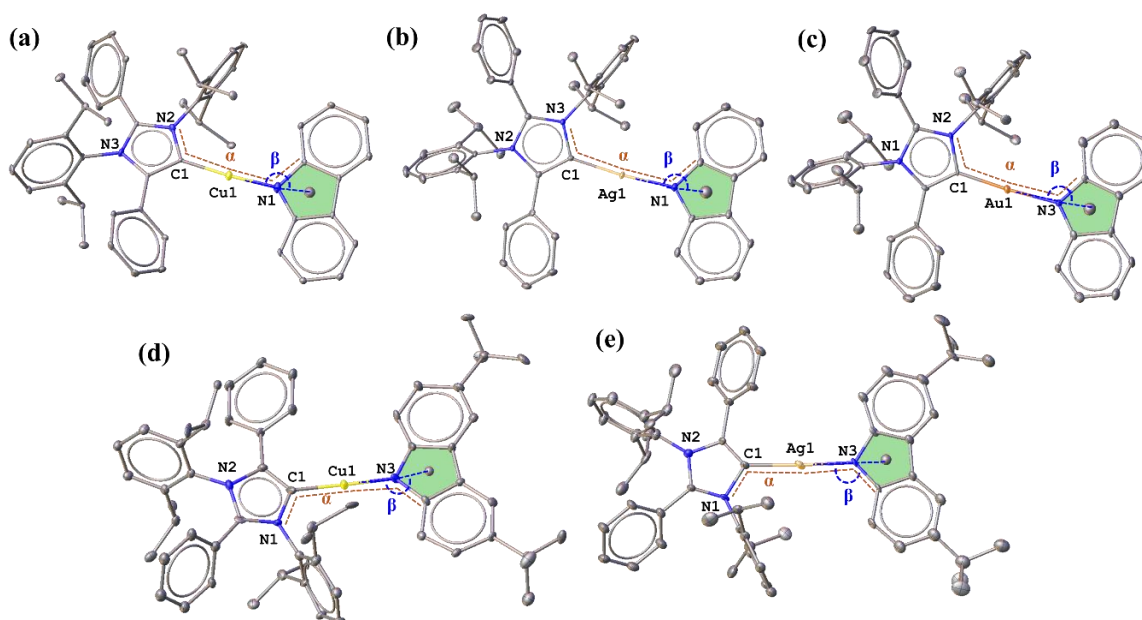


Figure 4A.A.14. α and β planes of complex 4A.5-4A.10.

4A.A.5. Thermogravimetric Analyses of Complexes 4A.2-4A.10

The thermogravimetric analyses (TGA) were performed using the PerkinElmer STA-6000 thermogravimetric analyser at a heating rate of 10 °C/min in a nitrogen atmosphere. Figure S38 contains TGA data for complexes 4A.2-4A.10.

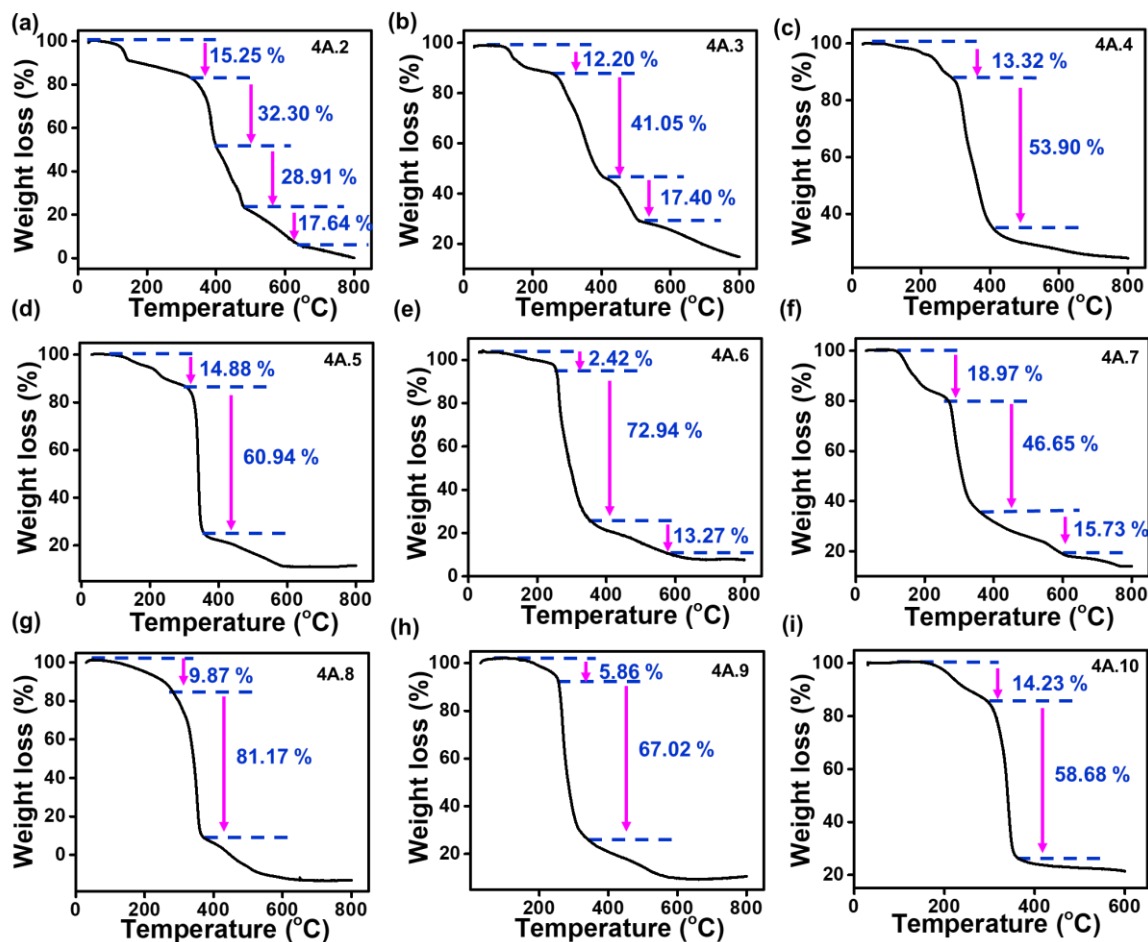


Figure 4A.A.15. TGA plots for complex (a) 4A.2, (b) 4A.3, (c) 4A.4, (d) 4A.5, (e) 4A.6, (f) 4A.7, (g) 4A.8, (h) 4A.9 and (i) 4A.10.

4A.A.6. Photophysical studies.

4A.A.6.1. Instrumentation and methods

Steady-state solution-based absorption spectra were recorded on a UV-2600 UV spectrophotometer (Shimadzu). Steady-state emission spectra and time-gated emission spectra of all the samples in solution and solid state were recorded using a Fluorolog-3 (HORIBA) instrument. Absolute quantum yields were measured in the Fluoromax-4C (HORIBA)

instrument by using an integrating sphere. For complex **4A.5**, temperature-dependent PL and PL decay profiles were recorded in an Edinburgh FLS980 Instrument coupled with a cryostat. The solid samples were placed between two sapphire plates and fixed in a gold-coated copper sample holder. The sample holder is fixed in a closed-cycle He cryostat (Advanced Research Systems) attached with a Lake Shore 335 temperature controller. For a three-state TADF model, under fast thermalisation conditions, the experimentally observed decay time or lifetime is found to be an average of the singlet and triplet states' lifetimes. The experimentally observed lifetime is a function of temperature owing to the Boltzmann thermal distribution of the population between singlet and triplet states. This experimentally observed temperature-dependent lifetime is denoted by $\tau(T)$, τ_{Av} (Av denotes average), and τ_{obs} (obs denotes observed). In our work, we have denoted it as τ_{obs} . For **4A.2-4A.10**, steady-state PL spectra were recorded on a JASCO FP-8500 spectrofluorometer instrument. The lifetime and low-temperature PL were measured in an Edinburgh FLS1000 photoluminescence spectrometer, attached with an Optistat DN cryostat. The temperature was controlled using a Mercury iTC temperature controller (Oxford Instruments). The sample was excited using a xenon lamp, and emission was collected from 320 to 800 nm.

4A.A.6.2. Absorption spectrum in the solution and solid phase

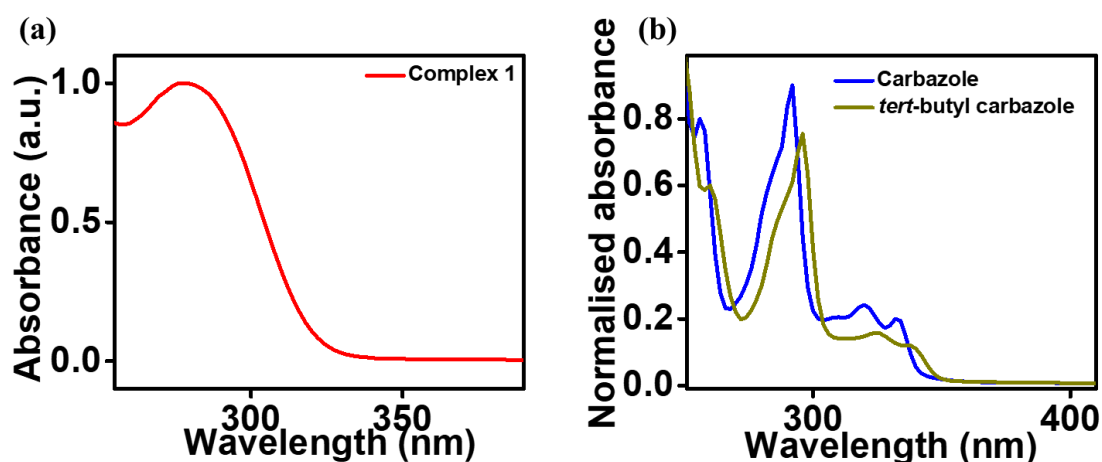


Figure 4A.A.16. (a) Absorption spectrum of complexes **4A.1** in DCM, (b) Absorption spectrum of carbazole and tert-butyl carbazole in DCM.

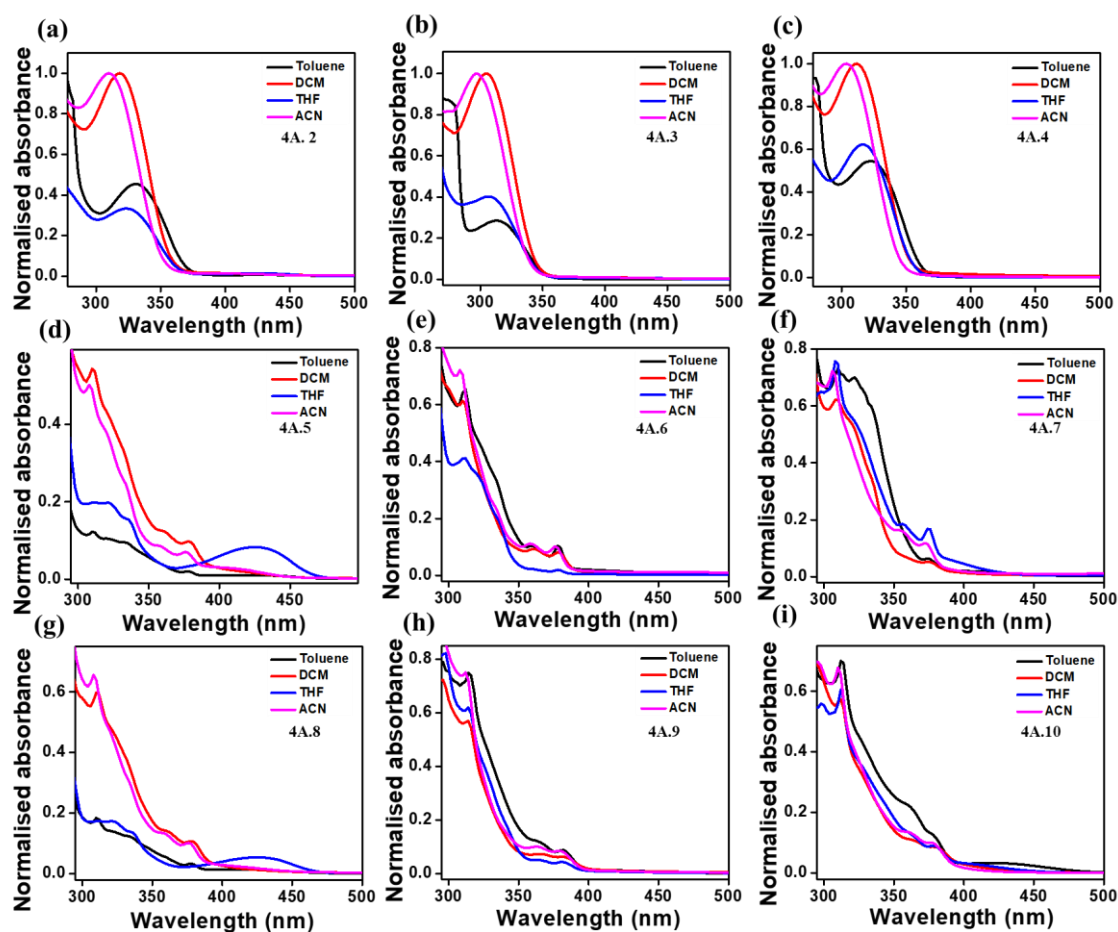


Figure 4A.A.17. The absorption spectra of complexes **4A.2-4A.10** (solvent polarities).

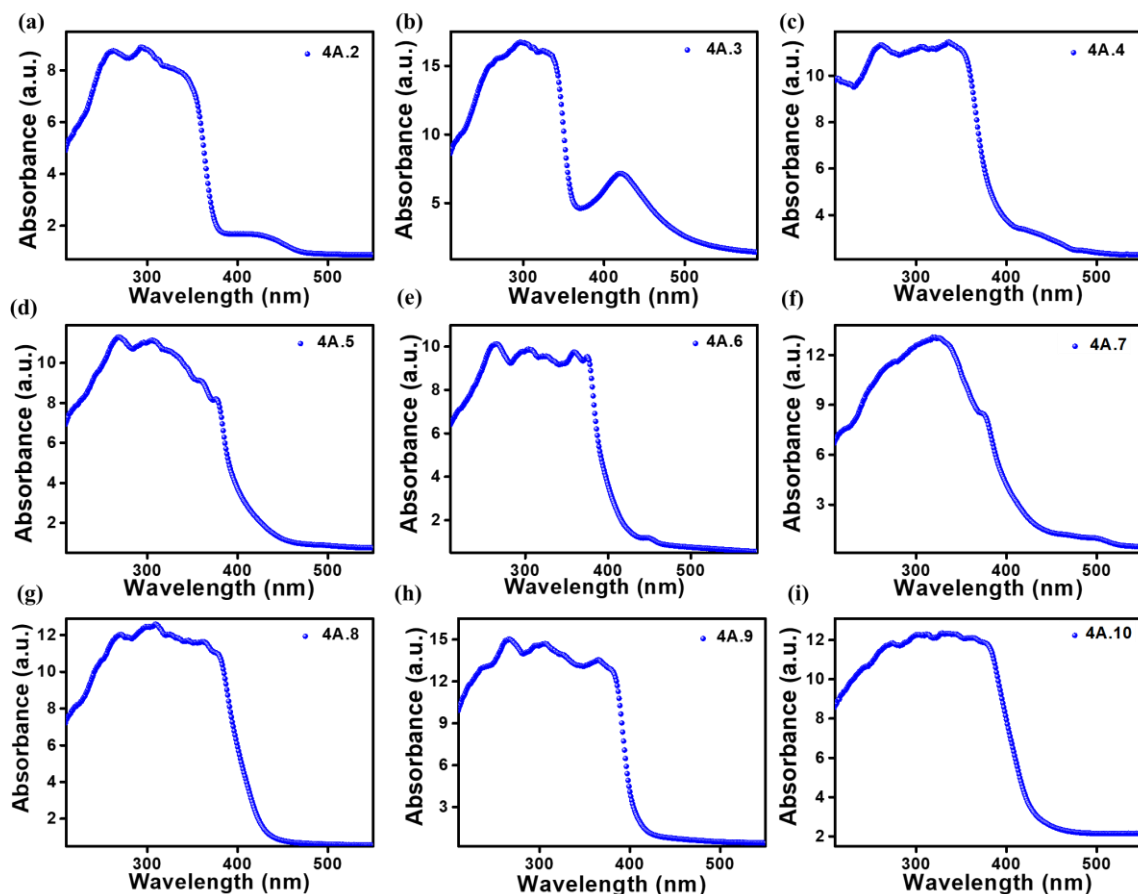


Figure 4A.A.18. The absorption spectra of complexes 4A.2-4A.10 in the solid state.

4A.A.5.3. Emission spectrum in the solution phase

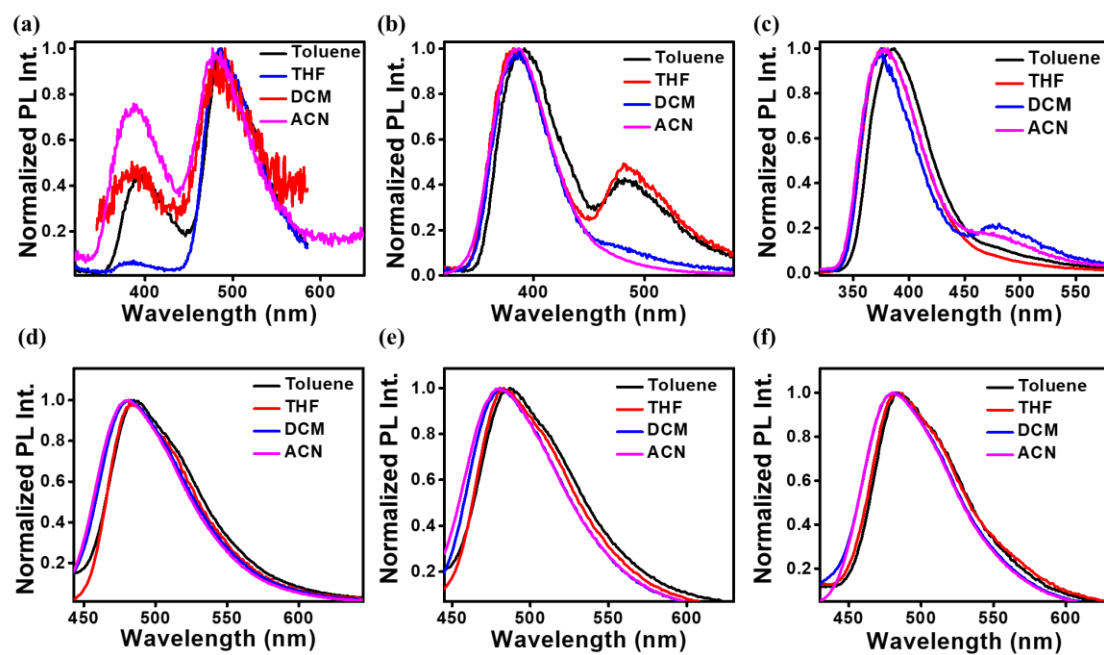


Figure 4A.A.19. The emission spectra of complex **4A.2-4A.4** in solvents of different polarity at 300 nm and 375 nm excitation wavelengths. (a) Complex **4A.2** ($\lambda_{\text{exc.}}$ 300 nm), (b) Complex **4A.3** ($\lambda_{\text{exc.}}$ 300 nm), (c) Complex **4A.4** ($\lambda_{\text{exc.}}$ 300 nm), (d) Complex **4A.2** ($\lambda_{\text{exc.}}$ 375 nm), (e) Complex **4A.3** ($\lambda_{\text{exc.}}$ 375 nm), and (f) Complex **4A.4** ($\lambda_{\text{exc.}}$ 375 nm).

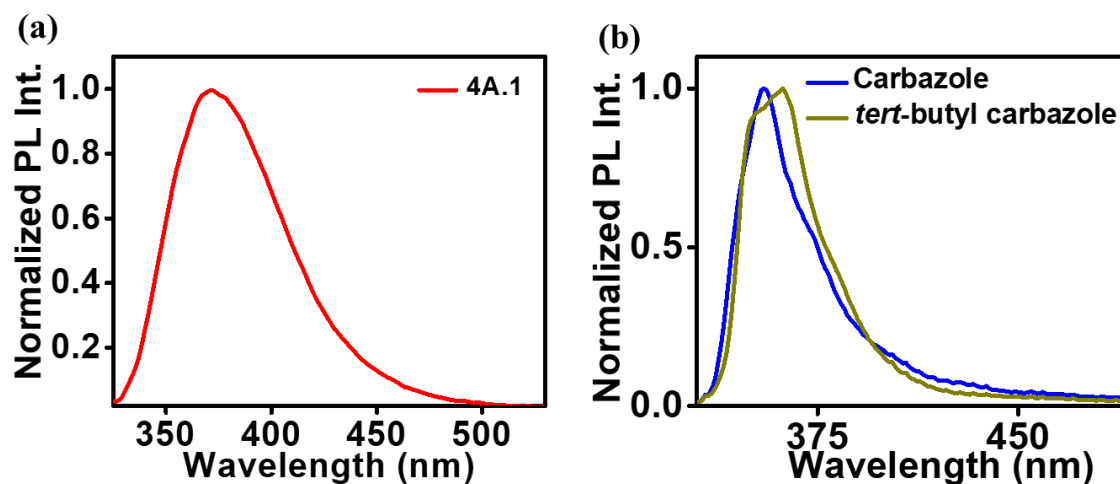


Figure 4A.A.20. The emission spectra of complex **4A.1**, carbazole, and *tert*-butyl carbazole in DCM at 300 nm excitation wavelength. (a) Complex **4A.1** ($\lambda_{\text{exc.}}$ 300 nm), (b) Carbazole and *tert*-butyl carbazole ($\lambda_{\text{exc.}}$ 300 nm).

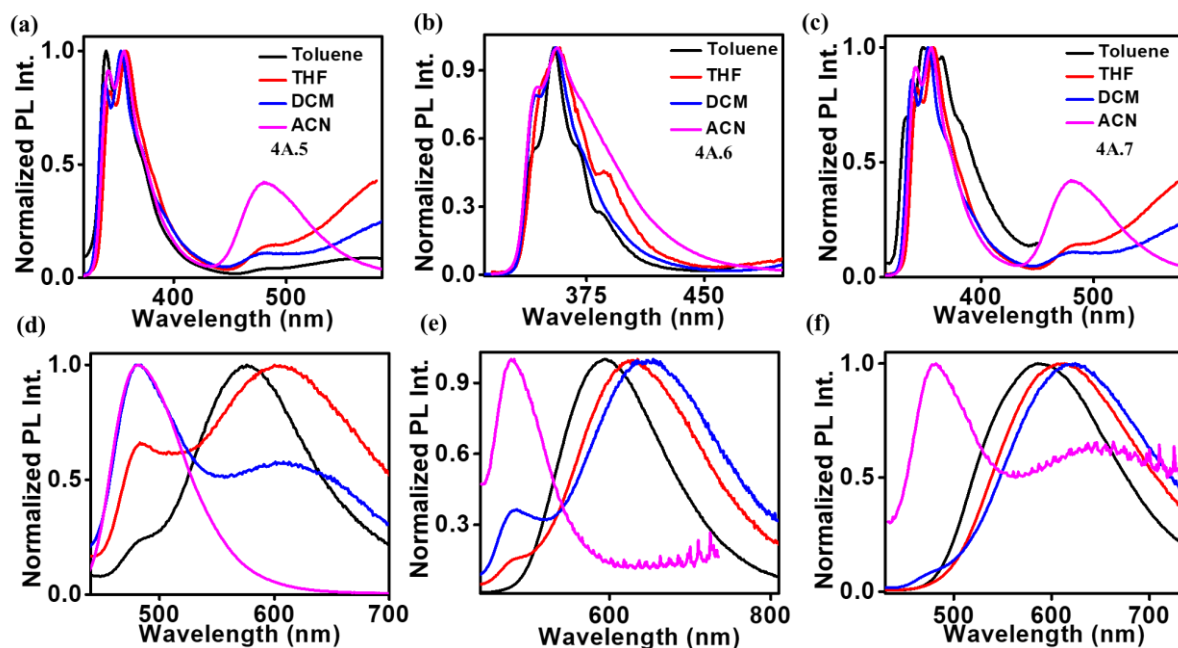


Figure 4A.A.21. The emission spectra of complex **4A.5-4A.7** in different solvents at 300 nm and 375 nm excitation wavelengths. (a) Complex **4A.5** ($\lambda_{\text{exc.}}$ 300 nm), (b) Complex **4A.6** ($\lambda_{\text{exc.}}$ 300 nm), (c) Complex **4A.7** ($\lambda_{\text{exc.}}$ 300 nm), (d) Complex **4A.5** ($\lambda_{\text{exc.}}$ 375 nm), (e) Complex **4A.6** ($\lambda_{\text{exc.}}$ 375 nm), and (f) Complex **4A.7** ($\lambda_{\text{exc.}}$ 375 nm).

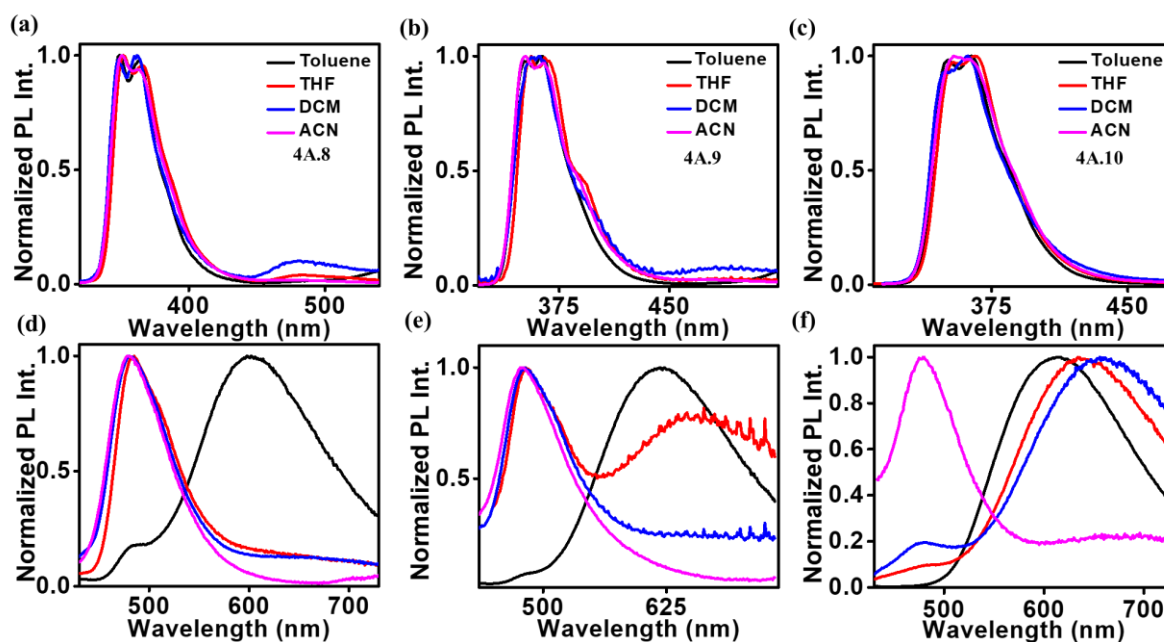


Figure 4A.A.22. The emission spectra of complex **4A.8-4A.10** in different solvents at 300 nm and 375 nm excitation wavelengths. (a) Complex **8** ($\lambda_{\text{exc.}}$ 300 nm), (b) Complex **4A.9** ($\lambda_{\text{exc.}}$ 300 nm), (c) Complex **4A.10** ($\lambda_{\text{exc.}}$ 300 nm), (d) Complex **4A.8** ($\lambda_{\text{exc.}}$ 375 nm), (e) Complex **4A.9** ($\lambda_{\text{exc.}}$ 375 nm), and (f) Complex **4A.10** ($\lambda_{\text{exc.}}$ 375 nm).

4A.A.6.4. Long and prompt lifetime of complexes in the solution phase.

4A.A.6.4a. Prompt lifetime

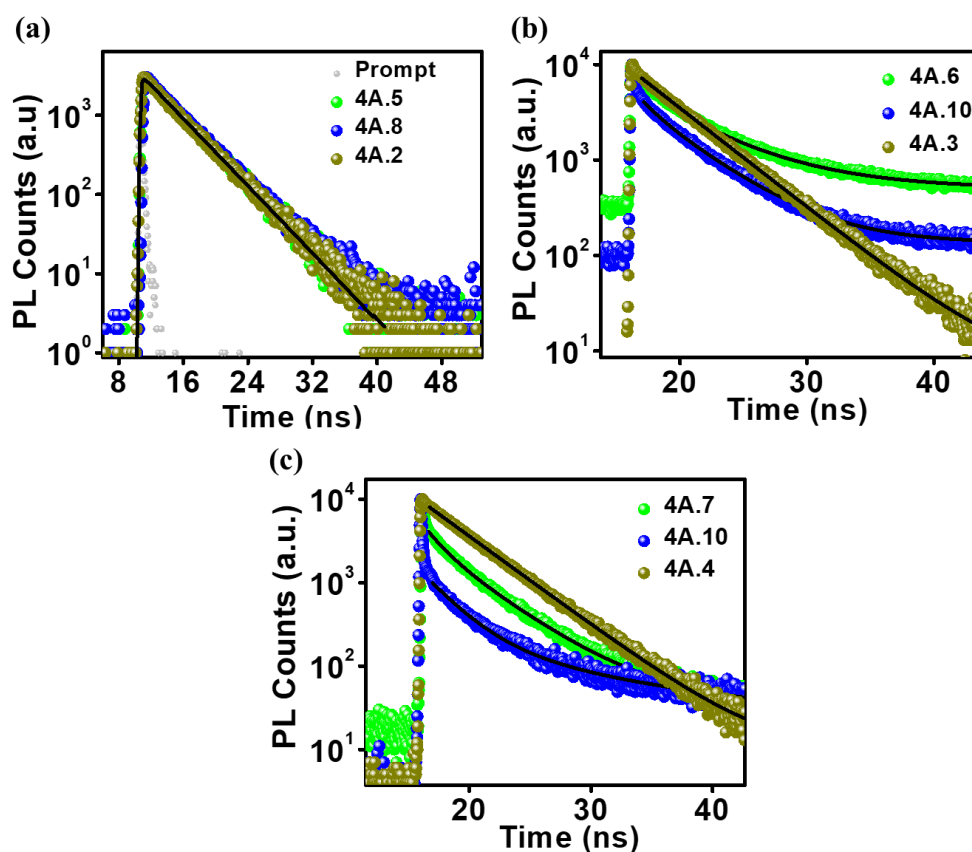


Figure 4A.A.23. Fluorescence lifetimes of 4A.2-4A.10 in toluene collected at 485 nm.

Table 4A.A.3: Prompt lifetimes of complexes at 485 nm.

Complex	Emission (nm)	Decay transient	Average lifetime
4A.2	485	4.1 ns	4.1 ns
4A.3	485	4.2 ns	4.2 ns
4A.4	485	4.1 ns	4.1 ns
4A.5	485	4.1 ns	4.1 ns
4A.6	485	6 ns (57%), 2.1 ns (43%)	4.3 ns
4A.7	485	4.3 ns (62%), 1.5 ns (38%)	3.2 ns
4A.8	485	4.1 ns	4.1 ns
4A.9	485	4.5 ns (80%), 1.4 ns (20%)	3.9 ns
4A.10	485	2.6 ns (81%), 11.2 ns (19%)	4.2 ns

4A.A.6.4b. Long lifetime

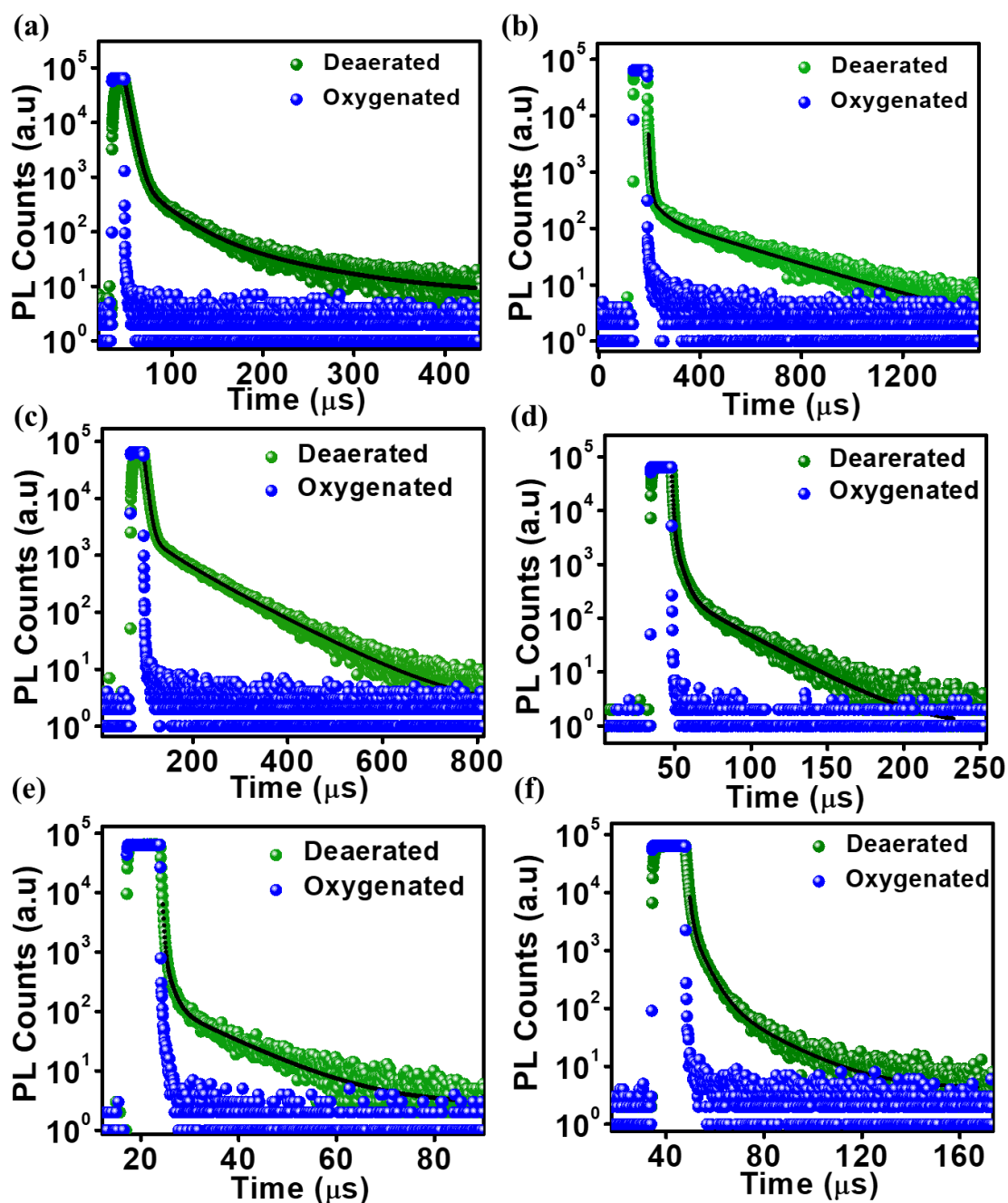


Figure 4A.A.24. TRPL data of complexes **4A.5-4A.10** in toluene solution under deaerated and oxygenated conditions at the CT emission maxima. (a) Complex **4A.5** at emission 575 nm. (b) complex **4A.6** at emission 593 nm. (c) Complex **4A.7** at emission 587 nm. (d) Complex **4A.8** at emission 600 nm. (e) Complex **4A.9** at emission 618 nm. (f) Complex **4A.10** at emission 612 nm.

4A.A.6.5. PMMA film emission, lifetime and quantum yield:

4A.A.6.5a. Emission Spectra

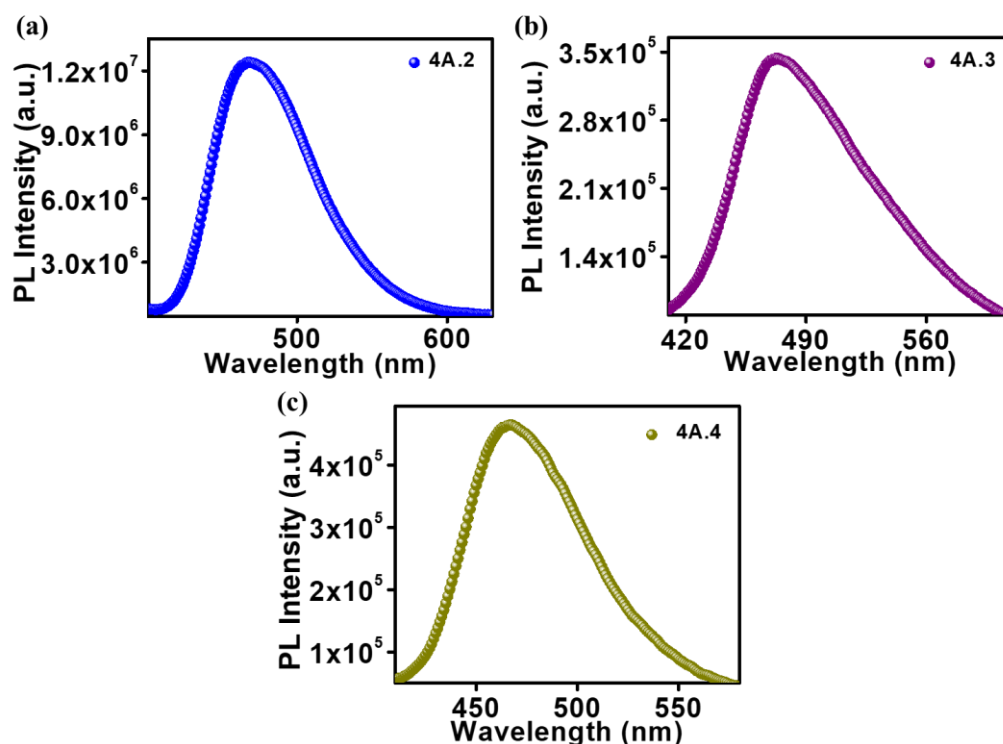


Figure 4A.A.25. The emission spectra of complex 4A.2-4A.4 in PMMA film at 375 nm excitation wavelength. (a) Complex 4A.2, (b) Complex 4A.3, (c) Complex 4A.4.

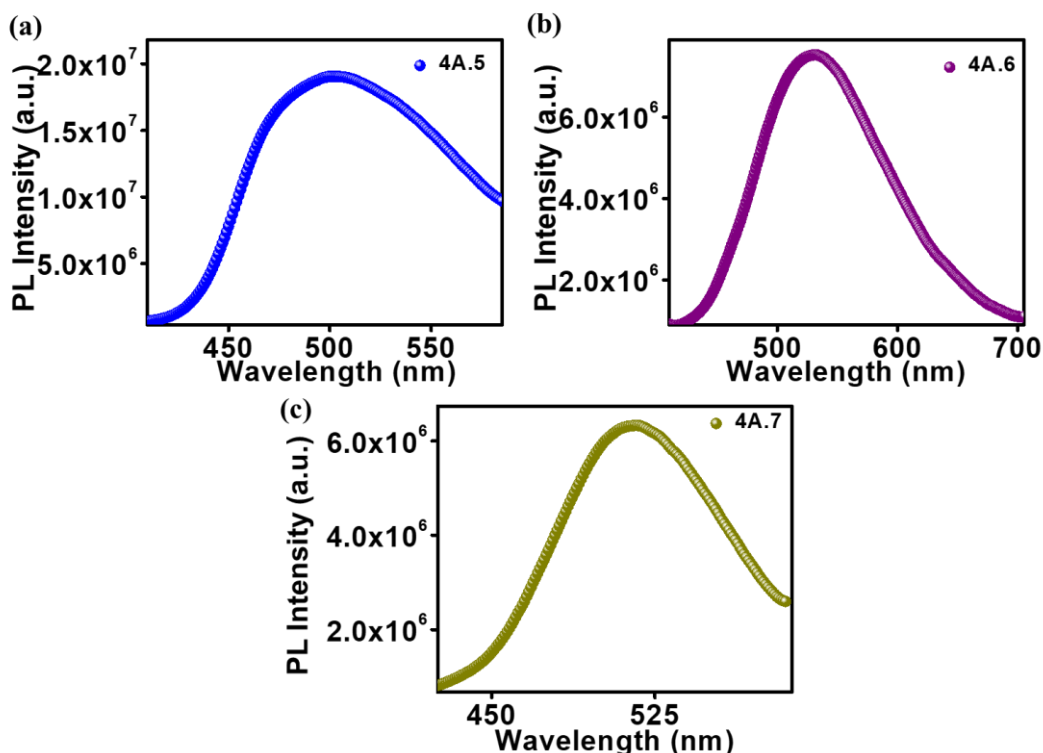


Figure 4A.A.26. The emission spectra of complex 4A.5-4A.7 in PMMA film at 375 nm excitation wavelength. (a) Complex 4A.5, (b) Complex 4A.6, (c) Complex 4A.7.

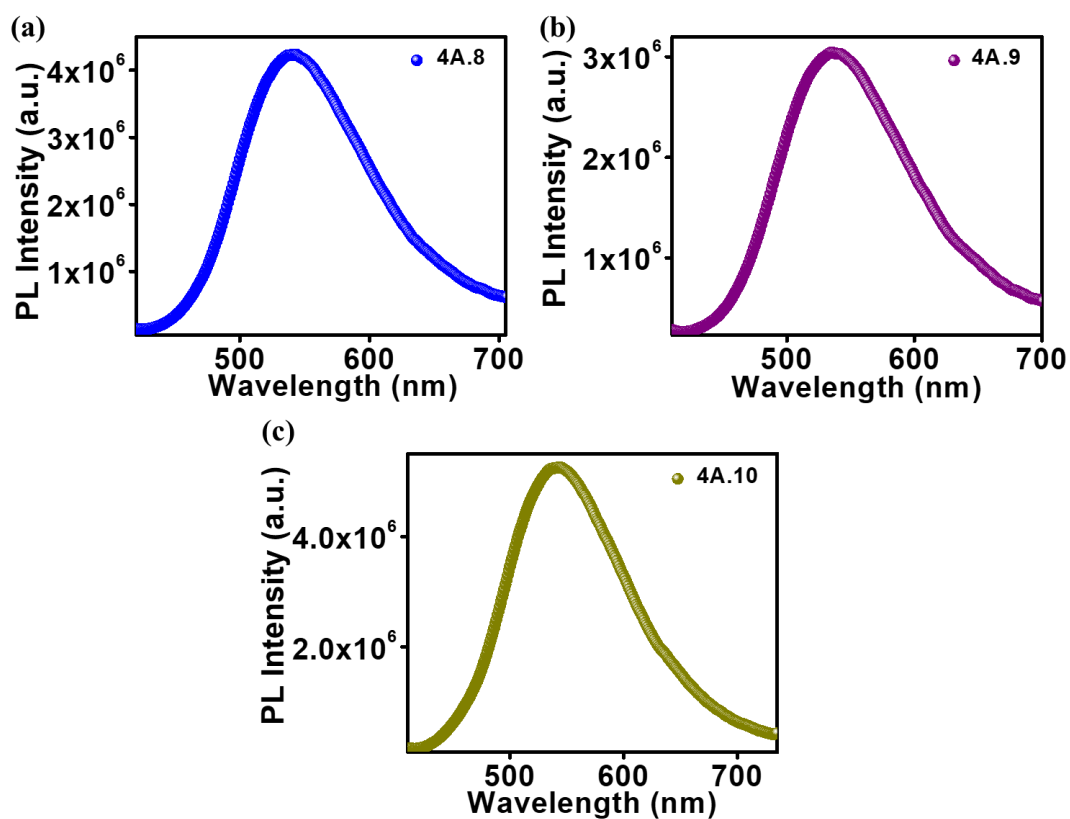


Figure 4A.A.27. The emission spectra of complex 4A.8-4A.10 in PMMA film at 375 nm excitation wavelength. (a) Complex 4A.8, (b) Complex 4A.9 (c) Complex 4A.10

4A.A.6.5b. Lifetime measurement

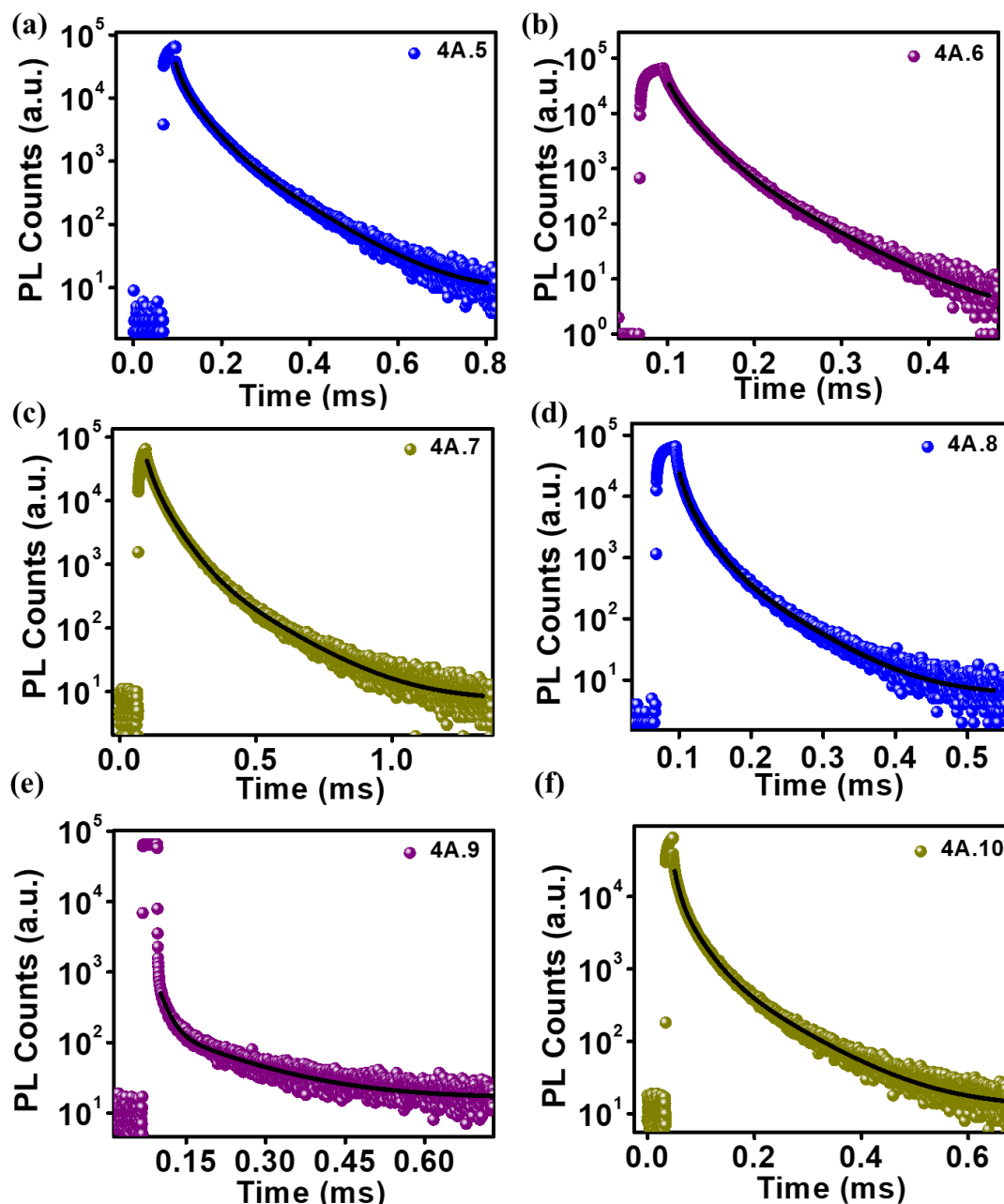


Figure 4A.A.28. Lifetime of complexes 4A.5-4A.10 in film in presence of PMMA host collected at their respective emission maxima. (a) Lifetime data of complex 4A.5 collected at emission 502 nm. (b) Lifetime data of complex 4A.6 collected at emission 531 nm. (c) Lifetime data of complex 4A.7 collected at emission 515 nm. (d) Lifetime data of complex 4A.8 collected at emission 541 nm. (e) Lifetime data of complex 4A.9 collected at emission 537 nm. (f) Lifetime data of complex 4A.10 collected at emission 541 nm.

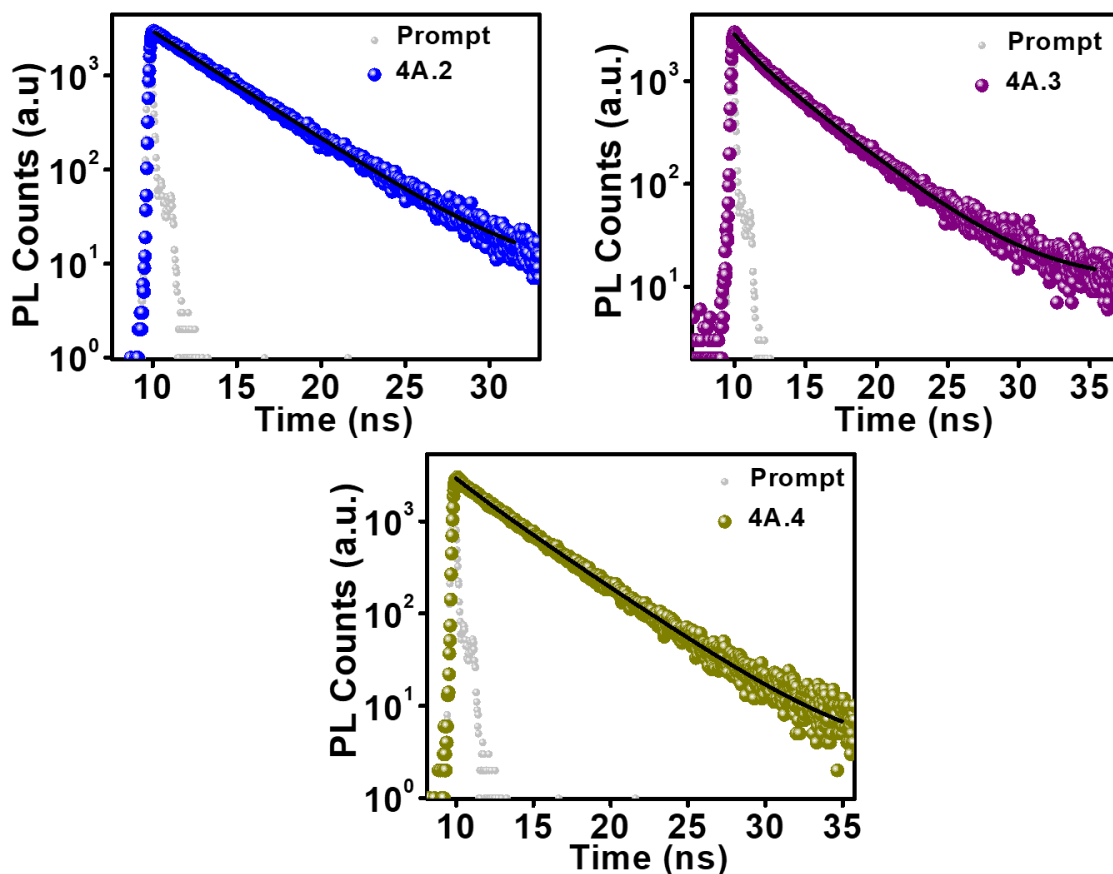


Figure 4A.A.29. Lifetime of complexes 4A.2-4A.4 in film in presence of PMMA host collected at the emission maxima.

Table 4A.A.4. Average lifetime and Decay transient of complex 5-10.

Complex	Emission (nm)	Decay transient	Average lifetime
4A.2	470	3.8 ns	3.8 ns
4A.3	473	4 ns (73%), 1.2 ns (27%)	3.2 ns
4A.4	468	3.9 ns (84%), 1.8 ns (16%)	3.6 ns
4A.5	502	38.8 μ s (48%), 10.6 μ s (41%), 0.1 ms (11%)	33.7 μ s
4A.6	531	22.7 μ s (56%), 8.6 μ s (37%), 53.8 μ s (7%)	19.7 μ s
4A.7	515	57.7 μ s (48%), 20.1 μ s (47%), 0.17 ms (4%)	44.5 μ s
4A.8	541	6.6 μ s (53%), 21.1 μ s (41%), 60 μ s (6%)	15.6 μ s
4A.9	537	16.8 μ s (74%), 0.14 ms (26%)	47.1 μ s
4A.10	541	8.1 μ s (56%), 30.1 μ s (38%), 97.6 μ s (7%)	22.2 μ s

4A.A.6.6. Steady state emission, lifetime and quantum yield:

4A.A.6.6a. Emission Spectra

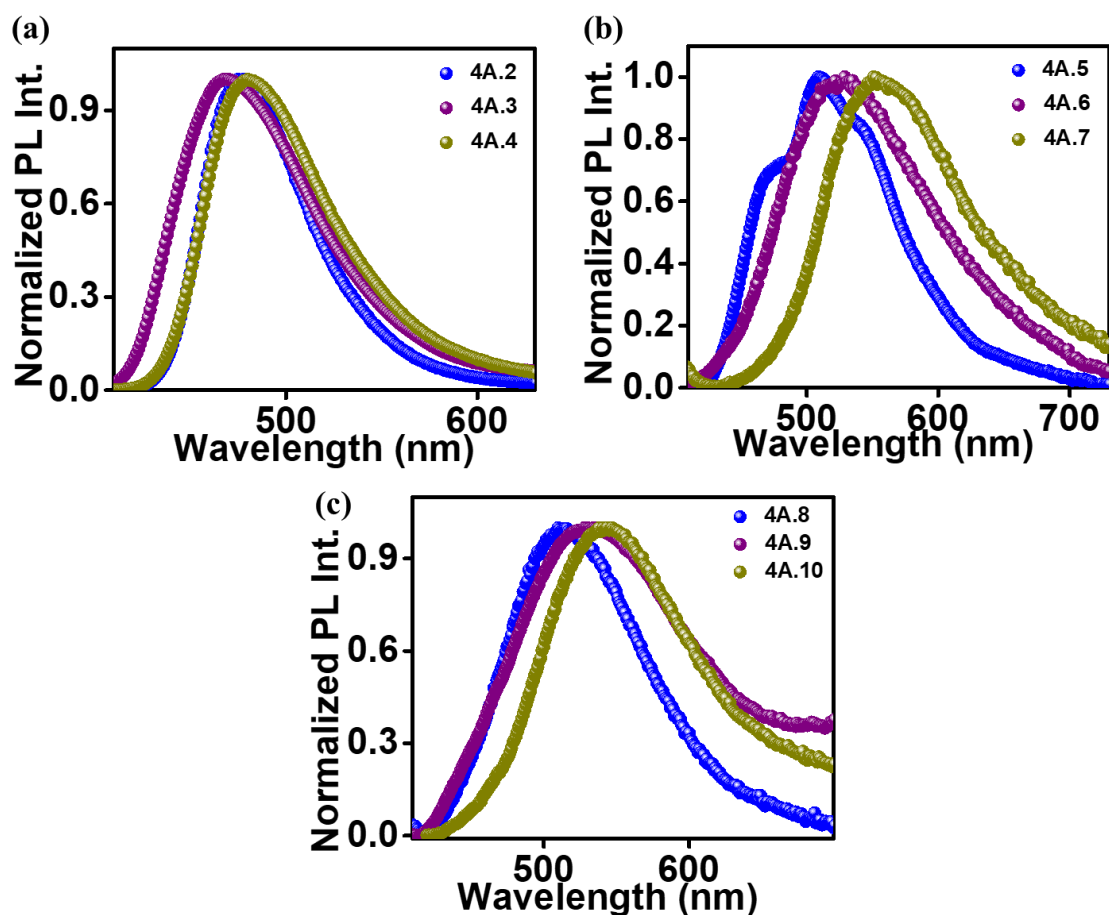


Figure 4A.A.30. The emission spectrum of complex 4A.2-4A.10 in the solid state at 375 nm excitation wavelength. (a) Complex 4A.2, 4A.3, and 4A.4 (b) Complex 4A.5, 4A.6, and 4A.7 (c) Complex 4A.8, 4A.9, and 4A.10.

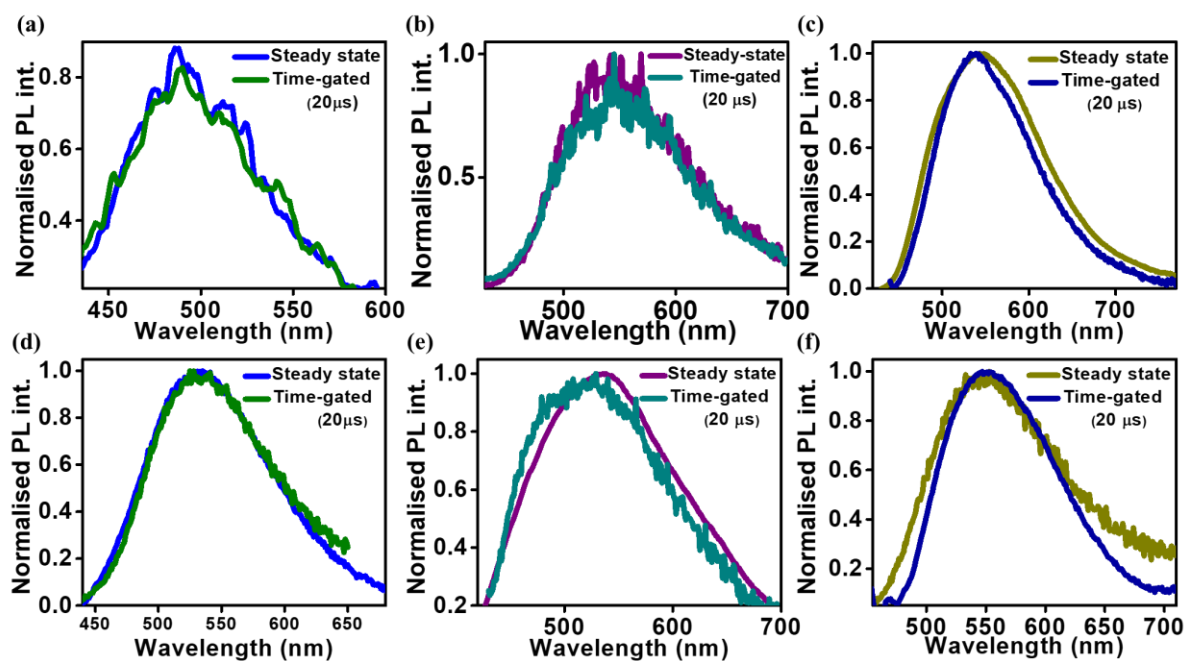


Figure 4A.A.31. The steady-state emission spectra and time-gated emission spectra (20 μ s detector-delay and 10ms sample window) of complex 4A.5-4A.10 in the solid state at 375 nm

excitation wavelength. (a) Complex 4A.5, (b) Complex 4A.6 (c) Complex 4A.7 (d) Complex 4A.8, (e) Complex 4A.9 (f) Complex 4A.10

4A.A.6.6b. Lifetime measurement

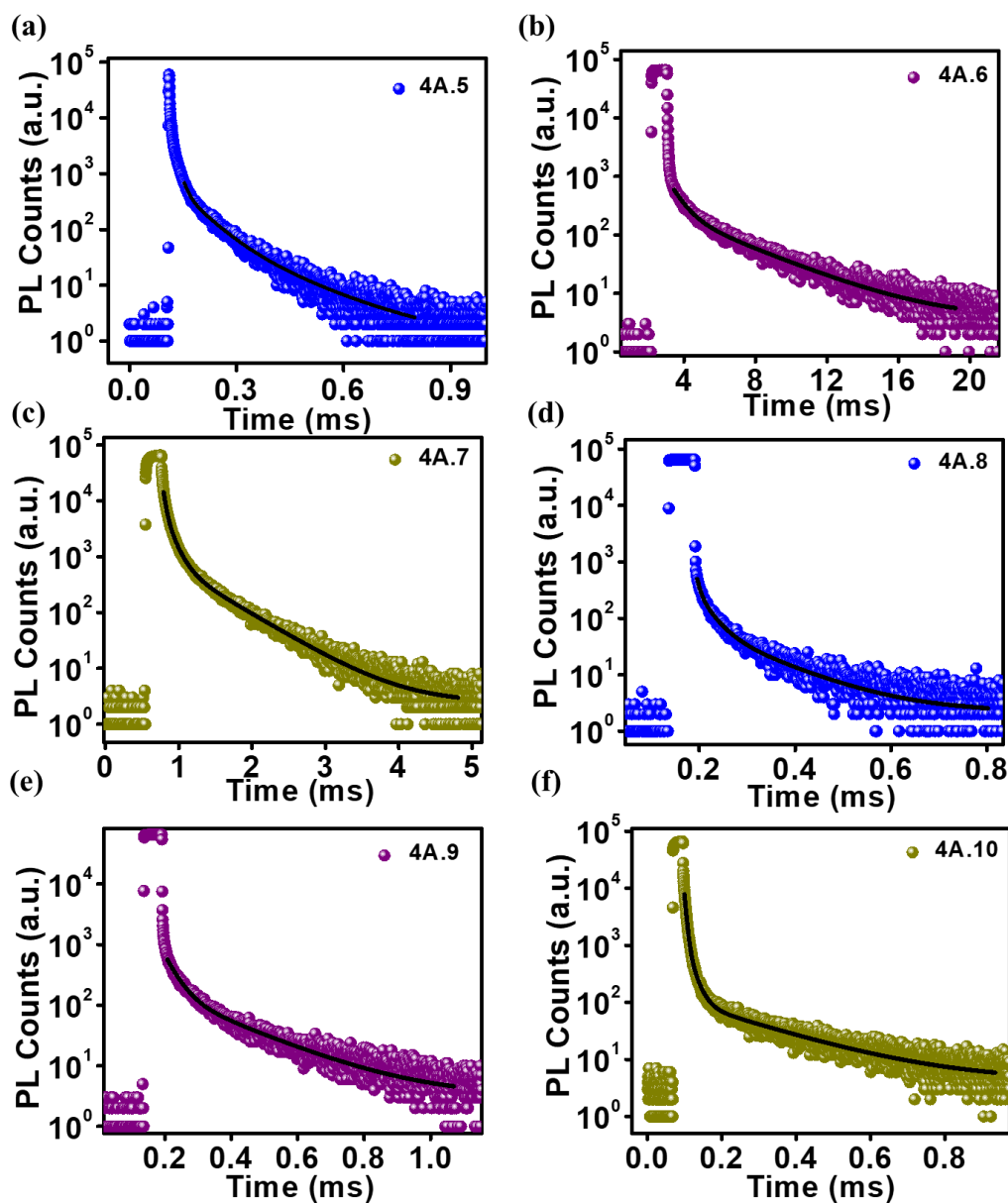


Figure 4A.A.32. Lifetime of complexes 4A.5-4A.10 in the solid state at the CT emission maxima.

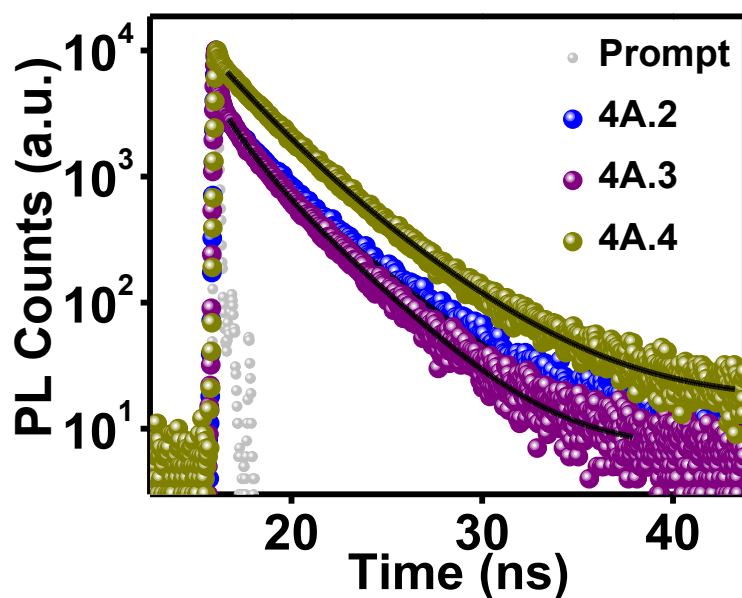


Figure 4A.A.33. The fluorescence lifetime of complexes 4A.2-4A.4 in the crystalline state collected at respective emission maxima.

Table 4A.A.5. Various contributing components in the lifetime data of complex 4A.5-4A.10.

Complex	Emission	Decay transient	Average lifetime
4A.2	478	3.5 ns (66%), 1.3 ns (34%)	2.7 ns
4A.3	468	3.1 ns (58%), 1.2 ns (42%)	2.3 ns
4A.4	478	2.2 ns (66%), 4.2 ns (34%)	2.9 ns
4A.5	485	12.3 μ s (99.96%), 62.4 μ s (0.03%), 0.12 ms (0.0037%)	12.4 μ s
4A.6	529	0.6 ms (64%), 3.4 ms (36%)	1.6 ms
4A.7	553	35.1 μ s (59%), 0.1 ms (36%), 0.5 ms (6%)	93.3 μ s
4A.8	510	12.6 μ s (49%), 21.4 μ s (48%), 48.6 μ s (3%)	17.9 μ s
4A.9	530	35 μ s (75%), 0.18 ms (25%)	0.7 ms
4A.10	541	5.3 μ s (85%), 18.8 μ s (14%), 0.2 ms (1%)	9.7 μ s

Table 4A.A.6. Various contributing components in the lifetime data of complex 4A.5.

Temperature (K)	τ_1 (μ s)	α_1 (%)	τ_2 (μ s)	α_2 (%)	τ_3 (μ s)	α_3 (%)	τ_{avg} (μ s)
300	12.3	99.96	62.4	0.03	168	0.0037	12.36
280	40.7	63.12	111.36	18.65	272.21	3.84	56.91
260	6.16	99.99	105.99	Neg.	324.63	-	6.17
240	23.66	94.31	150.12	3.01	50.4	2.68	41.52
220	12.72	99.99	166.83	Neg.	777.13	Neg.	12.81

200	133.14	71.73	929.71	28.27	-	-	704.541
180	128.68	75.25	1251.97	24.75	-	-	974.753
160	841.09	79.7	4282.72	20.3	-	-	3585.742
140	785.450	87.24	7753.56	12.76	-	-	6866.492
120	1167.52	84.96	10882.5	15.04	-	-	9423.867
100	2318.68	82.65	12633.5	17.35	-	-	10830

4A.A.6.7. Mechanochromism (mechano-inactive) of complexes 4A.2, 4A.3, and 4A.4.

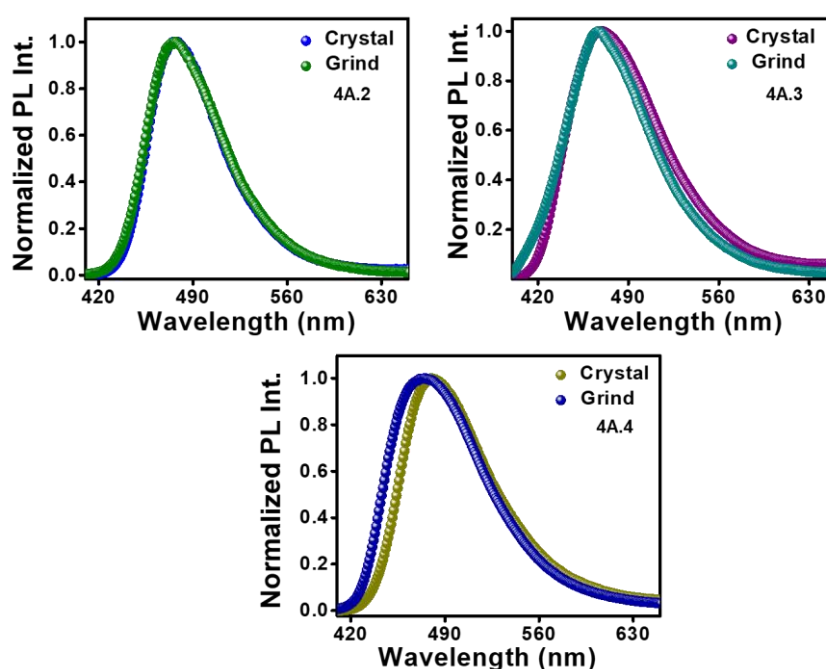


Figure 4A.A.34. Complex 4A.2-4A.4 is mechanochemically inactive.

4A.A.7. Powder X-Ray Diffraction (PXRD) patterns of complex 4A.5-4A.10.

The room-temperature powder X-ray diffraction (PXRD) measurements were performed using a BRUKER D8 Advance X-ray diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$).

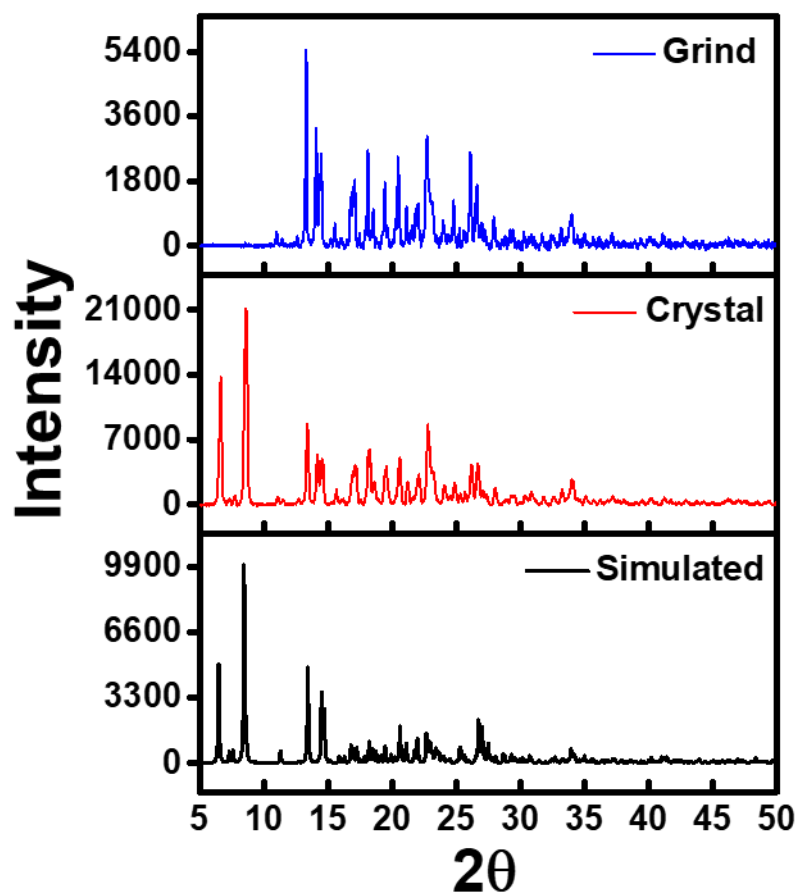


Figure 4A.A.35. Comparison between the experimentally obtained crystal and grinded PXRD pattern (measured at room temperature) with the simulated pattern from CIF of complex **4A.5**.

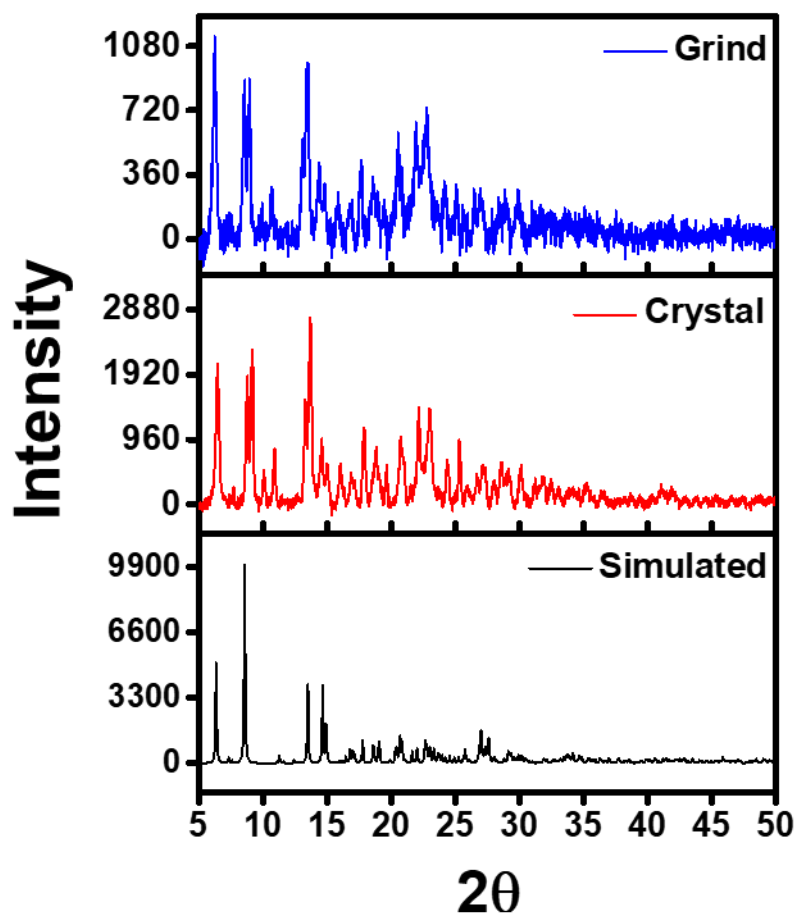


Figure 4A.A.36. Comparison between the experimentally obtained crystal and grinded PXRD pattern (measured at room temperature) with the simulated pattern from CIF of complex **4A.6**.

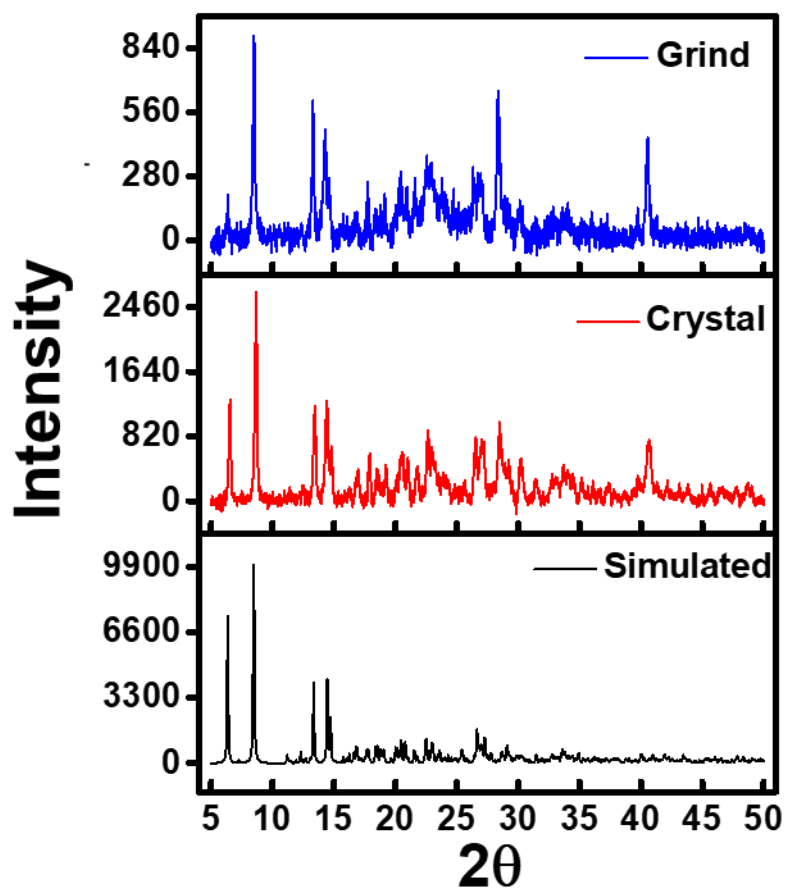


Figure 4A.A.37. Comparison between the experimentally obtained crystal and grinded PXRD pattern (measured at room temperature) with the simulated pattern from CIF of complex **4A.7**.

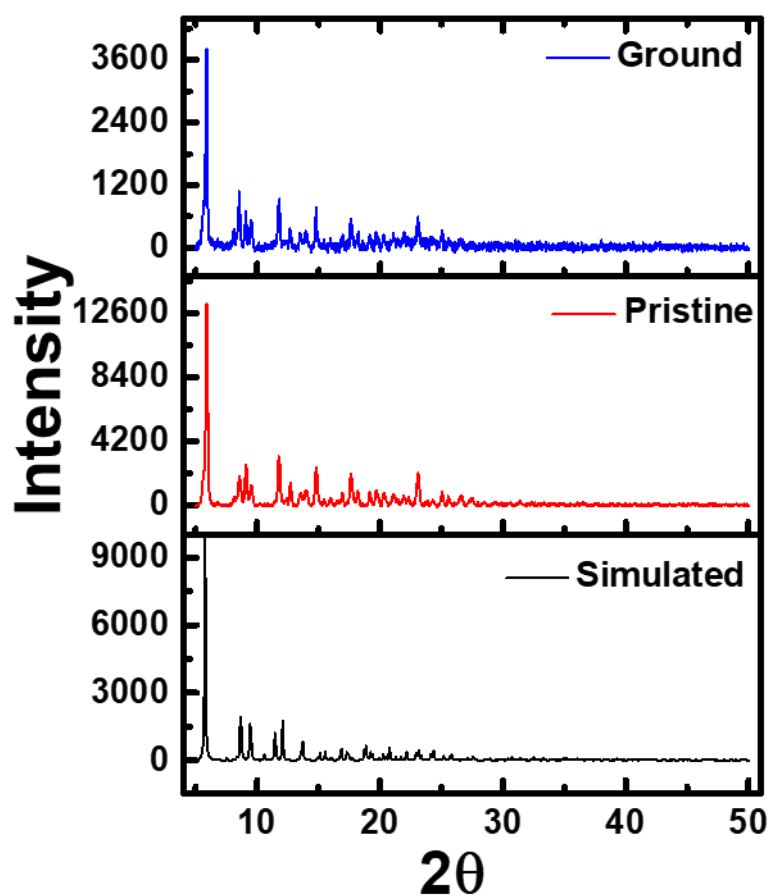


Figure 4A.A.38. Comparison between the experimentally obtained crystal and grinded PXRD pattern (measured at room temperature) with the simulated pattern from CIF of complex **4A.8**

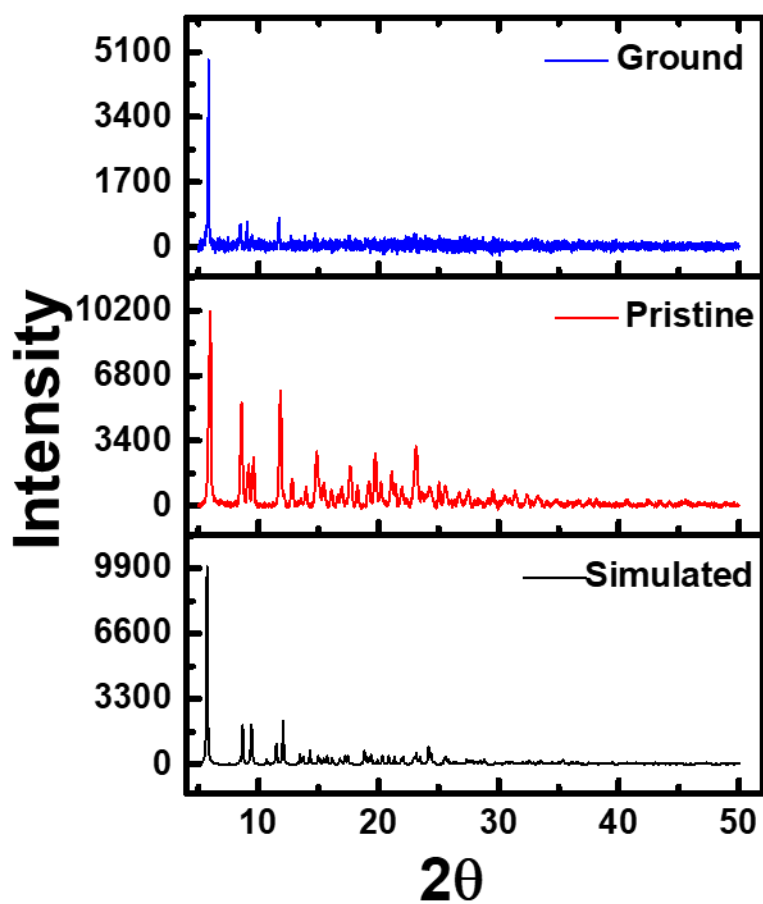


Figure 4A.A.39. Comparison between the experimentally obtained crystal and grinded PXRD pattern (measured at room temperature) with the simulated pattern from CIF of complex **4A.9**.

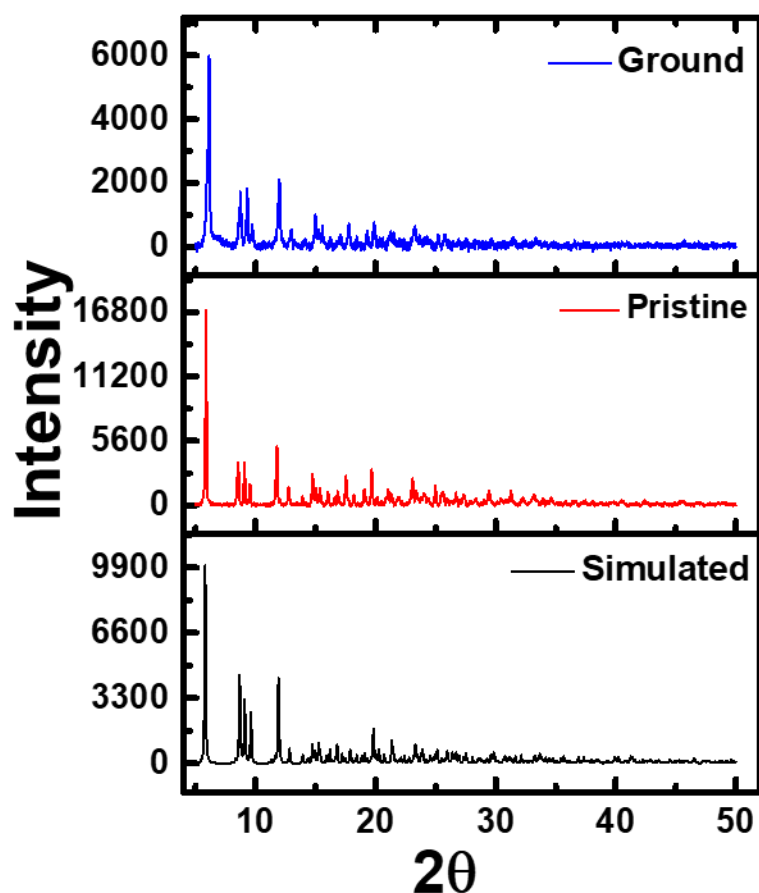


Figure 4A.A.40. Comparison between the experimentally obtained crystal and grinded PXRD pattern (measured at room temperature) with the simulated pattern from CIF of complex **4A.10**

4A.A.8. Fabrication of c-LEDs

Commercially accessible InGaN chips (power = 3W, λ_{EL} = 390-395 nm, VF = 3.1 V, IF = 700 mA) were acquired from ASIAN ELECTRONICS, India. 1 mM sample was mixed in chloroform, and the mixture was coated on the UV chip, dried under an IR light, and then utilised to quantify emission.

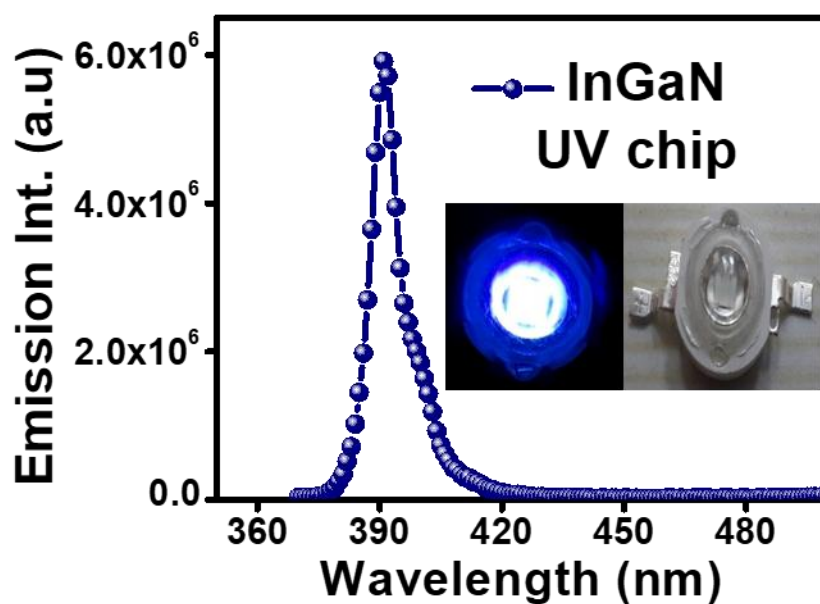


Figure 4A.A.41. Electroluminescence spectra of the InGaN chip centered at the 390-395 nm region.

4B.A.1 Crystallographic data for complexes 4B.1-4B.3.

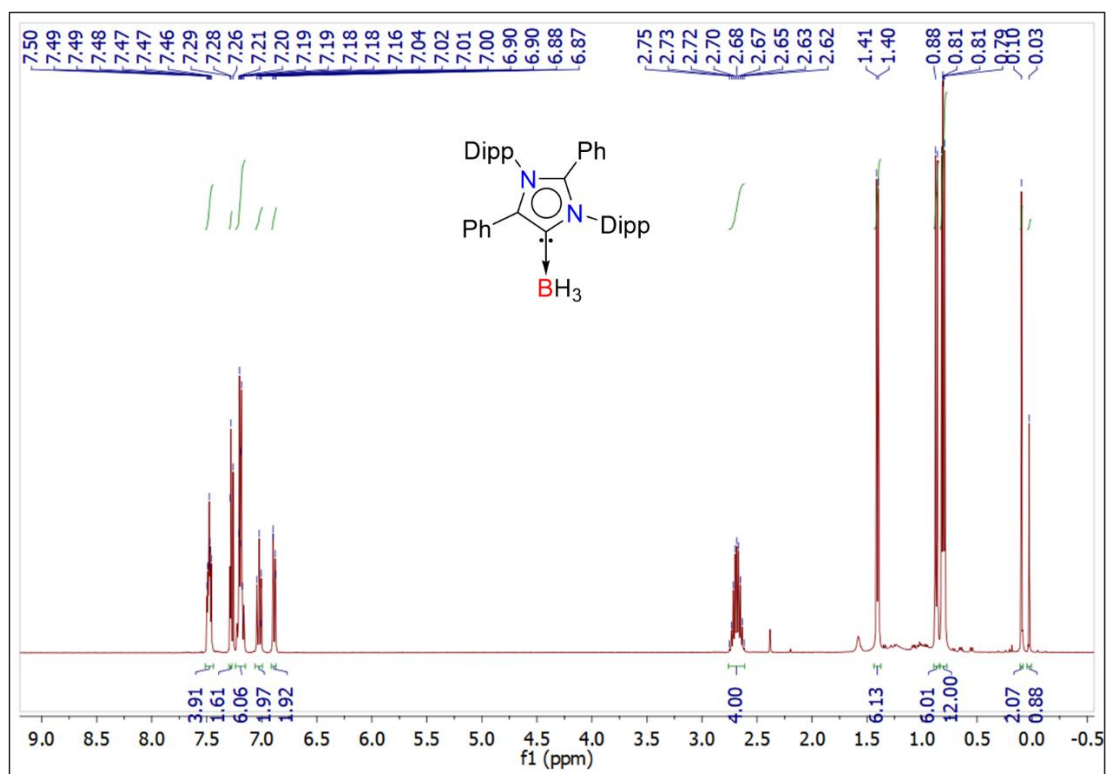
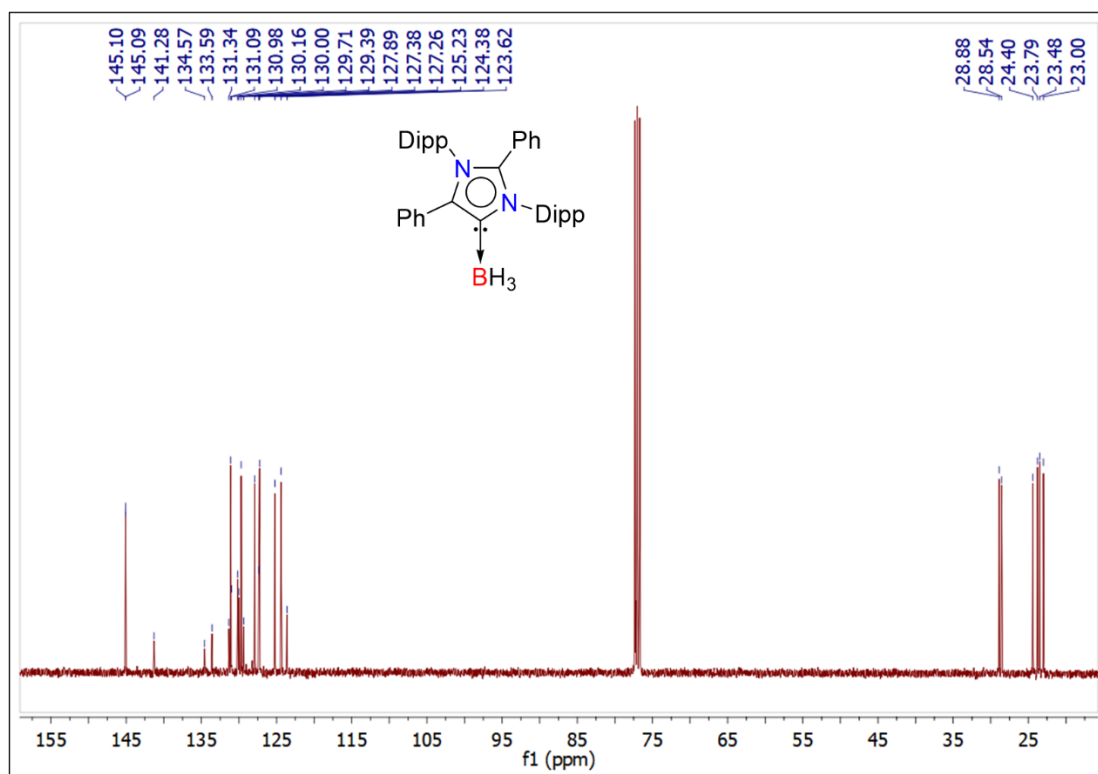
Table 4B.A.1: Crystallographic data for complexes 4B.1-4B.2

Identification code	4B.1	4B.2a	4B.2b
Empirical formula	C ₃₉ H ₄₇ BN ₂	C ₉₅ H ₁₀₂ B ₂ Cr ₂ N ₄ O ₁₀	C ₄₃ H ₄₆ BCrN ₂ O ₄
Formula weight	554.59	1585.42	717.63
Temperature/K	150.15	150.15	150.15
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Aea2	C2/c	P21/n
a/Å	21.319(4)	38.803(14)	19.381(4)
b/Å	20.857(3)	9.818(3)	11.302(2)
c/Å	15.146(4)	23.004(9)	20.920(4)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	90	104.190(12)	112.86(3)
$\gamma/^\circ$	90	90	90
Volume/Å ³	6735(3)	8497(5)	4222.4(16)
Z	8	4	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.094	1.239	1.129
μ/mm^{-1}	0.062	0.317	0.311
F(000)	2400.0	3352.0	1516.0
Crystal size/mm ³	0.147 × 0.123 × 0.114	0.177 × 0.162 × 0.147	0.162 × 0.144 × 0.135
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	3.82 to 50	4.33 to 50.392	3.662 to 50.15
Index ranges	-25 ≤ h ≤ 25, - 24 ≤ k ≤ 24, -17 ≤ l ≤ 18	-46 ≤ h ≤ 46, -11 ≤ k ≤ 11, -27 ≤ l ≤ 27	-23 ≤ h ≤ 22, -12 ≤ k ≤ 13, -24 ≤ l ≤ 24
Reflections collected	90334	33485	59974
Independent reflections	5931 [R _{int} = 0.3096, R _{sigma} = 0.1535]	7575 [R _{int} = 0.1033, R _{sigma} = 0.0950]	7377 [R _{int} = 0.3516, R _{sigma} = 0.2367]
Data/restraints/parameters	5931/1/353	7575/111/550	7377/6/476
Goodness-of-fit on F ²	1.025	1.054	1.070
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0766, wR ₂ = 0.1590	R ₁ = 0.0658, wR ₂ = 0.1723	R ₁ = 0.1147, wR ₂ = 0.1378
Final R indexes [all data]	R ₁ = 0.1531, wR ₂ = 0.2063	R ₁ = 0.1217, wR ₂ = 0.2079	R ₁ = 0.2419, wR ₂ = 0.1695
Largest diff. peak/hole / e Å ⁻³	0.35/-0.29	1.39/-0.77	0.84/-0.49
Flack parameter	0(9)		

Table 4B.A.1: Crystallographic data for complexes **4B.3**

Identification code	4B.3
Empirical formula	C ₉₅ H ₁₀₂ B ₂ N ₄ O ₁₀ W ₂
Formula weight	1849.12
Temperature/K	150.15
Crystal system	Monoclinic
Space group	C2/c
a/Å	39.306(14)
b/Å	9.863(4)
c/Å	23.330(8)
α /°	90
β /°	104.559(9)
γ /°	90
Volume/Å ³	8754(5)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.403
μ/mm^{-1}	2.686
F(000)	3752.0
Crystal size/mm ³	0.736 × 0.311 × 0.16
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.266 to 50.368
Index ranges	-46 ≤ h ≤ 46, -11 ≤ k ≤ 11, -27 ≤ l ≤ 27
Reflections collected	125050
Independent reflections	7831 [R _{int} = 0.0723, R _{sigma} = 0.0268]
Data/restraints/parameters	7831/60/562
Goodness-of-fit on F ²	1.117
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0255, wR ₂ = 0.0570
Final R indexes [all data]	R ₁ = 0.0314, wR ₂ = 0.0597
Largest diff. peak/hole / e Å ⁻³	1.05/-0.89

4B.A.2 NMR spectrum for 4B.1-4B.2.

Figure 4B.A.1. ¹H NMR spectrum of 4B.1 (CDCl₃, 400 MHz, 298 K)Figure 4B.A.2. ¹³C{¹H} NMR spectrum of 4B.1 (CDCl₃, 100.613 MHz, 298 K)

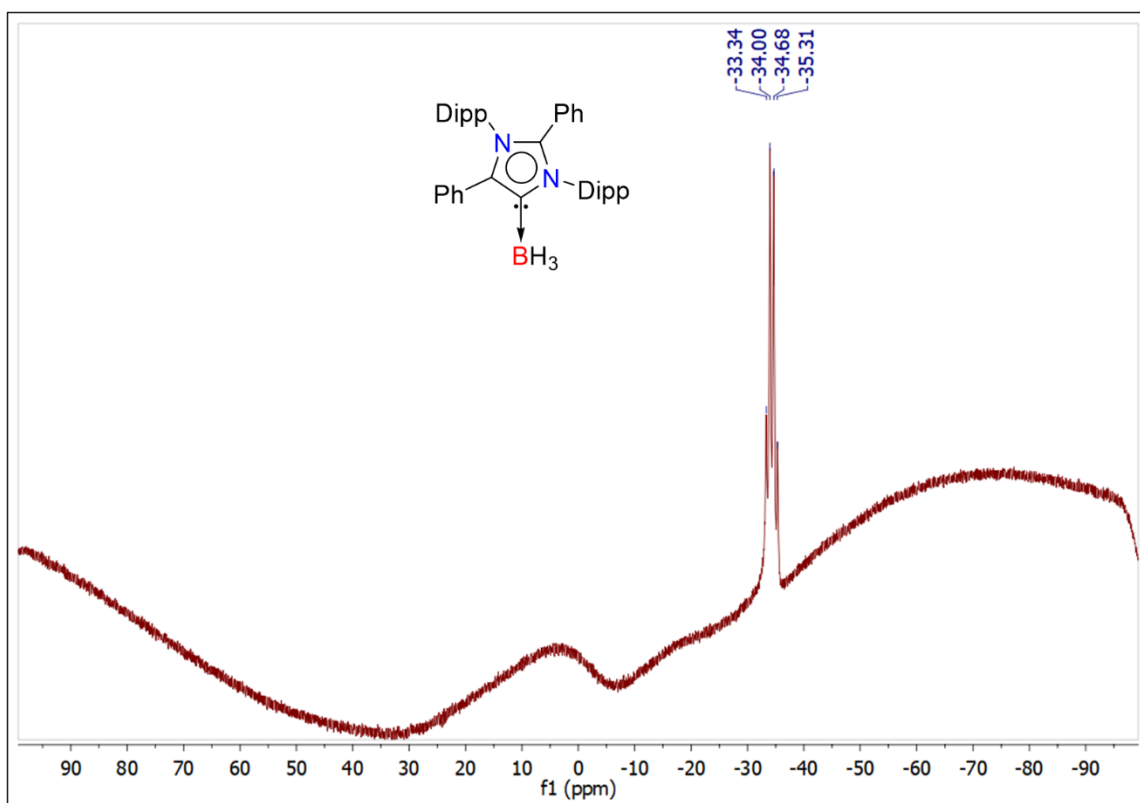


Figure 4B.A.3. ^{11}B NMR spectrum of compound 4B.1 (CDCl₃, 129 MHz, 298 K)

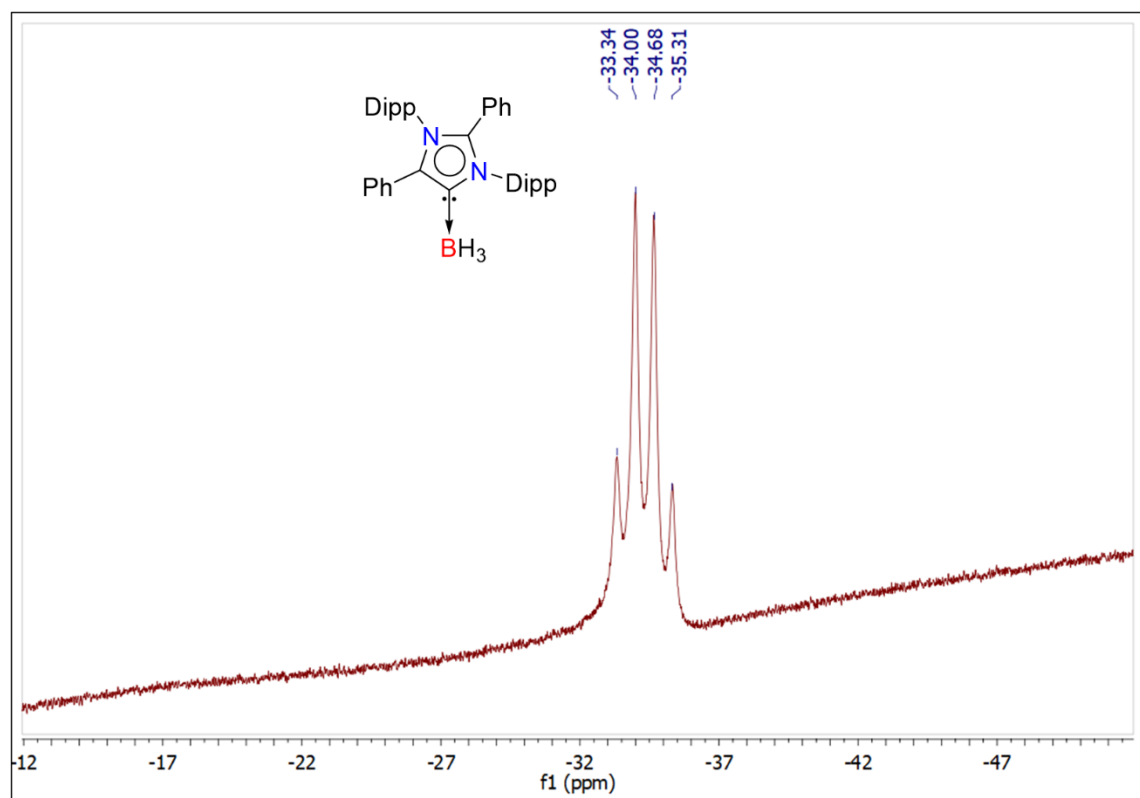


Figure 4B.A.4. ^{11}B NMR spectrum of compound 4B.1 (CDCl₃, 129 MHz, 298 K)

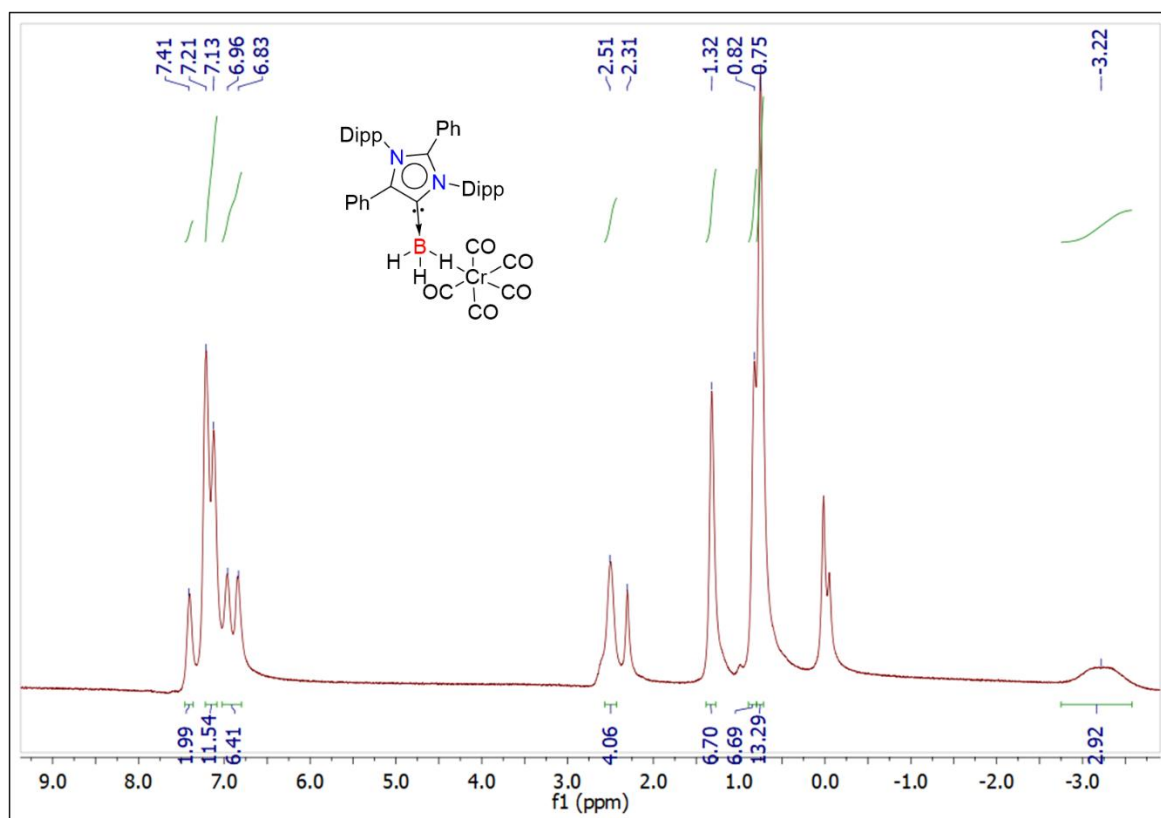


Figure 4B.A.5. ¹H NMR spectrum of **4B.2** (C₆D₆, 400 MHz, 298 K)

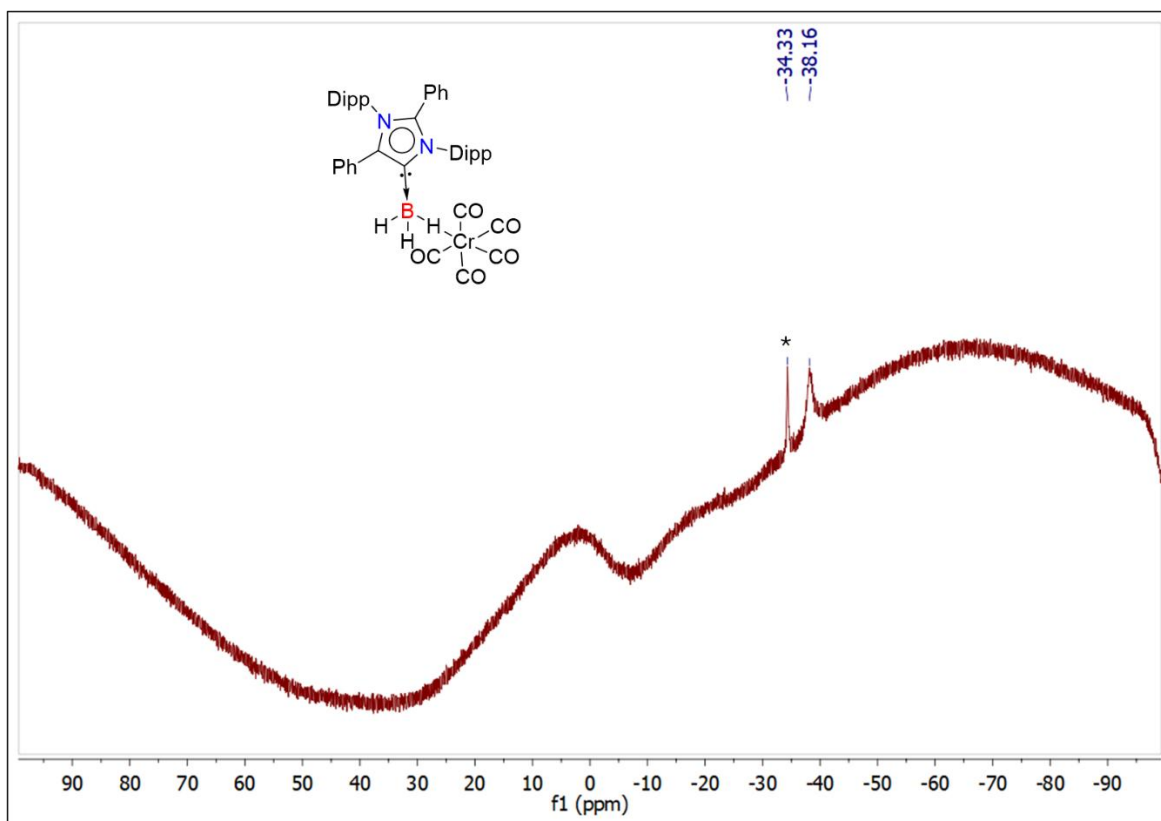


Figure 4B.A.6. ¹¹B{¹H} NMR spectrum of compound **4B.2** (C₆D₆, 129 MHz, 298 K). *Starting material

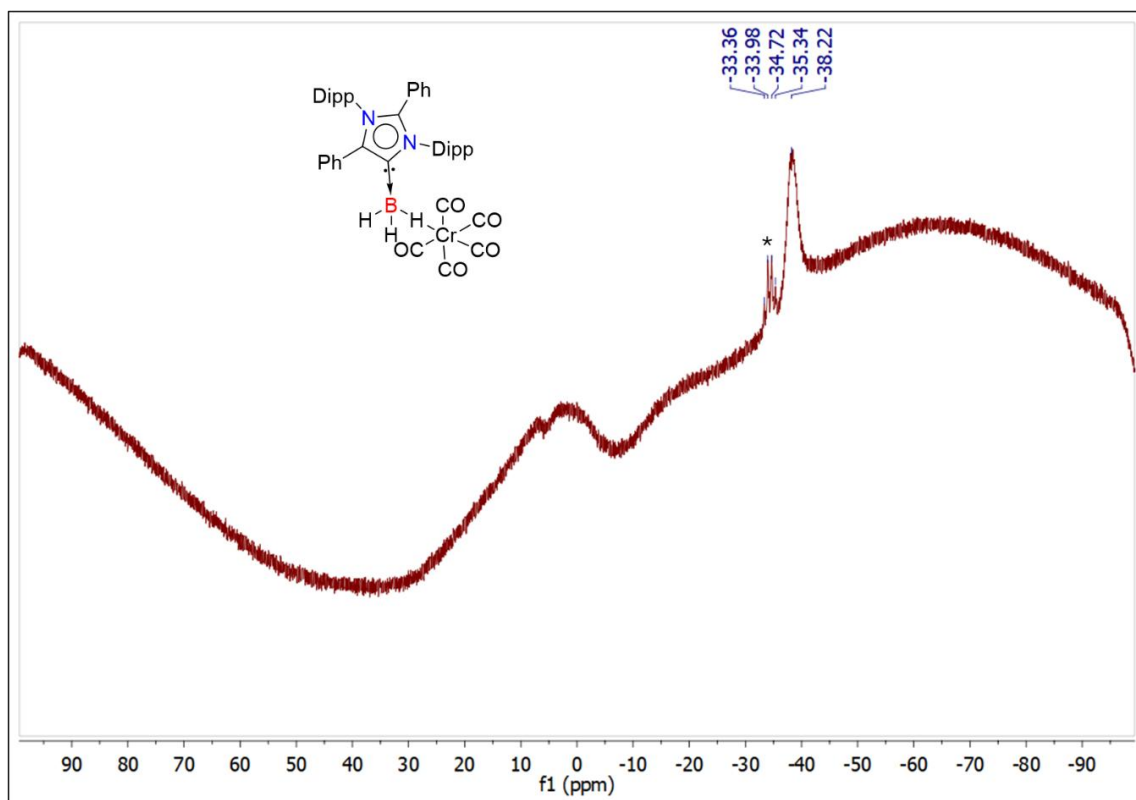


Figure 4B.A.7. ^{11}B NMR spectrum of compound **4B.2** (C_6D_6 , 129 MHz, 298 K). *Starting material

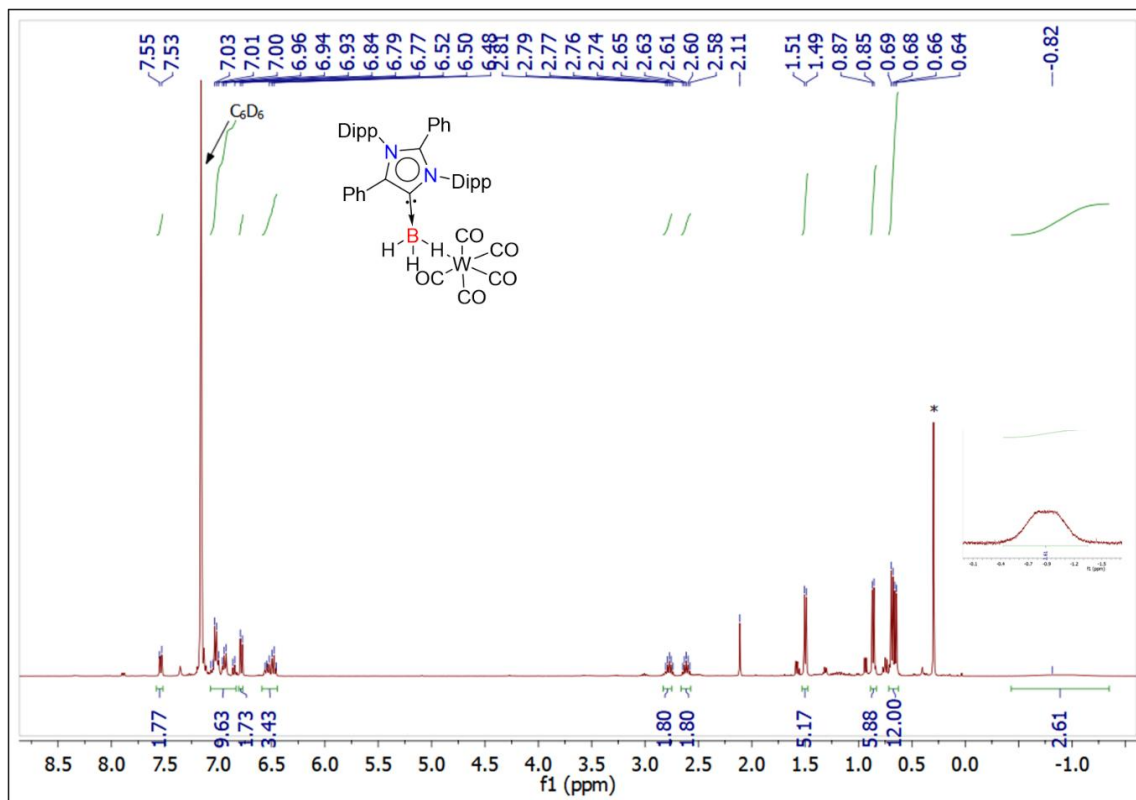


Figure 4B.A.8. ^1H NMR spectrum of **4B.3** (C_6D_6 , 400 MHz, 298 K)

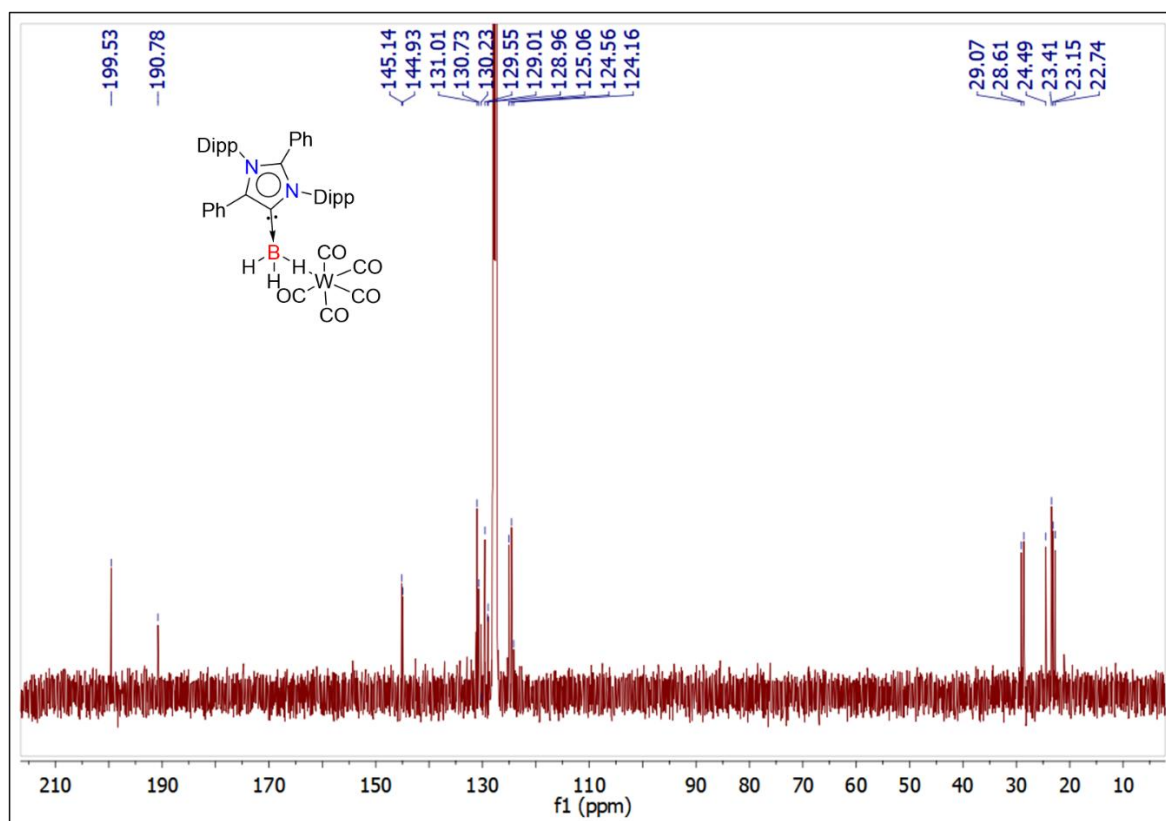


Figure 4B.A.9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4B.3 (C_6D_6 , 100.613 MHz, 298 K)

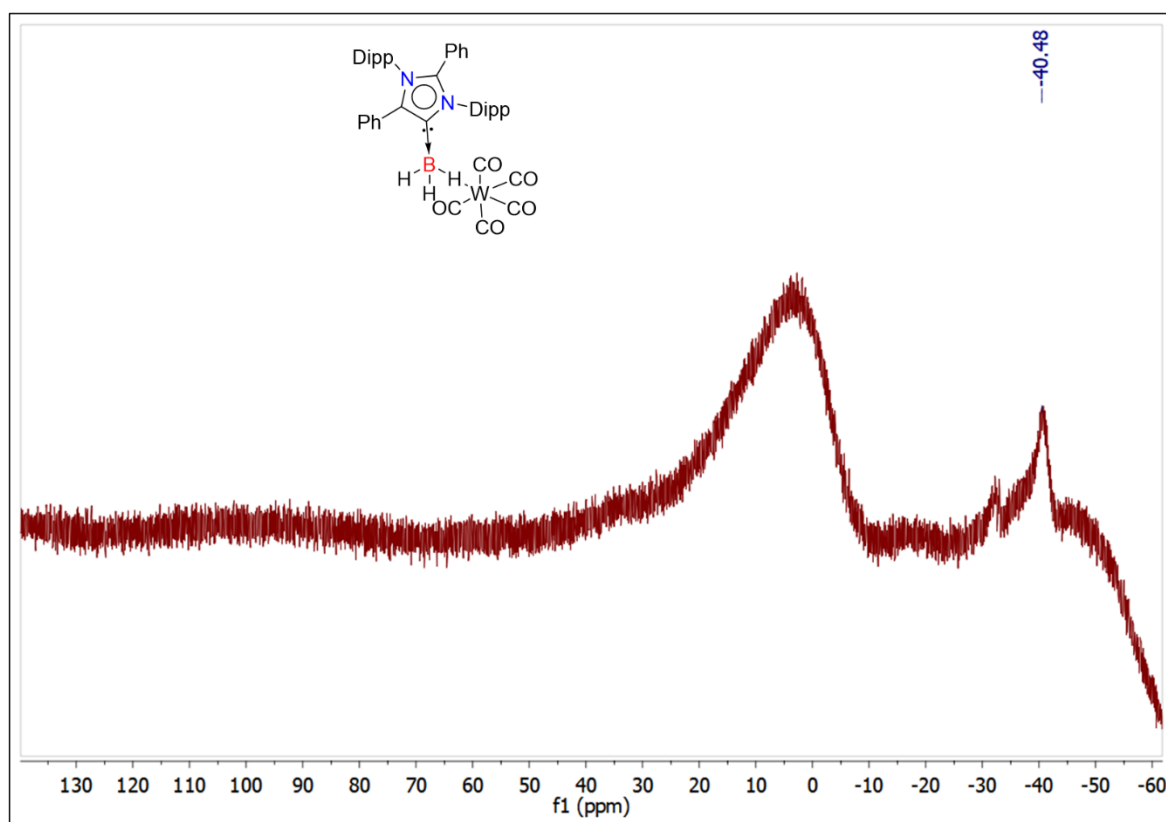


Figure 4B.A.10. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 4B.3 (C_6D_6 , 129 MHz, 298 K).

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First-Row Transition Metal Complexes of a Phosphine-Silylene-Based Hybrid Ligand

Author: Ruksana Akhtar, Sandeep H. Kaulage, Mayur P. Sangole, et al

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