Synthesis and Reactivity of Low-Valent Group 13 and 14
(Semi)Metal Complexes

vorgelegt von

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DISSERTATION

by

M. Sc. Chemistry

Gengwen Tan

from Jiangxi (P. R. China)
Die vorliegende Arbeit entstand in der Zeit von Oktober 2011 bis April 2015 unter der Betreuung von Prof. Dr. Matthias Driess am Institut für Chemie der Technischen Universität Berlin.

Von Herzen kommend gilt mein Dank meinem verehrten Lehrer

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und für die Forschungsfreiheit.
“千里之行，始于足下”
-- 老子

“A Journey of a thousand miles begins with a single step”
-- Laozi
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Publications during doctoral study

   Synthesis of Mixed Silylene-Carbene Chelate Ligands from *N*-Heterocyclic Silylcarbenes Mediated by Nickel


   Elucidating the Effect of the Nucleophilicity of the Silyl Group in the Reduction of CO$_2$ to CO Mediated by Silyl-Copper(I) Complexes

   Mechanistic Studies of CO$_2$ Reduction to Methanol Mediated by an *N*-Heterocyclic Germylene Hydride (Front Cover)

   Facile Access to Mono- and Dinuclear Heteroleptic *N*-Heterocyclic Silylene Copper Complexes

   From Elusive Thio- and Selenosilanoic Acids to Copper(I) Complexes with Intermolecular Si=E→Cu–O–Si Coordination Modes (E = S, Se).

   Unprecedented Silicon(II)→Calcium Complexes with *N*-Heterocyclic Silylenes

From Unsymmetrically Substituted Benzamidinato and Guanidinato Dichlorohydrido-silanes to Novel Hydrido N-Heterocyclic Silylene Iron Complexes


Synthesis and Unexpected Reactivity of Germiumylidene Hydride [:GeH]+ Stabilized by a Bis(N-Heterocyclic Carbene)borate Ligand


Bis-N-Heterocyclic Carbene (NHC) Stabilized $\eta^6$-Arene Iron(0) Complexes: Synthesis, Structure, Reactivity, and Catalytic Activity


A Cyclic Germadicarbene (“Germylone”) from Germiumylidene
Low-valent main group chemistry is one of the main research topics in contemporary organometallic chemistry. In this dissertation, the syntheses of monovalent Group 13 and divalent Group 14 (semi)metal compounds and their reactivities towards small molecules and transition metal reagents were investigated. In addition, the reactivities as well as the catalytic properties of the obtained transition metal complexes were studied.

In the first part of the dissertation, a distinctively different reaction feature between the NHSi\(_1\)(X)Si: (L\(_1\) = PhC(NtBu)\(_2\), X = functional group) and L\(_2\)Si: (L\(_2\) = CH(C=CH\(_2\))(CMe)(NAr)\(_2\), Ar = 2,6-iPr\(_2\)C\(_6\)H\(_3\)) towards copper(I) reagents was demonstrated. The reactions of the amidinato-substituted NHSi\(_1\)(X)Si: (X = Cl, O\(_t\)Bu, NMe\(_2\)) with [(tmeda)Cu(NCCH\(_3\))]OTf (tmeda = tetramethylethylenediamine; OTf = CF\(_3\)SO\(_3\)) afforded only the second isolable examples of NHSi copper(I) [L\(_1\)(X)Si:→Cu(tmeda)]OTf complexes as ionic compounds. The substituent X at the Si(II) center has a large influence on the structure of the NHSi copper(I) complex. In the case of X = Cl, the OTf\(^-\) counter anion exhibits a strong interaction with the [L\(_1\)(Cl)Si:→Cu(tmeda)] cation through the O···Cu contact. In contrast, when X = O\(_t\)Bu or NMe\(_2\), a much weaker interaction between the OTf\(^-\) anion and the complex cation can be observed in the solid state. Moreover, the dinuclear NHSi copper(I) complex [Cu\(_2\){η\(^1\),η\(^1\)-L\(_1\)Si:(O):SiL\(_1\)}\(_2\)]\(^{2+}\)(OTf\(_2\)) featuring a metallacyclooctane dicationic core was isolated through the reaction of the bis-NHSi ligand L\(_1\)Si:(O):SiL\(_1\) with [Cu(NCCH\(_3\))\(_4\)]OTf.

In contrast to the coordination of the amidinato-substituted NHSis towards copper(I) centers, the zwitterionic NHSi ligand L\(_2\)Si: is capable of activating the Cu–O and Cu–H bonds of (IPr)CuX (X = O\(_t\)Bu, OH, H and OC\(_6\)F\(_5\); IPr = (CHNAr)\(_2\), Ar = 2,6-iPr\(_2\)C\(_6\)H\(_3\)) affording the silyl copper(I) complexes L\(_2\)Si(X)Cu(IPr). The latter complexes bear different substituents at the silicon centers which can tune the nucleophilicity of the silyl groups. These silyl copper(I) complexes show different activities for CO\(_2\) reduction to CO. The complex bearing the electron-withdrawing substitutent OC\(_6\)F\(_5\) is the least active in CO\(_2\) reduction to CO, whereas the complexes containing electron-donating groups, such as O\(_t\)Bu and OH, exhibit the highest activity. These results suggest that the stronger the nucleophilicity of the silyl group, the higher the activity of the silyl copper(I) complex for CO\(_2\) reduction to CO.

Besides the activation of the Cu–O and Cu–H bonds of copper(I) reagents, the NHSi L\(_2\)Si: also serves as a starting material to afford several unprecedented silicon compounds, such as L\(_2\)(H)Si(CH\(_2\))NHC (NHC = 3,4,5-trimethylimidazol-2-yliden-6-yl) and L\(_2\)Si(=E)OH(dmap)
the chemist

Abstract

(L^3 = CH(MeCNAr)_2, Ar = 2,6-iPr_2C_6H_3; E = S, Se; dmap = 4-dimethylaminopyridine). In the second part of the dissertation, the compounds L^2(H)Si(CH_2)NHC and L^3Si(=E)OH(dmap) (E = S, Se) were employed as ligands for Ni(0, II) and Cu(I) complexes, respectively. The former compound serves as an elegant precursor to realize the first mixed NHSi-NHC chelate ligand supported Ni(II) complex [L^3Si:(CH_2)NHC]NiBr. The reduction of the Ni(II) complex to Ni(0) complexes as well as its catalytic properties for Kumada-Corriu type cross-coupling reactions were investigated.

The Ni(II) complex [L^3Si:(CH_2)NHC]NiBr was facilely accessible through the Ni(II)-mediated tautomerization of L^2(H)Si(CH_2)NHC via the hydride migration from the silicon center to the backbone of the L^2 ligand. Reduction of [L^3Si:(CH_2)NHC]NiBr with KC_8 in the presence of PMe_3 furnished [L^2Si(CH_2)NHC]Ni(II)Br(PMe_3) and [η^2(Si–H)][L^2Si(H)(CH_2)NHC]Ni(0)(PMe_3) complexes depending on the employed reaction time. When the chelate DMPE ligand (DMPE = 1,2-bis(dimethylphosphino)ethane) was utilized as an exogenous ligand, the analogous reduction resulted in the chelate NHSi-NHC ligand supported Ni(0) complex [L^3Si:(CH_2)NHC]Ni(dmpe). The corresponding dicarbonyl Ni(0) complex [L^3Si:(CH_2)NHC]Ni(CO)_2 could also be synthesized and isolated by the reduction of [L^3Si:(CH_2)NHC]NiBr with two molar equivalents of K(BHEt_3) in a CO atmosphere. In addition, the complex [L^3Si:(CH_2)NHC]NiBr exhibits excellent properties as a precatalyst for Kumada-Corriu type cross-coupling reactions, highlighting the potential of the chelate NHSi-NHC ligand supported TM complexes in homogeneous catalysis.

In another sub-chapter, the utilization of the L^3Si(=E)OH(dmap) compounds (E = S, Se) as ligands for Cu(I) complexes is described. The L^2Si(=S)OH(dmap) compound was reported previously, and its heavier analogue L^3Si(=Se)OH(dmap) could be accomplished for the first time in this work. Both adducts were facilely deprotonated by (MesCu)_4 (Mes = 2,4,6-Me_3C_6H_2) affording the two novel dimeric copper(I) complexes [L^3Si(=E)OCu]_2 featuring an intermolecular Si=E→Cu−O−Si interaction. The latter copper(I) complexes are efficient precatalysts for the Cu(I)-mediated aziridination reaction of styrene with PhI=N(Ts) (Ts = tosyl).

In the third part of this dissertation, the chemistry of germylene-, aluminum(I)- and gallium(I)-hydrides was investigated. Conversion of CO_2 into other valuable fine chemicals, such as formic acid, methanol and methane, is a highly interesting topic especially owing to environmental and energy aspects. The thermally labile germylene hydride L^{Cy}GeH (L^{Cy} = cyclo-C_6H_2-1-NAr-2-C(Ph)NAr, Ar = 2,6-iPr_2C_6H_3) could be generated in situ and be utilized to activate CO_2 affording the corresponding formate compound L^{Cy}GeOCH(=O) via CO_2
Abstract

insertion into the Ge(II)−H bond. The latter compound and the previously reported L\(^3\)GeOCH(=O) were further converted into methanol with the amine-alane adduct NMe\(_3\cdot\)AlH\(_3\) as a hydrogen source upon workup with water. A plausible mechanism for the conversion of the formate complexes into methanol was proposed based on the results from the model reaction of L\(^3\)GeOCH(=O) with the milder hydride delivery agent L\(^3\)AlH\(_2\).

In contrast to the well-developed chemistry of divalent Group 14 element hydrides, the field of Group 13 (semi)metal(I) monohydride has not been comprehensively investigated with only one example of Ga(I)-monohydride complex, but no report on Al(I)-monohydride complexes. Therefore, the syntheses of Al(I)- and Ga(I)-monohydride complexes stabilized through M(I):→Fe(CO)\(_4\) donor-acceptor interaction (M = Al, Ga) were studied in order to gain more structural and reactivity information on these species. Remarkably, the Al(I)-monohydride complex bisNHC-Al(H)[Fe(CO)\(_4\)] (bisNHC = bis-(N-Ar-imidazole-2-ylidene)methylene, Ar = 2,6-iPr\(_2\)C\(_6\)H\(_3\)) turned out to be highly reactive and capable of activating the \(\alpha\)-C−H and C−O bonds of cyclic ethers (tetrahydrofuran and tetrahydropyran) affording bisNHC-Al(2-cyclo-OC\(_4\)H\(_7\))[Fe(CO)\(_4\)], bisNHC-Al(2-cyclo-OC\(_5\)H\(_9\))[Fe(CO)\(_4\)] and bisNHC-Al(O\(_n\)Bu)[Fe(CO)\(_4\)], respectively. In contrast, the Ga(I)-monohydride complex bisNHC-Ga(H)[Fe(CO)\(_4\)] could be successfully isolated and fully characterized by structural and spectroscopic methods. Density functional theory (DFT) calculations revealed that both \(\alpha\)-C−H and C−O bond activations of THF with bisNHC-Al(H)[Fe(CO)\(_4\)] as the reaction intermediate are exothermic processes with a feasible energy barrier for each elementary step, whereas the \(\alpha\)-C−H bond activation of THF with bisNHC-Ga(H)[Fe(CO)\(_4\)] is an endothermic reaction and the C−O bond activation of THF with bisNHC-Ga(H)[Fe(CO)\(_4\)] needs to overcome a high energy barrier (34.3 kcal/mol) for the Ga−H bond activation (only 16.9 kcal/mol in the case of aluminum) which hampers the process. The pronouncedly different reactivity between the Al(I)-monohydride and Ga(I)-monohydride species towards cyclic ethers is likely attributed to the higher electronegativity of gallium versus aluminum which leads to a stronger Ga−H bond.
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**ABBREVIATIONS**

<table>
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<th>Abbreviation</th>
<th>Definition</th>
<th>Unit</th>
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<td>APCI</td>
<td>atmospheric-pressure chemical ionization</td>
<td>MHz</td>
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<tr>
<td>Ar</td>
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<tr>
<td>ca.</td>
<td>about</td>
<td>NBO</td>
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<td>R</td>
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<td>R.T.</td>
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<tr>
<td>eV</td>
<td>Electronvolt</td>
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<td>(mili)gram(s)</td>
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<td>UV-vis ultraviolet-visible</td>
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<tr>
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<td>lowest unoccupied molecular orbital</td>
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<td>weak</td>
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1. INTRODUCTION

Carbenes are neutral compounds bearing a divalent carbon atom with six electrons in its valence shell. Most of the carbenes feature a bent geometry with a sp\(^2\)-type hybridized carbon center, whereas an extreme case is the linear carbene in which the center carbon is sp hybridized with two nonbonding degenerate orbitals (2p\(_x\) and 2p\(_y\)). In the bent carbene, the 2p\(_y\) orbital remains almost unchanged, and it is normally described as p\(_\pi\); the 2p\(_x\) orbital is stabilized by hybridization with 2s orbital and represents the \(\sigma\) orbital of carbenes. The p\(_\pi\) and \(\sigma\) orbitals represent the frontier orbitals of bent carbenes (Figure 1-1).\[^1\]

![Figure 1-1. The nature of the frontier orbitals of linear vs bent carbenes (left) and electronic configuration of triplet vs singlet carbenes (right).](image)

The two nonbonding electrons at the carbene center can be filled separately in p\(_\pi\) and \(\sigma\) orbitals with parallel spin resulting in a triplet state, while they can also be paired in the same \(\sigma\) orbital affording a singlet carbene (Figure 1-1). This is depending on the energy difference between p\(_\pi\) and \(\sigma\) orbitals. A singlet state is favored with a large energy gap, and an energy difference of at least 2 eV is necessary to have a singlet ground state, whereas a value below 1.5 eV usually affords a triplet carbene.\[^2\] The best way to stabilize triplet carbenes is employing sterically congested ligands. The most well-known singlet carbenes nowadays are the N-heterocyclic carbenes (NHCs) stabilized by two adjacent nitrogen atoms. The first isolable NHC (CHNAd)\(_2\) I-1 was reported by Arduengo and coworkers through the reduction of 1,3-diadamantylimidazolium chloride I-2 with sodium hydride in the presence of catalytic amounts of dimethyl sulfoxide anion or with potassium tert-butoxide alone in THF (Scheme 1-1).\[^3\] In NHCs, the –I effect of the the two electronegative nitrogen atoms lowers the energy of the \(\sigma\) orbital, which is occupied by the free electron pair at the carbene carbon atom, and the \(\pi\) interaction of the electron pairs on the nitrogen atoms with the p\(_x\) orbital closes the octet...
shell at the carbene carbon atom. This leads to a particularly large HOMO/LUMO gap, and the carbene can be stable in its free form.

\[
\begin{align*}
\text{I-2} & \quad \text{NaH (cat.}^6 \text{CH}_2\text{S(O)CH}_3) \\
& \quad \text{or KOrBu} \\
& \quad - \text{NaCl,} \frac{1}{2} \text{H}_2 \\
& \quad \text{or KCl, HorBu} \\
& \quad \text{Ad} \\
\end{align*}
\]

Ad = adamantyl

**Scheme 1-1.** Synthesis of the first isolable carbene.

Remarkably, the NHCs are not only thermally stable but also readily accessible in a large amount, some of which are even commercially available nowadays.\[^4\] Since the first isolation of NHCs, their chemistry has been developed rapidly, and they play a crucial role as steering ligands for transition metal mediated homogeneous catalysis.\[^1, 5\] For instance, the second generation of Grubbs’ catalyst for olefin metathesis reaction which is stabilized by an NHC ligand shows significantly higher activity and stability than the first generation catalyst bearing two phosphine ligands (Scheme 1-2); this is owing to the stronger \(\sigma\)-donating ability and \textit{trans} effect of the applied NHC ligand in comparison to the phosphine ligands and therefore a more stable Ru–C bond is formed.\[^6\]

**Scheme 1-2.** Comparison of the first and second generation of Grubbs’ catalysts.

Moreover, NHCs have also proven to be practical in stabilizing the low-valent main group element species as well as main group (semi)metal centered radicals.\[^7\] One remarkable
application is the utilization of NHCs for stabilizing the :E=E: (E₂) and :E: species (E₂ = Si₂,[⁸] Ge₂,[⁹] and Sn₂,[¹⁰]; E = Si[¹¹] and Ge[¹²]) (Scheme 1-3). The NHC→:E=E:←NHC complexes containing a singlet E₂ fragment feature a trans-bent geometry with one lone pair of electrons at each metal center, whereas the bisNHC(:E:) complexes bear two lone electron pairs at the corresponding metal centers, and they are termed silylone and germylone, which are dicoordinate Si(0) and Ge(0) complexes, respectively.[¹³]

![Scheme 1-3. NHCs as supporting ligands for E₂ and :E: species.]

The strategy for stabilizing carbenes with two electronegative nitrogen atoms affording NHCs has also been successfully applied to realize other isoelectronic species, such as silylenes, which are heavier homologues of carbenes, and monovalent Group 13 metal compounds.[¹⁴]

### 1.1 N-Heterocyclic silylenes

The first isolable N-heterocyclic silylene (NHSi) I-3 was reported by Denk and West et al. through the reduction of a dichlorosilane precursor with elemental potassium (Scheme 1-4). Silylene I-3 is thermally stable even after heating to 150 °C in toluene for four months.[¹⁵] The saturated version of NHSi I-4,[¹⁶] benzo- and pyrido-fused NHSis (I-5[¹⁷] and I-6[¹⁸], respectively) analogous to I-3 were also reported afterwards by the reduction of the respective dichlorido precursors with suitable reducing agents.
Introduction

Scheme 1-4. Synthesis of the first isolable N-heterocyclic silylene and the Chemdraw structures of its analogues.

In 2006, the novel NHSi L^2Si: I-8 (L^2 = CH(C=CH_2)(CMe)(NAr)_2, Ar = 2,6-iPr_2C_6H_3) featuring a zwitterionic character based on the well-known Nacnac ligand L^3H (L^3 = CH(MeC=NAr)_2, Ar = 2,6-iPr_2C_6H_3) was reported by Driess et al.\textsuperscript{[19]} The NHSi I-8 was facilely obtained by the reduction of the dibromosilane precursor I-7 with KC_8. And the starting material I-7 was readily accessible through the reaction of SiBr_4 with the lithiated Nacnac ligand in the presence of TMEDA (tetramethylethlenediamine) (Scheme 1-5). Strikingly, except for the electrophilic nature of the dicoordinate Si(II) center, the NHSi I-8 contains two possible nucleophilic centers, the typical nucleophilic Si(II) center and the unsaturated C_3N_2-backbone, which is also supported by the resonance structure I-8a as depicted in Scheme 1-5, rendering rather rich reactivity of the NHSi I-8.

Scheme 1-5. Synthesis of the zwitterionic NHSi I-8 and the depiction of its resonance structure I-8a.

Ar = 2,6-iPr_2C_6H_3
TMEDA = tetramethylethlenediamine
Since small molecule activations with low-valent main group element complexes are one of the research frontiers in contemporary organometallic chemistry, the NHSi I-8 has been successfully applied to activate various interesting bonds containing substrates, including O–O, N–O, O–H, N–H and C–H bonds. These results have been recently summarized in two reviews published in 2010\(^{20}\) and 2011\(^{21}\) by Driess et al., thus the details will not be discussed here again. However, it is worthy to mention two recent remarkable examples. The first one is the activation of N\(_2\)O with the dmap-I-8 adduct (dmap = dimethylaminopyridine) affording an isolable base stabilized silanone I-9, which could further be converted into the first example of thiosilanoic acid-base adduct I-10 (Scheme 1-6).\(^{22}\) Compound I-10 was employed as a building block for preparing the manganese(II) silathiocarboxylate complex I-11 bearing a Si(=S)–O–Mn(II) moiety (Scheme 1-6).\(^{23}\) Another example is the ‘metal-free’ sp\(^3\) C–H bond activation of 1,3,4,5-tetramethylimidazol-2-ylidene with I-8 affording an unique N-heterocyclic hydrosilycarbene L\(^2\)Si(H)(CH\(_2\))NHC (L\(^2\) = CH(C=CH\(_2\))(CMe)(NAr)\(_2\), Ar = 2,6-iPr\(_2\)C\(_6\)H\(_3\); NHC = 3,4,5-trimethylimidazol-2-yliden-6-yl) complex I-12 (Scheme 1-7).\(^{24}\) Complex I-12 might serve as an elegant ligand for realizing transition metal complexes containing both NHC and silyl moiety as donors owing to the characteristic reactivity of the Si–H group in I-12 which can undergo oxidative addition to a transition metal center affording a silyl-NHC metal complex. Moreover, I-12 might also tautomerize through hydride migration from the silicon center to the L\(^2\) ligand backbone owing to the pronounced Brønsted basicity of the exocyclic methylene carbon yielding a mixed NHC-NHSi chelate ligand I-12a supported transition metal complex when a suitable transition metal reagent is employed to assist the hydride migration (Scheme 1-7).

**Scheme 1-6.** Syntheses of the thiosilanoic acid-base adduct I-10 and the manganese(II) silathiocarboxylate complex I-11.
**Scheme 1-7.** Synthesis of the $N$-heterocyclic silylcarbene I-12 and two possible reaction routes of I-12 toward transition metal reagents.

Apart from small molecule activations mediated by the NHSi I-8, it can also react with various organometallic reagents either through the coordination of the Si(II) to metal ions affording NHSi metal complexes or the Si(II) insertion into M–C or M–H bonds of organometallic compounds leading to the formation of silyl-metal complexes. These two reactivity features will be discussed in detail in the following part of this section.

Another widely investigated NHSi is the chlorosilylene $L^1$ClSi: ($L^1 = \text{Ph(CNtBu)}_2$) I-13 reported by Roesky and coworkers in 2006. At the beginning, this NHSi could only be isolated in very low yield (10%) through the reduction of the trichlorosilane precursor with two molar equivalents of elemental potassium in THF (Scheme 1-8).\textsuperscript{[25]} Later on, the yield was significantly improved through dehydrochlorination of the corresponding amidinato dichlorosilane precursor I-15 with an NHC or LiN(TMS)$_2$, and 90% yield was achieved when LiN(TMS)$_2$ was employed as a reducing agent. The substantial improvement of the reaction yield is the key factor for the fruitful chemistry derived from the chlorosilylene I-13. For instance, the NHSi I-13 and its derivatives have been successfully applied as ligands toward transition metal ions; some of the emerging NHSi transition metal complexes even exhibit remarkable catalytic performances in organic transformations. The details of this nice chemistry will be discussed in the following part of this section.
**Scheme 1-8.** Synthesis of the chlorosilylene I-13 through two different synthetic routes.

### 1.2 The reactivity of NHSis toward organometallic reagents

As divalent silicon species, NHSis can either react with metal sources through the coordination of the Si(II) to metal centers (Si:→M) or oxidative addition of the M−X (X = C, H, O etc.) bond of metal reagents to the Si(II) center affording silyl-metal complexes. Both of the reactive modes have been reported in literature, and the details will be discussed in the following part.

#### 1.2.1 Reactions of NHSis with organometallic reagents affording silyl-metal complexes

The reactions of the first isolable NHSi I-3 with transition metal hydrides have been investigated for molybdenum and tungsten affording two silyl-metal (CHNtBu)₂Si(H)-M(H)Cp₂ complexes (I-16: M = Mo, I-17: M = W) via the Si(II) insertion into the M−H bonds of Cp₂MH₂ (Scheme 1-9).[26]

**Scheme 1-9.** Synthesis of the silyl-molybdenum complex I-16 and silyl-tungsten complex I-17, respectively.

The reactivity of the benzo-fused NHSi I-5b with alkaline metal reagents has also been investigated extensively. The reactions of the organolithium and organosilyl lithium reagents with I-5b afforded the corresponding silyl-lithium products I-18 through the oxidative addition of the Li−X (X = C or Si) bond to the Si(II) center of I-5b (Scheme 1-10a).[27]
similar reaction also occurred when 1-5b was treated with lithium amides (LiNMe₂ and LiNiPr₂).[28]

Remarkably, when lithium amides [LiNrBu(TMS) and LiN-2,6-dimethylphenyl(TMS)] bearing one silyl group attached to the nitrogen atom were treated with 1-5b, the expected silyl-lithium complexes could not be obtained, whereas two new lithium amide complexes 1-20a and 1-20b were isolated from the respective reactions. This is likely due to the oxidative addition of the lithium amide to the Si(II) center affording the silyl-lithium intermediate, which is unstable and undergoes the exchange of the TMS group with the lithium moiety forming the final product 1-20a or 1-20b. In fact, the oxidative addition product 1-19 could be isolated when Li[N-2,6-dimethylphenyl(TMS)] was used as the starting material, and the migration of the TMS group only occurred at elevated temperatures (Scheme 1-10b). A similar TMS and lithium moiety exchange was also observed when MN(TMS)₂ (M = Li, Na, K) was allowed to react with 1-5b affording 1-21, and more interestingly if the reaction was carried out in 2:1 ratio of 1-5b to MN(TMS)₂, complex 1-22 could be isolated resulting from twice TMS migration (Scheme 1-10c). The reaction of sodium methoxide with 1-5b afforded a novel methoxy-substituted sodium silanide 1-23 as a dimeric complex via direct oxidative addition of the Na−O bond to the Si(II) center followed by dimerization through the O−Na interaction (Scheme 1-10d).
Introduction

Scheme 1-10. Reactions of organoalkali metal reagents with NHSi I-5b.

The activations of M−H and M−C bonds with the zwitterionic silylene I-8 have also been studied. With AlMe₃, AlH₃•NMe₃ and LiMe as starting materials, the reactions with I-8 afforded L²Si(Me)AlMe₂(THF) I-24, L²Si(H)AlH₂(NMe₃) I-25 and L²Si(Me)Li(THF)₃ I-26, respectively (L² = CH(C=CH₂)(CMe)(NAr)₂, Ar = 2,6-iPr₂C₆H₃) (Scheme 1-11). Interestingly, in constrast to the cases of organolithium and organoaluminum reagents, when ZnMe₂ was applied to react with I-8, the doubly Zn−C bond activation product [L²Si(Me)]₂Zn I-27 could be isolated in high yields (Scheme 1-11).[32]


Strikingly, when the NHSi I-8 was treated with Cp*Ir(V)H₄ (Cp* = C₅Me₅), the reaction firstly resulted in the formation of the Ir−H bond activation product L²Si(H)Ir(V)H₃Cp* I-28, which could be further converted into a novel hydridosilylene Ir(III) L³(H)Si:→Ir(III)H₂Cp* complex I-29 (L³ = CH(MeC=NAr)₂, Ar = 2,6-iPr₂C₆H₃) via hydride migration from the Cp*Ir(V)H₃ moiety to the exocyclic methylene carbon center owing to the pronounced Brønsted basicity of the terminal methylene carbon of I-8 (Scheme 1-12).[33]
**Introduction**

Scheme 1-12. Reaction of the NHSi 1-8 with Cp*IrH₄ affording the silyl-iridium(V) complex I-28 and hydridosilylene-iridium(III) complex I-29.

In contrast to the dicoordinate NHSis I-5 and I-8, treatments of the tricoordinate chlorosilylene I-13 with organoalkaline metal reagents afforded only the salt metathesis products with retention of the silylene character. For instance, the reaction of I-13 with KOtBu exclusively furnished the functionalized NHSi L’(OrBu)Si: with concomitant elimination of KCl. With this synthetic protocol, a series of functionalized amidinato-substituted silylenes with finely tuned electronic properties have been isolated. Moreover, the ferrocenyl-bridged bisNHSi and two NHSi based pincer ligands with the silylene moieties as coordination arms have been realized through the reaction of NHSi I-13 with the corresponding dilithium salts (Scheme 1-13). These amidinato-substituted silylenes have found to be useful as ligands in transition metal chemistry.


### 1.2.2 Coordination of NHSis toward transition metal ions

The application of NHSis as ligands for transition metal chemistry is a very interesting topic owing to the similar electronic structure of NHSis to that of NHCs, which have been widely used as ligands in coordination chemistry as well as homogeneous catalysis. And the
chemistry of NHSi transition metal complexes has been developed rapidly during the last decades.

Since the first isolation of NHSi 1-3, it has been utilized to react with various metal reagents affording NHSi metal complexes via the Si(II)→M interaction. However, most of the metals that have been studied are late transition metals, including Cr, Mo, W, (Group 6) Fe, Ru, (Group 8) Rh, (Group 9) Ni, Pd and Pt (Group 10) (see Scheme 1-14 for selected examples). Moreover, several NHSi f-block metal and Ca(II) complexes have also been reported and structurally characterized by single-crystal X-ray diffraction analysis. Other five-membered NHSis, analogous to 1-3, have also found to be useful as starting materials to access NHSi transition metal complexes. For instance, the only example of NHSi Group 11 metal complex, which is a copper(I) complex, was reported by Lappert and coworkers through the reaction of the benzo-fused NHSi 1-5b with (PhP3)3CuI with concomitant elimination of one PhP3 moiety (Scheme 1-14).

\[
\text{M} = \text{Cr, Mo, W}
\]

Scheme 1-14. Selected examples of the five-membered NHSi metal complexes.

In comparison to other NHSis aforementioned, there are only a few examples of NHSi transition metal complexes based on the zwitterionic NHSi I-8 reported till now. However, these NHSi metal complexes exhibited fantastic performance for small molecule activations owing to the extra reactive site at the exocyclic methylene center in comparison to other NHSIs. A remarkable example is the NHSi tricarbonyl nickel(0) complex I-30, which is facilitate accessible by the reaction of I-8 with Ni(cod)2 (cod = cyclooctadiene) followed by ligand exchange with CO. Complex I-30 can efficiently activate substrates bearing O−H, S−H and N−H bonds (Scheme 1-15).
As mentioned above, the chlorosilylene I-13 serves as an important starting material to access NHSis bearing various functional groups at the Si(II) center and NHSi based pincer ligands. These novel derivatives of I-13 have been employed as ligands to prepare transition metal complexes, some of which turned out to be efficient precatalysts for organic transformations. For instance, the NHSi I-13 and its derivatives have shown to exhibit remarkable ability in terms of coordination to a variety of transition metals including, for example, Ti,\(^{[46]}\) V and Co,\(^{[47]}\) Cr, Mo and W,\(^{[48]}\) Mn and Re,\(^{[49]}\) or Fe (see selected examples in Scheme 1-16).\(^{[50]}\) For example, the reaction of (η\(^5\)-C\(_5\)H\(_5\))Ti(PMe\(_3\))\(_2\) with two molar equivalents of I-13 afforded the first example of NHSi Group 4 metal L\(^1\)(Cl)Si:→Ti(η\(^5\)-C\(_5\)H\(_5\))←:Si(Cl)L\(^1\)I-31 with concomitant liberation of PMe\(_3\). Complex I-31 could further be converted into L\(^1\)(Me)Si:→Ti(η\(^5\)-C\(_5\)H\(_5\))←:Si(Me)L\(^1\)I-32 and L\(^1\)(H)Si:→Ti(η\(^5\)-C\(_5\)H\(_5\))←:Si(H)L\(^1\)I-33 through salt metathesis reactions with MeLi and Li(BHEt\(_3\)), respectively.\(^{[46]}\) Another remarkable example is the electron-rich NHSi iron(0) complex L\(^1\)(H)Si:→Fe(dmpe\(_2\))I-35 (dmpe = 1,2-bis(dimethylphosphino)ethane) bearing a hydride group at the silicon center with the iron center additionally stabilized by two dmpe ligands. Compound I-35 can serve as a highly active precatalyst for ketone hydrosilylations, and a reaction mechanism for the catalytic process was proposed which involves the hydride group migration from the Si(II) to Fe(0) center triggered by a ketone coordination to the Si(II) center based on NMR spectroscopic studies, which was also supported by DFT calculations.\(^{[50b]}\) Very recently, Roesky Junior and coworkers reported the first NHSi Zn(II) \([L^1(\text{Et})\text{Si}:]_2\rightarrow\text{ZnCl}_2\) complex I-38 through the reaction of I-13 with ZnEt\(_2\) via ligand...
exchange between the zinc and silicon moieties with a concomitant Si(II)→Zn(II) bond formation.\textsuperscript{[51]}

\textbf{Scheme 1-16.} Selected examples of the amidinato-substituted silylene transition metal complexes.

Two bidentate ligands featuring two amidinato-substituted silylene moieties as the coordination sites have also been prepared. They have been utilized as supporting ligands for synthesizing bisNHSi Co(I) and Ni(0) complexes, which exhibited moderate to high activity as precatalysts for organic transformations. The ferrocenyl-connected bis-NHSi cobalt(I) complex \textbf{I-39} is active for [2+2+2] cyclotrimeration of alkynes and nitriles;\textsuperscript{[52]} the oxo-bridged bis-NHSi nickel(0) complex \textbf{I-40} has proven to be an efficient precatalyst for Kumada-Corriu and Nigishi-type cross-coupling reactions (Scheme 1-17).\textsuperscript{[53]}
Scheme 1-17. Bis-NHSi supported cobalt(I) and nickel(II) complexes and their applications in homogeneous catalysis.

The NHSi based pincer ligands containing two amidinato-substituted silylene moieties as coordination arms have shown to be useful as ligands for transition metal chemistry. The synthesis of these pincer ligands is rather straightforward. For instance, the first example of NHSi based pincer ligand I-42 could be facilely accessible by the reaction of the dilithium salt I-41 with two molar equivalents of I-13. Unexpectedly, treatment of I-42 with Pd(PPh₃)₄ resulted in the formation of an NHSi hydridosilyl-Pd(II) complex I-44. The reaction might firstly proceed via oxidative addition of the arene-C–H bond to the Pd(0) center affording I-43 bearing a Pd–H bond as an intermediate, which is likely labile and undergoes hydride migration from the Pd–H to one of the Si(II) centers with concomitant coordination of an NHSi moiety from another ligand molecule to the Pd(II) center affording the NHSi silyl–Pd(II) complex I-44 (Scheme 1-18).[^54]

In contrast to the reaction of Pd(PPh$_3$)$_4$ with 1-42, the reactions of 1-42 with [IrCl(coe)$_2$]$_2$ (coe = cyclooctene), IrH(CO)(PPh$_3$)$_2$ and [RhCl(PPh$_3$)$_2$]$_2$ afforded pincer ligand scaffold ligated Ir(III) (1-45 and 1-46) and Rh(III) 1-47 complexes, respectively (Scheme 1-19). The Ir(III) complexes were found to be catalytically active for arene-C–H borylation reactions. More importantly, the comparison of the electron-donating capacity of the Group 14 metallhylenes (silylene and germlylene) with the traditional phosphine ligands showed that the metallhylenes are not simply isoelectronic analogues of phosphines, but indeed can tune the electronic property of the metal centers and ultimately change the reactivity of the metal complexes, highlighting the potential of NHSis as ligands in transition metal chemistry.\textsuperscript{[35b]}

\begin{center}
\textbf{Scheme 1-19.} Synthesis of the NHSi based pincer type Ir(III) and Rh(III) complexes.
\end{center}

Moreover, treatment of the ligand 1-42 with NiBr$_2$(dme) (dme = 1,2-dimethoxylethane) in the presence of an excess amount of NEt$_3$ (10 equiv.) resulted in the formation of the pincer-type nickel(II) complex 1-48. Complex 1-48 was an efficient precatalyst for the nickel-catalyzed Sonogashira cross-coupling reaction. Importantly, from the stoichiometric reaction of 1/n molar equivalent of [Cu–C≡C–2,6-Ph$_2$C$_6$H$_3$]$_n$ oligomer with 1-48, one of the possible catalytic intermediates 1-49 for the nickel-catalyzed Sonogashira cross-coupling reaction could be successfully isolated and fully characterized by structural and spectroscopic methods (Scheme 1-20).\textsuperscript{[35c]}
Introduction

Scheme 1-20. Synthesis of the pincer-type nickel(II) complex and isolation of one of the possible catalytic intermediates I-49 for the nickel-catalyzed Sonogashira cross-coupling reaction.

1.3 Low-valent Group 13 and Group 14 element hydrides

(Semi)Metal hydrides and their complexes are valuable synthons in chemical synthesis. It has been shown that main group and transition (semi)metal hydride compounds are important intermediates or catalysts in various catalytic processes\(^\text{[55]}\). They have also been widely applied as precursors for preparing high-purity elements and alloy devices for the electronic industry\(^\text{[56]}\). Low-valent main group chemistry represents one of the most attractive research frontiers in contemporary organometallic chemistry, particularly owing to the pursuit of transition metal free small molecule activation reactions and transformations\(^\text{[20]-[21], [57]}\). Low-valent Group 14 element hydrides received numerous attention since they have already exhibited some interesting applications in the activation of unsaturated substrates, such as alkynes, ketones, imines, as well as carbon dioxide, either stoichiometrically or catalytically\(^\text{[50b], [57c], [58]}\). The remarkable examples are the two-coordinate germylene and stannylene hydrides 2,6-(CHPh\(_2\))\(_2\)-4-iPr-C\(_6\)H\(_2\)(SiMe\(_3\))N-M(H) (M =Ge and Sn), which have shown to be efficient precatalysts for hydroboration of a variety of unactivated carbonyl compounds (Scheme 1-21)\(^\text{[58b]}\).
Introduction

Scheme 1-21. Hydroboration of carbonyl substrates catalyzed by two-coordinate Ge(II)-H and Sn(II)-H species.

1.3.1 Divalent Group 14 element hydrides

To date, tremendous efforts have been undertaken in synthesizing divalent Group 14 element hydrides (EH₂, E = Si-Sn), and dozens of complexes with the stabilization of sterically demanding ligands R in REH (E = Si-Sn) or through Lewis-type donor-acceptor stabilization have been reported[46, 58a, 59]. For instance, Power and coworkers reported the first example of a divalent Group 14 element hydride (Ar⁺SnH)₂ bearing a sterically encumbered aryl group Ar⁺ (Ar⁺ = C₆H₃-2,6-(C₆H₂-2,4,6-iPr)₃). Rivard and coworkers recently reported the stabilization of the parent metallylene hydrides SiH₂, GeH₂ and SnH₂ by employing an NHC as a donor and BH₃ or a metal carbonyl fragment as an acceptor (Scheme 1-22).[59d, 59f, 60] Robinson et al. also reported the synthesis of a SiH₂ complex stabilized by a NHC ligand and a boron moiety through the activation of BH₃ with the NHC stabilized disilicon(0) complex.[61] In the case of silicon, most of the Si(II)-hydrides that have been reported till now are obtained through the Lewis-type donor-acceptor stabilization. Strikingly, there are two examples of Si(II)-hydrides known with the absence of Lewis acid stabilization as reported by Baceiredo et al.[58a] and Inoue et al.[59e], respectively (Scheme 1-22).

Scheme 1-22. Selected examples of divalent Group 14 metal hydrides.
In contrast to the Si(II)-hydrides, there are several reported examples of isolable germylene-hydrides without Lewis acid stabilization (Scheme 1-23).\textsuperscript{62} The first one, the Nacnac ligand (L\textsuperscript{3}H, L\textsuperscript{3} = CH(MeC=NAr)\textsubscript{2}, Ar = 2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) stabilized germylene-hydride L\textsuperscript{3}GeH \textbf{I-50}, was reported by Roesky and coworkers in 2006.\textsuperscript{62a} It was first prepared by the hydride exchange of L\textsuperscript{3}GeCl with AlH\textsubscript{3}•NMe\textsubscript{3}. Later on, the authors found that \textbf{I-50} could be facilely prepared by the salt metathesis reaction of L\textsuperscript{3}GeCl with K[BH\textsubscript{s}Bu\textsubscript{3}],\textsuperscript{58e} and this became a general method to prepare low valent main group hydride complexes.

\textbf{Scheme 1-23.} Reported examples of germylene hydrides without the stabilization of Lewis acids.

The germylene hydride \textbf{I-50} has been intensively investigated for small molecule activations, including ketones, alkynes, diazo and azo compounds as well as CO\textsubscript{2}.\textsuperscript{57c} One of the interesting cases is the activation of CO\textsubscript{2}. It was shown that complex \textbf{I-50} could activate CO\textsubscript{2} at ambient conditions affording the germylene formate compound \textbf{I-52} (Scheme 1-24).\textsuperscript{58e} The latter compound could further be converted into methanol and formic acid by treatment with NH\textsubscript{3}•BH\textsubscript{3} and LiNH\textsubscript{2}•BH\textsubscript{3}, respectively, after workup with water. Moreover, the reaction mechanism for the formation of methanol from \textbf{I-52} with NH\textsubscript{3}•BH\textsubscript{3} as a hydride source was proposed based on NMR spectroscopic studies. The authors suggested that the first step is the formate group transfer from the Ge(II) to the boron center of NH\textsubscript{3}•BH\textsubscript{3} affording H\textsubscript{3}N•BH\textsubscript{2}(-OCH(=O)) \textbf{I-53} with concomitant regeneration of L\textsuperscript{3}GeH. Species \textbf{I-53} is further reduced to H\textsubscript{3}N•BH\textsubscript{2}(OCH\textsubscript{2}O)BH\textsubscript{2}•H\textsubscript{3}N \textbf{I-54} and ultimately the reaction affords H\textsubscript{3}N•BH\textsubscript{2}(OCH\textsubscript{3}) \textbf{I-55} which is hydrolyzed with D\textsubscript{2}O affording methanol-d\textsubscript{1} as the final product (Scheme 1-24).\textsuperscript{63}
Scheme 1-24. Activation of CO$_2$ with germylene hydride I-50 and the proposed mechanism for CO$_2$ reduction to methanol-d$_1$ mediated by I-50 based on NMR spectroscopic studies.

1.3.2 Monovalent Group 13 (semi)metal hydrides

In contrast to divalent Group 14 metal hydrides, the chemistry of monovalent Group 13 (semi)metal hydrides is far less developed. Matrix isolation studies revealed that aluminum and gallium monohydride could be generated by treatment of elemental aluminum and gallium, respectively, under UV-light radiation in a dihydrogen atmosphere at low temperatures. These species are extremely reactive and tend to react readily with another equivalent of dihydrogen molecule to form the corresponding metal trihydrides at elevated temperatures.$^{[64]}$
The isolable monovalent Group 13 (semi)metal hydride complexes are exceptionally scarce. The only existing examples so far reported are (CAAC)₂BH I-56 (CAAC = cyclic (alkyl)(amino) carbene)\(^{[65]}\), the mixed carbene ligands stabilized hydridoboron(I) I-57\(^{[66]}\) and (tmeda)Ga(H)[Cr(CO)\(_5\)] I-58 \(^{[67]}\) reported by Bertrand et al. and Fischer et al., respectively (Scheme 1-25). The hydridoboron(I) moieties in I-56 and I-57 are stabilized by two neutral carbene ligands, whereas the Ga(I)–H in I-58 is stabilized by tmeda and a Cr(CO)\(_5\) moiety acting as an electron donor and an electron acceptor, respectively. Additionally, Robinson et al. reported the NHC-stabilized diborene complex I-59 which could be described as a dimer of (NHC)BH.\(^{[68]}\) Until now, Al(I)-monohydride and complexes thereof have still escaped isolation.

2. MOTIVATION

Before 1994, silylenes were just elusive species that attracted the attention of inorganic chemists. However, the situation has been changed dramatically during the last decades with a series of N-heterocyclic silylenes (NHSis) having been successfully isolated. These NHSis exhibited excellent performance in small molecule activations, as silicon sources for synthesizing unprecedented organosilicon compounds, and as supporting ligands for transition metal chemistry. One of the main interests of my dissertation is to explore the reactivities of the NHSis and their derivatives (thio- and selenosilanoic acids) towards Cu(I) reagents and to realize one chelate ligand bearing both the NHSi and N-heterocyclic carbene (NHC) moieties in its scaffold. The objectives of the work are (Chart 1):

- Gaining more structural information about the bonding features between the amindinato ligand L\(^1\) (PhC(NH\(\text{Bu}\)_2)) supported NHSis and copper(I) ions.
- Developing a novel methodology for preparing silyl-copper(I) complexes with various functional groups at the silicon centers through the insertion of the Si(II) of L\(^2\)Si: into the Cu–X bonds of copper(I) reagents, and probing their activities for CO\(_2\) reduction.
- Preparing a mixed chelate NHSi-NHC ligand supported Ni(II) [L\(^3\)Si(CH\(_2\)NHC)NiBr\(_2\)] (L\(^3\) = CH(MeC=NAr), Ar = 2,6-iPr\(_2\)C\(_6\)H\(_3\); NHC = 3,4,5-trimethylimidazol-2-yliden-6-yl). Investigating the reduction of the NHSi-NHC Ni(II) complex to Ni(0) complexes and evaluating its catalytic performance for nickel-catalyzed Kumada-Corriu type cross-coupling reactions.
- Utilizing the derivatives of the NHSi L\(^2\)Si\(_2\)_; the thio- and selenosilanoic acid-base adducts L\(^3\)Si(=E)(OH)(dmap) (E = S, Se; dmap = dimethylaminopyridine) as building blocks for synthesizing novel copper(I) complexes, and employing the copper(I) complexes as precatalysts for aziridination reaction.
Motivation

Chart 1. The reactions of NHSis and their derivatives towards copper(I) and nickel(II) reagents.

Low-valent main group element hydrides have attracted tremendous attention in contemporary organometallic chemistry, particularly owing to the pursuit of transition metal-free small molecule activations as well as homogeneous catalysis. The chemistry of low-valent main group hydrides is also a main research interest of my dissertation.

N-heterocyclic germylene hydrides have shown to be capable of activating CO$_2$ affording germylene formates, one of which ($L^3$GeH) could further be converted into methanol when BH$_3$•NH$_3$ was used as the hydride source after hydrolysis with water. However, there are only two examples of N-heterocyclic germylene hydrides known that can activate CO$_2$, and the mechanism for converting the germylene formate species into methanol in the presence of an exogeneous hydride source is still not well-understood. Thus, it is desirable to synthesize more germylene hydrides with different ligand scaffolds, and study the reaction mechanism in detail for germylene hydride mediated CO$_2$ reduction to methanol.

Inspired by the applications of divalent Group 14 element hydrides in small molecule activations, I was interested to synthesize their Group 13 element analogues. However, there
is a rather limited understanding of Group 13 (semi)metal(I) hydrides. As shown in the introduction part, there are only four examples of Group 13 metal(I) hydrides, and there is no report of isolable Al(I)-hydride and only one example of Ga(I)-hydride complex. Therefore, it would be interesting to prepare Al(I)-hydride and Ga(I)-hydride complexes in order to fill these gaps, and garner more structural and chemical information about these species.
3. RESULTS AND DISCUSSION

3.1 The reactivities of N-heterocyclic silylenes (NHSis) towards copper(I) reagents

3.1.1 Synthesis of mono- and dinuclear NHSi-copper(I) complexes

Owing to the novelty of the NHSi transition metal chemistry, there are still only a few complexes reported in comparison to the vast number of NHC metal complexes known to date. Most of the NHSi metal complexes that have been reported till now are of transition metals of the Groups 5 through 10, with NHSi Group 10 metal complexes being the most numerous. In contrast, NHSi Group 4 metal complexes are still very rare, and reports of NHSi group 11 or 12 metal complexes are also scant. Lappert and co-workers reported the first isolable NHSi copper(I) [(PPh₃)₂ICu(→:Si{N(CH₂Bu)}₂Ph)] complex featuring a tetrahedral copper(I) center through the reaction of the homoleptic NHSi 1-5b with [CuI(PPh₃)₃] under concomitant elimination of one PPh₃ ligand. In addition, Frenking and coworkers carried out theoretical studies on the stability and bonding situation of NHSi Cu, Ag and Au complexes.

Considering the apparent gap in NHSi Group 11 metal chemistry, it is desirable to synthesize more NHSi copper(I) complexes in order to garner more structural and spectroscopic information about these complexes as well as to understand more about their reactivities.

3.1.1.1 Synthesis of mononuclear NHSi copper(I) complexes

The amidinato-stabilized chlorosilylene L₁(Cl)Si: 1 (L₁ = PhC(N₆Bu)₂) has been widely utilized in transition metal chemistry, and it has shown to be a suitable supporting ligand to form a variety of NHSi transition metal complexes, including, for example Ti, V and Co, Cr, Mo and W, Mn and Re, or Fe. Considering the success of 1 in coordination chemistry, it was firstly employed as a ligand to explore the coordination chemistry of the NHSi towards copper(I) ions.

Accordingly, the reaction of 1 with the copper (I) precursor [Cu(tmeda)(CH₃CN)][OTf] (tmeda = N,N,N',N'-tetramethylethlenediamine, OTf = triflate) was carried out in toluene, and the expected NHSi copper(I) [L₁(Cl)Si:→Cu(tmeda)][OTf] complex 2 was formed as an
Results and Discussion

An ionic compound in high yield in a straightforward fashion. Complex 2 represents only the second example of an isolable NHSi copper complex (Scheme 2-1).

**Scheme 2-1.** Facile access to the amidinato-substituted NHSi copper (I) complex 2.

Prompt by the facile access to the NHSi copper(I) complex 2, the previously reported L\(^1\)(OtBu)Si: and L\(^1\)(NMe\(_2\))Si: \[^{[34a]}\] were further employed as NHSi ligands to react with [Cu(tmeda)(CH\(_3\)CN)][OTf], in order to explore how the substituent at the Si(II) center can influence the structural features of the respective NHSi copper(I) complexes. In analogy to the synthesis of complex 2, the reactions proceeded selectively in both cases affording the desired NHSi copper (I) \([L^1(OtBu)Si:\rightarrow Cu(tmeda)][OTf] \ (3) and [L\(^1\)(NMe\(_2\))Si:\rightarrow Cu(tmeda)][OTf] \ (4) complexes as colorless solids in good yields, respectively (Scheme 2-2).

**Scheme 2-2.** Facile access to the NHSi copper (I) complexes 3 and 4, respectively.

Complexes 2-4 were fully characterized by multinuclear \(\{^1\text{H}, ^{13}\text{C}, ^{19}\text{F}, ^{29}\text{Si}\}\}\) NMR spectroscopy, elemental analyses and single-crystal X-ray diffraction analyses. All three complexes exhibit singlet resonance signals in the \(^1\text{H}\) NMR spectra in CD\(_2\)Cl\(_2\) corresponding for the N\(_{\text{rBu}}\) protons of the coordinated NHSis (Table 2-1). This either indicates a highly symmetrical rigid structure or free-rotation of the coordinated NHSis on the NMR time-scale. Moreover, the expected two sets of resonance signals (NMe\(_2\) and NCH\(_2\)CH\(_2\)N) for TMEDA coordinated to the copper centers are also clearly observed in all three complexes as relatively broad signals. Complex 3 shows an additional singlet resonance
signal at $\delta = 1.51$ ppm corresponding to the protons of the OtBu group, while 4 exhibits an additional resonance signal at $\delta = 2.57$ ppm corresponding to the NMe$_2$ protons, in accordance with the expected structures for complexes 3 and 4 (Scheme 2-2). A key feature in the $^{13}$C{$^1$H} NMR spectra for the complexes is the somewhat deshielded chemical shift position of the amidinate NCN carbon nuclei, which seems to be rather invariant on changing the substituent on the Si center (Table 2-1).

**Table 2-1.** Summary of some key chemical shifts (in ppm, spectra recorded in CD$_2$Cl$_2$) observed in complexes 2-4.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{29}$Si{$^1$H}</th>
<th>$^1$H of tBu</th>
<th>$^{13}$C{$^1$H} of NCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>32.9</td>
<td>1.20</td>
<td>174.9</td>
</tr>
<tr>
<td>3</td>
<td>5.4</td>
<td>1.23</td>
<td>172.9</td>
</tr>
<tr>
<td>4</td>
<td>18.3</td>
<td>1.11</td>
<td>170.9</td>
</tr>
</tbody>
</table>

The most significant difference is the $^{29}$Si chemical shifts of complexes 2-4, which are revealed as sharp singlet resonance signals in the corresponding $^{29}$Si{$^1$H} NMR spectra (Table 2-1). This is most likely attributed to the changing of substituents attached to the Si(II) centers. In previous reports, for similar NHSi complexes of Ti$^{[46]}$ and Fe$^{[50b]}$ a negative correlation was found to exist between the values of chemical shift position in the $^{29}$Si{$^1$H} NMR spectra and the Hammet constant ($\sigma_p$)$^{[74]}$ of the substituents at the Si centers (where the substituents Cl, H and CH$_3$ were studied). In contrast, complexes 2-4 reveal no such correlation, and so these substituents do not obey this trend. However, complex 2 clearly exhibits the most deshielded Si nucleus in the series. While it is tempting to explain this by the presence of the electronegative Cl substituent in 2, resulting in electronic withdrawal from the Si(II) center, in a deshielded nucleus and concomitant increase in the chemical shift position. Whereas, both silicon atoms in complexes 3 and 4 bear electron-donating substituents OtBu and NMe$_2$, respectively, which lead to upfield shifted $^{29}$Si resonance signals in comparison to that of 2 (Table 2-1).

The molecular structures of these novel NHSi copper(I) complexes 2-4 were unambiguously determined by single-crystal X-ray diffraction analyses.$^{[75]}$ The single-crystals were obtained in all three cases in concentrated toluene solutions upon storage at $-30$ °C for 24 hours
Results and Discussion

(Figure 2-1 for 2 and Figure 2-2 for 3 and 4). The silicon atoms feature slightly distorted tetrahedral geometries in all three complexes. The Si–Cu bond lengths are somewhat comparable to each other within narrow limits: 2.1716(12)-2.2003(6) Å. This metrical parameter is clearly a reflection of the electronic effect of the featuring substituent at the Si center. This can be explained by the high s-character of the lone pair at the silicon atom of 2, resulting in a relatively short Si→Cu bond. A similar phenomenon was noted before in a series of iron complexes of the type [(dmpe)\(_2\)Fe←:Si(X)L)] (X = Cl, H, CH\(_3\)) (dmpe = 1,2-bis(dimethylphosphino)ethane) for X = Cl\(^{[50b]}\) and also for a series of aluminum and gallium complexes by Fischer, Frenking and co-workers, the latter work also contained detailed theoretical calculations elucidating the effect of s-character of the lone pair of electrons at the aluminum or gallium on Al–M or Ga–M bond length.\(^{[67]}\) The authors explained that the high s character results in a more ‘compact’ lone pair of a donor center and concomitant a bond length contraction upon coordination to a metal ion.

![Figure 2-1](image_url)

**Figure 2-1.** ORTEP representation of the molecular structure of 2. Thermal ellipsoids set at the 50 % probability level, H atoms and counter anion omitted for clarity. Selected bond lengths and angles [\(^\circ\)] (Å): Cl1–Si1 2.1198(15), Si1–N1 1.828(3), Si1–N2 1.839(3), Si1–Cu1 2.1716(12), Cu1–N3 2.102(3), Cu1–N4 2.136(3) Cu1–O2 2.312 Å; N1–Si1–N2 71.13(13), N1–Si1–Cl1 101.44(12), N2–Si1–Cl1 101.57(11), N1–Si1–Cu1 125.11(11), N2–Si1–Cu1 128.61(11), Cl1–Si1–Cu1 118.24(6), N1–Si1–C7 35.81(12), N2–Si1–C7 35.51(12), Cl1–Si1–C7 106.92(10), Cu1–Si1–C7 134.77(11), N3–Cu1–N4 85.58(12).
Results and Discussion

**Figure 2-2.** ORTEP representation of the cations in complex 3 (left) and 4 (right). Thermal ellipsoids set at the 50% probability level, H atoms and counter anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: 3: Cu1−N4 2.0876(17), Cu1−N3 2.1058(16), Cu1−Si1 2.2003(6), N1−Si1 1.8528(16), N2−Si1 1.8345(18), O1−Si1 1.6406(14); N4−Cu1−N3 85.78(7), N4−Cu1−Si1 142.49(5), N3−Cu1−Si1 131.51(5), O1−Si1−N2 102.79(8), O1−Si1−N1 105.69(7), N2−Si1−N1 70.94(7), O1−Si1−Cu1 128.89(6), N2−Si1−Cu1 118.49(6), N1−Si1−Cu1 115.01(5). 4: Cu1−N4 2.101(3), Cu1−N3 2.125(4), Cu1−Si2 2.1981(12), Si2−N5 1.710(4), Si2−N1 1.854(3), Si2−N2 1.870(4); N4−Cu1−N3 85.59(14), N4−Cu1−Si2 139.03(10), N3−Cu1−Si2 135.23(10), N5−Si2−N1 106.05(16), N5−Si2−N2 107.82(17), N1−Si2−N2 69.85(15), N5−Si2−Cu1 120.21(14), N1−Si2−Cu1 122.34(11), N2−Si2−Cu1 119.77(11).

Of particular interest is the trigonal-planar coordination geometry of the copper(I) centers in complexes 3 and 4, evidenced by the sum of angles around the copper atom of ca. 360°. However, this is notably not the case for complex 2, which deviates from trigonal planarity at the copper center as shown by the sum of angles of 348.72°. This difference, is a result of the rather short contact distance, in the solid state, between the copper center in the cation and one of the oxygen atoms of the OTf⁻ counter anion (d = 2.312 Å). Hence, complex 2 is a contact ion pair in the solid state. This is particularly interesting, since it is likely a result of the increased Lewis acidity of the Cu(I) center in 2, influenced by the electron-withdrawing chloro substituent of the coordinated NHSi ligand (Figure 2-1). Complex 3, in contrast to the case of complex 2, exhibits a very large separation between the copper center and the O atom of the OTf⁻ anion, while in complex 4 a Cu−O distance of 3.277 Å is observed as a result of electrostatic interaction. These results further highlight that changing the substituent at the Si center can not only cause significant electronic change of the donor properties of the NHSi.
ligands, but also influence greatly the interaction of the complex cation and counter anion in the solid state structures of the NHSi metal complexes.

3.1.1.2 Synthesis of dinuclear N-heterocyclic silylene copper(I) complex

Intrigued by the facile access to the NHSi copper(I) complexes 2-4 with monodentate NHSi ligands, I further tried to explore the reactivity of a bidentate NHSi ligand towards copper(I), targeting the isolation of a bisNHSi-Cu(I) complex. Therefore, the bidentate bisNHSi :Si(L\textsuperscript{1})(O)(L\textsuperscript{1})Si: 5 bearing an oxo bridge between the two silicon(II) centers and [Cu(CH\textsubscript{3}CN)\textsubscript{4}]OTf\textsuperscript{76} were employed as starting materials. Accordingly, the reaction of 5 with one molar equivalent of [Cu(CH\textsubscript{3}CN)\textsubscript{4}]OTf in toluene at room temperature afforded the dinuclear NHSi copper(I) complex 6 selectively featuring a metallacyclooctane core (Scheme 2-3). Complex 6 was isolated as a colorless solid in high yield in a concentrated toluene solution at −20 °C. It is noteworthy that the bisNHSi 5 has previously shown to be a suitable chelate ligand for preparing the bisNHSi-Ni(0) [:Si(L\textsuperscript{1})(O)(L\textsuperscript{1})Si:]Ni(cod) (cod = cyclooctadiene) complex,\textsuperscript{77} which is an active precatalyst for Kumada-Corriu and Nigishi-type cross-coupling reactions.\textsuperscript{53b}

![Scheme 2-3. Synthesis of the dinuclear NHSi copper(I) complex 6. (6 is represented as a charge separated salt for simplicity, although OTf does interact with the Cu centers both in the solid state and in solution).](image)

Complex 6 has been characterized by NMR spectroscopy, elemental analysis as well as single-crystal X-ray diffraction analysis. The multinuclear NMR spectra of complex 6, at ambient temperature in CD\textsubscript{2}Cl\textsubscript{2}, suggest a fluxional solution behavior of the triflate counter anions in addition to a discrete charge separated dication coexisting in solution. For instance, in the \textsuperscript{1}H NMR spectrum, two signals (one broad, and one sharp) corresponding to the \textit{t}Bu groups of the amidinato ligand are observed, with an integral ratio of approximately 1: 0.63.
Results and Discussion

(Figure 2-3). The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra exhibits two resonance signals, with one sharp ($\delta = 3.26$) and one broad ($\delta = 7.73$ ppm) (Figure 2-3). Both of these signals are downfield shifted in comparison to that of the ‘free’ bisNHSi 5, which features a resonance signal at $\delta = -16.1$ ppm, clearly indicating the coordination of the silicon(II) centers to copper(I) ions. Moreover, two signal sets are also observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, exemplified by the NCN signals which appears at $\delta = 172.8$ and 174.9 ppm, the latter also being somewhat broadened. Collectively, these data clearly indicate the presence of two species in solution. The sharp signals correspond most likely to the discrete charge separated ion pair of $[\text{Cu}_2\{\eta^1, \eta^1-L\text{Si(\mu-O)SiL}\}_2]^{2+}$. The latter dication is highly symmetric and should exhibit a single resonance signal in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum, and one set of signals in the $^1\text{H}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, respectively. The broad components in the spectra are hence attributed to the dynamic coordination/de-coordination of the OTf$^-$ counter anion to the dication $[\text{Cu}_2\{\eta^1, \eta^1-L\text{Si(\mu-O)SiL}\}_2]^{2+}\ldots(\text{OTf})_n^-, n = 1$ or 2). These findings are akin to recently reported Cu(I) complexes featuring chelating pyrazole ligands, which also feature similar dynamic behavior of a coordinating iodide anion.$^{[78]}

![Figure 2-3. $^1\text{H}$ (left) and $^{29}\text{Si}\{^1\text{H}\}$ (right) NMR spectra of complex 6 in CD$_2$Cl$_2$ solutions at 298 K.](image)

Crystals of complex 6 suitable for single-crystal X-ray diffraction analysis were obtained in a THF / hexane solutions (2:1 v:v) upon standing at room temperature for 24 hours. The solid state structure of 6 is depicted in Figure 2-4. The asymmetric unit possesses one molecule bearing a symmetry operation rendering half of it metrically invariant to the other (symmetry element $C_s$). The compound bears a unique dicationic metallacyclooctane ring with the elements copper, silicon and oxygen.$^{[79]}$ The two OTf$^-$ counter anions are strongly associated with the copper centers, evidenced by a rather short Cu–O (O atom of SO$_3$) bond length of 2.141 Å, rendering 6 a contact ion pair, akin to what was observed in complex 2 ($\text{vide supra}$: d(Cu–O) = 2.312 Å).
Figure 2-4. ORTEP representation of complex 6 in the solid state. Thermal ellipsoids set at the 50 % probability, H atoms omitted for clarity. Operation symmetric: -x+1, -y, -z+1. Selected bond lengths [Å] and angles [°]: Cu1–O2 2.141(4), Cu1–Si1 2.2719(13), Cu1–Si2 2.2853(14), Si1–O1 1.642(3), Si1–N2 1.845(4), Si1–N1 1.859(4), Si2–O1 1.639(3), Si2–N3 1.846(4), Si2–N4 1.863(4); O2–Cu1–Si1 115.39(12), O2–Cu1–Si2 99.85(12), Si1–Cu1–Si2 143.90(5), O1–Si1–N2 103.16(17), O1–Si1–N1 104.91(17), N2–Si1–N1 70.58(17), O1–Si1–Cu1 119.02(13), N2–Si1–Cu1 127.73(13), N1–Si1–Cu1 120.78(13).
3.1.2 Synthesis of silyl-copper(I) complexes and their application in CO₂ reduction to CO

In the previous part, the coordination of NHSis towards copper(I) ions have been discussed. Except for the coordination of an NHSi to a transition metal center via Si(II)→M interaction, the divalent silicon can also active the M–X bond (X = H, C, O etc.) of organometallic reagents yielding the corresponding silyl-metal complex with a X group at the silicon center. As discussed in the introduction part, the zwitterionic NHSi $L^2Si$: 7 can facilely activate the M–H and M–C bonds (M = Li, Zn, Al and Ir) of the organometallic reagents affording the respective silyl-metal complexes. Therefore, it would be desirable to explore the reaction of 7 with other metal complexes in an attempt to isolate some more interesting silyl-metal complexes, such as silyl-copper(I) complexes. Recently, the NHC stabilized silyl-copper(I) complex (IPr)Cu-SiMe₂Ph (IPr = (CHNAr)₂, Ar = 2,6-iPr₂C₆H₃) has proven to be an important intermediate in copper-mediated CO₂ reduction to CO with (IPr)CuOttBu as a precatalyst and PhMe₂Si-Bpin {Bpin = B[OC(CH₃)₂]₂} as an oxygen scavenger (Scheme 2-4). The computational investigation carried out by Yates et al. revealed that the nucleophilic attack of the electrophilic carbon of CO₂ with the silyl group is the rate-determining step in the catalytic process.

\[
\begin{align*}
\text{Ar} &\text{CuOttBu} \\
\text{Ar} &\text{Cu-SiMe₂Ph} \\
\text{pinB} = &\text{B[OC(CH₃)₂]₂} \\
\text{Ar} = &2,6-iPr₂C₆H₃
\end{align*}
\]

\[
\begin{align*}
\text{PhMe₂Si-Bpin} &\xrightarrow{-\text{pinB-OttBu}} \\
\text{CO₂} &\xrightarrow{\text{CO}} \\
\text{PhMe₂Si-Bpin} &\xrightarrow{-\text{pinB-OSiMe₂Ph}} \\
\text{Cu-OSiMe₂Ph}
\end{align*}
\]

**Scheme 2-4.** Reduction of CO₂ to CO mediated by the NHC silyl-copper(I) complex.

However, until now, no experimental work elucidating the effect of the nucleophilicity of the silyl group of the silyl-copper(I) complex on the activity of CO₂ reduction to CO has ever been demonstrated. This is likely due to the difficulties in introducing various functional groups at the silicon centers, which can tune the nucleophilicity of the silyl groups. Traditionally, the silyl-copper(I) complexes are prepared by the transmetalation reaction of
Results and Discussion

copper(I) salts with alkaline metal silyl reagents \[^{[82]}\] or through metathesis reaction of copper(I) alkoxide complexes with silylboranes \[^{[80]}\]. However, these organosilicon reagents are highly reactive, so the introduction of some special functional groups, such as OH and H, into silyl-copper(I) complexes is experimentally challenging. Since the silyl-metal complexes are readily accessible through the M−X bond activation with NHSi 7, it might be possible to prepare silyl-copper(I) complexes bearing different functional groups on the silicon centers by the activation of Cu−X bonds of copper(I) reagents with 7. In this chapter, the facile synthesis of a series of silyl-copper(I) complexes \(L^2\text{Si}(X)\text{Cu}(\text{IPr})\) (X = OtBu, OH, H and OC\(_6\)F\(_5\); IPr = (CHNAr)\(_2\), Ar = 2,6-\(i\)Pr\(_2\)C\(_6\)H\(_3\)) through the Cu−O and Cu−H bonds activation of the (IPr)CuX complexes with NHSi 7 is discussed. More importantly, those silyl-copper(I) complexes bear different functional groups on the silicon centers, rendering different nucleophilic nature of the silyl-groups. This leads to different activities of these complexes in CO\(_2\) reduction to CO, and the results suggest that the silyl-copper(I) complex bearing a stronger nucleophilic silicon center has a higher activity for this reaction.

3.1.2.1 Synthesis of the silyl-copper(I) complexes

The activation of Cu−O bond of (IPr)CuOtBu \[^{[83]}\] (IPr = (CHNAr)\(_2\), Ar = 2,6-\(i\)Pr\(_2\)C\(_6\)H\(_3\)) with NHSi 7 was firstly investigated. Accordingly, the reaction of (IPr)CuOtBu with one molar equivalent of 7 was carried out in toluene from \(-20^\circ\text{C}\) to room temperature. The \(^1\)H NMR spectrum of the reaction mixture in benzene-\(d_6\) indicated a clean reaction with only one new \(\gamma\)-H signal of the \(L^2\) ligand. From the reaction mixture after workup, the expected silyl-copper(I) \(L^2\text{Si}(\text{OtBu})\text{Cu}(\text{IPr})\) complex 8 bearing a OtBu group on the silicon center could readily be isolated as a colorless crystalline solid in 78\% yield (Scheme 2-5).

\[
\begin{align*}
\text{N} & \text{N} \quad \text{N} & \text{N} \\
\text{Si} & \text{Ar} & \text{Cu} & \text{X} \\
\text{Ar} & \text{Ar} & \text{Ar} & \text{Ar}
\end{align*}
\]

\(7\)

\(Ar = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\)

\[
\begin{align*}
\text{N} & \text{N} \quad \text{N} & \text{N} \\
\text{Si} & \text{Cu} & \text{X} & \text{Ar} \\
\text{Ar} & \text{Ar} & \text{Ar} & \text{Ar}
\end{align*}
\]

\(8\): X = OtBu

\(9\): X = OH

\(10\): X = H

\(11\): X = OC\(_6\)F\(_5\)

\textbf{Scheme 2-5.} Syntheses of the copper(I)-silyl complexes 8-11 through the Cu−O and Cu−H bonds activation of (IPr)CuX (X = OtBu, OH, H and OC\(_6\)F\(_5\)) with the NHSi 7.
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The facile access to compound 8 is striking, and it suggests that various functional groups can be introduced to the silyl-copper(I) complexes since a large number of (NHC)copper(I) compounds are available from literature. Therefore, the silyl-copper(I) complexes bearing a range of functional groups at the silicon centers, such as hydroxyl or hydride groups, were targeted. For this purpose, (IPr)CuOH, (IPr)CuH and (IPr)CuOC\textsubscript{6}F\textsubscript{5} containing electron-dонating OH and electron-withdrawing OC\textsubscript{6}F\textsubscript{5} groups were chosen as starting materials. (IPr)CuOH has shown to be an elegant reagent to activate and functionalize Y–H bond containing substrates (Y = C, O, P, S), while (IPr)CuH is considered to be a key intermediate in copper(I)-catalyzed hydrosilylation and hydroborylation reactions.

Accordingly, treatments of (IPr)CuOH, (IPr)CuH (in situ prepared according to the published procedure) and (IPr)CuOC\textsubscript{6}F\textsubscript{5} with one molar equivalent of the NHSi 7 in toluene cleanly afforded compounds \( \text{L}^{2}\text{Si(OH)}\text{Cu(IPr)} \), \( \text{L}^{2}\text{Si(H)}\text{Cu(IPr)} \) and \( \text{L}^{2}\text{Si(OC}_{6}\text{F}_{5})\text{Cu(IPr)} \) as colorless crystalline solids in good yields (76% for 9, 68% for 10, 74% for 11), respectively (Scheme 2-5). Compounds 8-10 are soluble in toluene and THF, marginally soluble in n-hexane, whereas compound 11 is soluble in all hydrocarbon solvents. Complexes 8-10 are thermally robust with relatively high decomposition temperatures (8: 254 °C; 9: 271 °C; 10: 242 °C), but rather air sensitive with decomposition upon exposure to air after several minutes.

Compounds 8-10 have been fully characterized by multinuclear \( ^{1}\text{H},^{13}\text{C}\{^{1}\text{H}\},^{29}\text{Si}\{^{1}\text{H}\} \) NMR spectroscopy, mass spectrometry, IR spectroscopy and elemental analyses, as well as single-crystal X-ray diffraction analyses. All of the \( ^{1}\text{H} \) NMR spectra (in THF-d\textsubscript{8}) of 8-11 are similar and feature two singlet resonance signals for the protons at the exocyclic methylene groups (8: \( \delta = 2.44, 3.18 \) ppm; 9: \( \delta = 2.13, 2.99 \) ppm; 11: \( \delta = 2.25, 3.13 \) ppm; 12: \( \delta = 2.37, 3.29 \) ppm), which is in accordance with the expected results for the 1,1-addition products obtained from the insertions of the Si(II) atom of 7 into Cu–O and Cu–H bonds of the substrates. The resonance signal for the protons of the OrBu group in 8 is observed at \( \delta = 0.20 \) ppm that is upfield shifted in comparison to that of the reactant (IPr)CuOrBu (\( \delta = 1.33 \) ppm).\textsuperscript{83} The proton of the OH group of 9 resonates at \( \delta = 3.12 \) ppm, and the Si–H proton resonance signal of 10 is located at \( \delta = 5.46 \) ppm with \( ^{29}\text{Si} \) satellites \( ^{1}J_{\text{Si}, \text{H}} = 149.5 \text{ Hz} \) in the corresponding \( ^{1}\text{H} \) NMR spectra. The stretching vibration mode of the Si–H bond of 10 is revealed at \( \nu = 1957 \text{ cm}^{-1} \) in the IR spectrum.

The molecular structures of complexes 8-10 were unambiguously determined by single-crystal X-ray diffraction analyses, and they are depicted in Figure 2-5.\textsuperscript{75} Suitable crystals
could be obtained in concentrated toluene solutions at 0 °C. Compound 8 crystallizes in the monoclinic space group \(P2_1/n\) with one toluene molecule in the unit cell. The silicon atom is tetrahedrally coordinated by N1, N2, O1 and Cu1. The Si1–N1 (1.795(3) Å) and Si1–N2 (1.806(3) Å) bond lengths are slightly longer than those in \(L^2\text{Si}(\text{Me})\text{Al}(\text{THF})\text{Me}_2\) (1.775(3) Å, 1.778(3) Å), which was prepared by the reaction of 7 with AlMe₃ in THF.\(^{[88]}\) The Cu1 atom is almost linearly coordinated by Si1 and C34 atoms with the Si1–Cu1–C34 bond angle of 174.20(11)°. The Cu1–C34 bond length (1.961(4) Å) is longer than those in NHC stabilized copper(I) complexes (1.862(10)-1.911(4) Å),\(^{[84b]}\) this is likely attributed to the steric hindrance from the bulky β-diketiminato ligand and the NHC (IPr) moiety. The Cu1–Si1 (2.2977(13) Å) distance is slightly shorter than those in \((\text{tBu}_3\text{Si})_2\text{CuNa}(\text{THF})_4\) (2.3581(13) and 2.3638(13) Å)\(^{[89]}\) and \((\text{PMe}_3)_2\text{CuSiPh}_3(2.340 (2) \text{ Å})\).\(^{[90]}\)

**Figure 2-5.** Molecular structures of compounds 8-10 (a-c). Thermal ellipsoids are drawn at 50% probability level and the Ar groups (Ar = 2,6-\text{iPr}_2\text{C}_6\text{H}_3) are drawn in a framewire style. The hydrogen atoms (except those at C1 in 8, O1 and C5 in 9, Si1 and C5 in 10) and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): 8: Cu1–C34
1.961(4), Cu1–Si1 2.2977(13), Si1–O1 1.665(3), Si1–N1 1.795(3), Si1–N2 1.806(3), C1–C2 1.351(5), C2–C3 1.464(5), C3–C4 1.362(5), C4–C5 1.509(6); C34–Cu1–Si1 174.20(11), O1–Si1–N1 103.18(16), O1–Si1–N2 103.42(15), N1–Si1–N2 97.31(16), O1–Si1–Cu1 111.10(12), N1–Si1–Cu1 116.41(12), N2–Si1–Cu1 122.83(13). 9: Si1–O1 1.686(3), Si1–N1 1.780(3), Si1–N2 1.780(3), Cu1–Si1 2.3248(10), Cu1–C30 1.964(3), C1–C2 1.469(5), C2–C3 1.375(5), C3–C4 1.423(5), C4–C5 1.389(5); C34–Cu1–Si1 172.94(10), O1–Si1–N1 101.42(13), O1–Si1–N2 104.28(13), N1–Si1–N2 99.10(13), N2–Si1–Cu1 119.93(10), N2–Si1–Cu1 119.33(10). 10: Si1–N1 1.789(2), Si1–N2 1.789(2), Si1–Cu1 2.3052(8), Cu1–C30 1.964(3); N1–Si1–Cu1 118.42(8), N2–Si1–Cu1 119.40(8), C30–Cu1–Si1 173.97(8).

Complexes 9 and 10 are isostructural, and crystallize isotopically in the monoclinic space group $P2_1/c$. In complex 9, the silicon atom is attached to a hydroxyl group, whereas in complex 10 it is coordinated to a hydrogen atom. As expected, all the remaining metrical parameters of compounds 9 and 10 are comparable to each other within narrow limits. Notably, the six-membered $C_3N_2Si$ ring in 9 and 10 is slightly puckered, and the Si1 and O1 atoms in 9 and Si1 and H1 in 10 are on the same side of the plane defined by N2C2C3C4N1, respectively. However, this is not the case for compound 8, in which the Si1 and O1 atoms are on different sides (Figure 2-5). This is likely due to the bulkiness of the OtBu group in complex 8, which, due to the steric repulsion with the bulky aromatic (Ar = 2,6-iPr$_2$C$_6$H$_3$) groups of the $\beta$-diketiminato ligand and IPr moiety, makes them ‘bend’ away from each other. The complexes 8-11 represent the first examples of silyl-copper(I) complexes bearing various functional groups at the silicon center, particularly complexes 9 and 10 feature the reactive hydroxyl and hydride groups at the respective silicon centers. Unfortunately, attempts to isolate crystals of 11 suitable for single-crystal X-ray diffraction analysis were hitherto unsuccessful.

**Table 2-2.** $\delta^{29}$Si) NMR values of 8-11 in THF-$d_8$ and 12-15 in benzene-$d_6$ at 298 K and comparison with Hammett constants ($\sigma_p$) of the substituents at the silicon atom.

<table>
<thead>
<tr>
<th>Complexes (X)</th>
<th>$\delta^{29}$Si (ppm)</th>
<th>Hammett Constant ($\sigma_p$)</th>
<th>Complexes (X)</th>
<th>$\delta^{29}$Si (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 (OtBu)</td>
<td>-9.4</td>
<td>-0.27</td>
<td>12 (OtBu)</td>
<td>-80.7</td>
</tr>
<tr>
<td>9 (OH )</td>
<td>-11.9</td>
<td>-0.37</td>
<td>13 (OH)</td>
<td>-71.4</td>
</tr>
<tr>
<td>10 (H)</td>
<td>-4.7</td>
<td>0</td>
<td>14 (H)</td>
<td>-59.6</td>
</tr>
<tr>
<td>11 (OC$_6$F$_5$)</td>
<td>-10.9</td>
<td>Not reported</td>
<td>15 (OC$_6$F$_5$)</td>
<td>-81.9</td>
</tr>
</tbody>
</table>

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The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of 8, 9, 11 and the $^{29}\text{Si}$(INEPT) NMR spectrum of 10 in THF-$d_8$ show single resonance signals in all cases (Table 2-2). They are upfield shifted when compared to that of NHSi 7 ($\delta = 88.4$ ppm), but are comparable to that observed for L$_2^2\text{Si}(\text{Me})\text{Al(THF)}\text{Me}_2$ ($\delta = -7.2$ ppm). The $^{29}\text{Si}$ nuclei chemical shifts for 8-10 also show a good correlation to the Hammett constant ($\sigma_p$) of the substituents at the silicon centers (Table 2-2). The direct correlation of the $^{29}\text{Si}$ nuclei chemical shifts to $\sigma_p$ suggests that the inductive and resonance effects of the substituents are contributory to the $\delta(29\text{Si})$ values. The complexes 8 and 9 have similar chemical shifts, and they are upfield shifted when compared to that of 10. This suggests that the silicon nuclei of complexes 8 and 9 are more shielded when compared to that of 10. This is due to the electron-donating OrBu and OH groups attached to the silicon centers in 8 and 9, respectively, whereas compound 10 has a hydrogen atom at the silyl group. The $^{29}\text{Si}$ chemical shift of 11 in THF-$d_8$ is at $\delta = -10.8$ ppm and thus upfield shifted compared to that of 10, although complex 11 bears an electron-withdrawing OC$_6$F$_5$ group at the silicon center. This is mainly due to the shielding effect from the aromatic C$_6$F$_5$ ring, which off-sets the deshielding through electron withdrawal.

3.1.2.2 Probing the activity of the silyl-copper(I) complexes 8-11 towards CO$_2$ reduction

As the functional groups at the silicon centers of compounds 8-11 feature different electronic effects, the respective silyl groups concomitantly exhibit different nucleophilicity. Therefore, in order to elucidate how the nucleophilicity of the silyl groups could effect the activities for CO$_2$ reduction to CO, the novel silyl-copper(I) complexes 8-11 were employed as starting materials for CO$_2$ reduction.

![Scheme 2-6](image)

Scheme 2-6. Reduction of CO$_2$ to CO with 8-11 affording the siloxy-copper(I) complexes 12-15, respectively.
Accordingly, the reductions of CO$_2$ with complexes 8-11 were carried out in toluene under strictly controlled reaction conditions in each case (in a CO$_2$ atmosphere (1 atm), Scheme 2-6). All compounds 8-11 turned out to be very efficient in the reduction of CO$_2$ to CO. Based on the $^1$H NMR spectroscopic studies, of the reactions under the analogous conditions, compounds 8 and 9 were consumed much faster than compounds 10 and 11. A similar time (less than 5 min)$^{[91]}$ for reaction completion in the case of 8 and 9 was observed, whereas for complexes 10 and 11, the reactions were completed within 40 min and 250 min, respectively. The kinetic studies with $^1$H NMR spectroscopy revealed that the reductions of CO$_2$ with 10 and 11 were zero-order reactions with respect to the silyl-copper(I) complexes, with determined reaction rate constants of $7.8 \times 10^{-6}$ mol•L$^{-1}$•s$^{-1}$ and $2.7 \times 10^{-8}$ mol•L$^{-1}$•s$^{-1}$, respectively (Figure 2-6). The computational studies by Yates et al. suggested that the nucleophilic attack of the electrophilic carbon of CO$_2$ with the silyl group was the rate-determining step in CO$_2$ reduction to CO.$^{[81]}$ Complexes 8 and 9 contain the electron-donating groups OtBu and OH at the silicon centers, respectively, whereas compound 11 bears the electron-withdrawing OC$_6$F$_5$ group. Consequently, the nucleophilicity of the silyl groups in complexes 8-11 approximate: 8 ($\approx$ 9) $>$ 10 $>$ 11. This nucleophilicity trend is consistent with the reactivity towards CO$_2$ reduction to CO which indicates that the stronger nucleophilicity of the silyl group is, the higher activity the silyl-copper complex has in CO$_2$ reduction to CO.

![Figure 2-6](image_url)  

**Figure 2-6.** Dynamic plots of the reactions of 10 and 11 with CO$_2$ in benzene-d$_6$ at 298 K determined by $^1$H NMR spectroscopy.

Attempts to isolate the potential intermediates in the reduction process, as proposed by Yates et al., failed owing to the high activity of 8-11 towards CO$_2$.$^{[81]}$ The only isolable products were the siloxy-copper(I) complexes 12-15 as depicted in Scheme 2-6, which are the final species in CO$_2$ reduction to CO mediated by silyl-copper(I) complexes. Complexes 12-
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15 were also fully characterized by spectroscopic and structural methods. In addition, the formation of CO has been determined by the reaction of $^{13}$CO$_2$ with compound 8 in a sealed off NMR tube in benzene-d$_6$, as the characteristic resonance for CO could be observed at $\delta = 179$ ppm in the $^{13}$C\{\textsuperscript{1}H\} NMR spectrum.$^{[84c]}$ The formation of 15 was confirmed by NMR spectroscopy and high resolution mass spectrometry (calcd.: m/z 1095.5026; found: m/z 1095.4974), however, attempts to obtain single-crystals of 15 suitable for X-ray diffraction analysis were unsuccessful.

Complexes 12-14 were isolated as colorless solids in high yield from concentrated toluene solutions at –20 °C and they are soluble in THF and toluene, whereas they are moderately soluble in benzene. The resonance signal for the protons at OtBu group in complex 12 is located at $\delta = 0.64$ ppm in the $^1$H NMR spectrum, the corresponding carbon resonance signals for OC(CH$_3$)$_3$ and OC(CH$_3$)$_3$ are observed at $\delta = 31.6$ ppm and $\delta = 71.1$ ppm in the $^{13}$C\{\textsuperscript{1}H\} NMR spectrum, respectively. The proton of the hydroxyl group in complex 13 resonates at $\delta = 1.42$ ppm, while the proton signal of the Si–H group in complex 14 is observed at $\delta = 5.08$ ppm flanked by the $^{29}$Si satellites ($^1$J(Si, H) = 250.1 Hz) in the $^1$H NMR spectrum. This indicates the retention of the Si–H group in compound 14 and that it is not involved in the reduction of CO$_2$.

As expected, all the silicon chemical shifts of complexes 12-15 are in the range of the resonances for four coordinate Si(IV) atoms ($\delta = -80.7$, –71.4, –59.6 and –81.9 ppm, respectively) (Table 2-2). The $^{29}$Si chemical shift of 14 is lower-field shifted in comparison to those of complexes 12, 13 and 15.

Single crystals of 12, suitable for X-ray diffraction analysis were obtained by slow diffusion of n-hexane into a CH$_2$Cl$_2$ solution at room temperature for 3 days. The molecular structure is portrayed in Figure 2-7 (a). It crystallizes in the monoclinic space group P2$_1$/n. According to the molecular structure, an oxygen atom is bounded to the silicon and copper atoms. Thus, the silicon center has a tetrahedral coordination geometry, and the copper atom is linearly coordinated by O1 and C30. The Si–N bond distances (1.736(5) and 1.752(5) Å) are comparable to those in compound 8 (1.795(3) and 1.806(3) Å). Unexpectedly, the Si1–O1 (1.568(4) Å) bond length is much shorter than that of Si1–O2 (1.621(4) Å), and the former is close to the Si–O bond distance (ca. 1.54 Å) in silanones which bear a Si=O bond.$^{[92]}$ Moreover, the angle of Si1–O1–Cu1 (152.9(2)$^\circ$) is larger than that of a typical sp$^3$ hybridized oxygen atom. This is similar to the case of the L$^3$Al(Me)OYbCp$_2$ (L$^3$ = CH(MeCNAr$_2$)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) complex, which has a nearly linear geometry (Al–O–Yb 169.5$^\circ$) for the oxygen
atom due to the $\pi$-donation of electrons in the 2p orbital of oxygen to the highly Lewis acidic metal center.\cite{93}

Figure 2-7. Molecular structures of compounds 12-14 (a-c). Thermal ellipsoids are drawn at 50% probability level and the Ar groups (Ar = 2,6-iPr$_2$C$_6$H$_3$) are drawn in a framewire style. H atoms (except those at C1 for 12 and 13, C5 and Si1 for 14) are omitted for clarity. Selected bond lengths (Å) and angles (deg): 12: Cu1–O1 1.816(4), Cu1–C30 1.877(6), Si1–O1 1.568(4), Si1–O2 1.621(4), Si1–N1 1.736(5), Si1–N2 1.752(5), C1–C2 1.383(8), C2–C3 1.431(8), C3–C4 1.359(8), C4–C5 1.496(7); O1–Cu1–C30 175.8(2), O1–Si1–O2 114.2(2), O1–Si1–N1 116.2(2), O2–Si1–N1 104.7(2), O1–Si1–N2 113.1(2), O2–Si1–N2 106.0(2), N1–Si1–N2 101.3(2), Si1–O1–Cu1 152.9(2). 13: Cu1–O1 1.793(2), Cu1–C30 1.849(3), Si1–N1 1.735(2), Si1–N2 1.740(3), Si1–O2 1.653(2), Si1–O1 1.557(2), C1–C2 1.383(4), C2–C3 1.441(4), C3–C4 1.376(4), C4–C5 1.479(4); O1–Cu1–C30 178.14(13), O1–Si1–O2 113.96(14), O1–Si1–N1 111.71(13), O2–Si1–N1 108.97(12), O1–Si1–N2 113.92(12), O2–Si1–N2 104.67(13), N1–Si1–N2 102.80(13), Si(1)–O(1)–Cu(1) 153.33(18). 14: Cu1–O1 1.7669(15), Cu1–C26 1.822(2), Si1–O1 1.5756(16), Si1–N2 1.7210(18), Si1–N1 1.7342(18),
O1–Cu1–C26 177.17(8), O1–Si1–N2 111.98(8), O1–Si1–N1 113.02(9), N2–Si1–N1 103.17(9), Si1–O1–Cu1 140.94(10).

Single crystals of complexes 13 and 14 were grown in concentrated toluene solutions at room temperature, and the results of X-ray crystallographic analyses are depicted in Figure 2-7 (b and c, respectively). Complex 13 crystallizes in the monoclinic space group $P2_1/c$ with one toluene molecule in the unit cell, while complex 14 crystallizes in the monoclinic space group $P2_1/n$. The geometry of the silicon and copper atoms in complexes 13 and 14 are in accordance with those in complex 12. As expected, all metric parameters of the corresponding bond lengths and angles of 13 and 14 are akin to those of compound 12.
3.2 The reactivities of the derivatives of N-heterocyclic silylenes with nickel(II) and copper(I) reagents

3.2.1 From an N-heterocyclic silylcarbene to chelate NHSi-NHC nickel(0, II) complexes

As discussed in the introduction part, NHSis are emerging as a novel class of versatile steering ligands in the coordination chemistry of the transition metals, and their complexes have demonstrated remarkable features in small molecule activation and as precatalysts for various types of organic transformations. N-heterocyclic carbenes (NHCs) represent one of the most widely utilized supporting ligands in transition metal chemistry in the last decades.\textsuperscript{[5a-c, 84d, 94]} These NHC metal complexes have exhibited numerous superior activities in comparison to related phosphine complexes owing to the stronger σ-donor ability of the NHC ligands.\textsuperscript{[6]}

According to previous studies, NHSi and NHC can exceed drastically the σ-donor ability of phosphines and feature strong trans effect. Combining these two ligand types in one chelate molecule could enable new coordination features at transition metal centers. Moreover, the presence of both strong σ-donating moieties might facilitate the coordination and dissociation of other ligands thereby improving the activity or catalytic performance of the respective transition metal complexes. However, until now no such mixed ligand system or a respective transition metal complex has been reported. The difficulty to synthesize a mixed NHSi-NHC chelated Ni(II) complex \([\text{L}^3\text{Si}(\text{CH}(\text{MeC} = \text{NAr})_2)]\text{NiBr}_2\) \(17\) through hydride migration (tautomerization) from the silicon center to the exocyclic methylene group of \(16\) mediated by NiBr\(_2\) is described. Remarkably, the reduction of \(17\) with KC\(_8\) in the presence of PMe\(_3\) does not lead to the expected NHSi-NHC \((\text{Me}_3\text{P})_2\text{Ni}(0)\) complex but to the silyl-NHC bromo-Ni(II)
complex 18 and the hydrosilyl-NHC Ni(0) complex 19 featuring an agostic Si–H→Ni bonding interaction, respectively. However, the analogous reduction of 17 in the presence of DMPE (DMPE = 1,2-bis(dimethylphosphino)ethane) furnishes the first mixed NHSi-NHC (dmpe)Ni(0) complex 20. Moreover, the remarkably high activity of complex 17 as a precatalyst for Kumada-Corriu-type cross-coupling reactions is demonstrated.

3.2.1.1 Synthesis of [L\textsuperscript{3}Si(CH\textsubscript{2})(NHC)]NiBr\textsubscript{2}

Treatment of L\textsuperscript{2}(H)Si(CH\textsubscript{2})NHC\textsubscript{16} with NiBr\textsubscript{2}(dme) (dme = 1,2-dimethoxyethane) in toluene at 50 °C afforded facilely the NHSi-NHC stabilized Ni(II) complex [L\textsuperscript{3}Si(CH\textsubscript{2})(NHC)]NiBr\textsubscript{2} 17 which could be isolated as deep red crystals in 82% yield in concentrated toluene solutions at −20 °C (Scheme 2-4).

\[ \text{Scheme 2-7. Synthesis of the first mixed NHSi-NHC ligand chelated Ni(II) complex 17.} \]

Although the detailed mechanism for the formation of complex 17 is still ambiguous, it might proceed firstly via the coordination of the NHC moiety of 16 to NiBr\textsubscript{2} affording 17\textsubscript{a}, which then triggers the hydride migration from the Si–H moiety to the terminal CH\textsubscript{2} group owing to the strong Brønsted basicity of this methylene carbon forming silylene species that spontaneously coordinates to the nickel center yielding complex 17 as the final product bearing the chelating NHSi-NHC ligand [L\textsuperscript{3}Si(CH\textsubscript{2})(NHC)] 16\textsubscript{a} (L\textsuperscript{3} = CH(MeCNAr)\textsubscript{2}, Ar = 2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) (Figure 2-8). The proposed mechanism was further supported by density functional theory (DFT) calculations, which revealed that the coordination of the NHC moiety to NiBr\textsubscript{2}(dme) with concomitant elimination of DME and the subsequent formation of complex 17 are exothermal (−4.2 kcal/mol and −29.1 kcal/mol, respectively; see Figure 2-8 for details).
Figure 2-8. Potential energy surface for the reaction of 16 with NiBr$_2$(dme) to form complex 17 (6-31G(d) for H, C, N, Si, LANL2DZ for Ni) and the optimized structure of 17a.$^{[95]}$

Compound 17 is well soluble in CH$_2$Cl$_2$ and THF, and moderately soluble in toluene. The protons of the methyl groups of the β-diketiminato ligand L$^3$ are observed at $\delta = 1.57$ and 1.66 ppm as singlet signals in the $^1$H NMR spectrum in CD$_2$Cl$_2$. Interestingly, the resonances of the methine protons of the iPr groups exhibit two septet signals at $\delta = 2.95$ and 5.03 ppm with one significantly downfield shifted signal (Figure 2-9). This is likely a consequence of intramolecular hydrogen bonding between the methine protons and one of the bromide atoms on the nickel center, which is consistent with the respective metric parameters observed in the molecular structure determined by single-crystal X-ray diffraction analysis (vide infra). The protons of the SiCH$_2$N moiety appear at $\delta = 2.73$ ppm as a singlet resonance. The $^{13}$C signals for the SiCH$_2$N and N-CH$_3$ moieties could not be observed in the $^{13}$C{$_^1$}H NMR spectrum, which might be due to the long relaxation time for these two $^{13}$C nuclei. However, both of them can be unambiguously assigned at around $\delta = 37.3$ ppm from $^1$H-$^{13}$C{$_^1$}H HMQC NMR spectrum with correlations to the corresponding proton signals (Figure 2-10). The $^{29}$Si resonance signal is shown at $\delta = 8.3$ ppm in the $^{29}$Si{$_^1$}H NMR spectrum, which is upfield shifted when compared to that of the pincer-type bis(NHSi)-Ni(II) [2,6-(OSi:L$^1$)$_2$-3,5-tBuC$_6$H]NiBr complex ($\delta = 20.2$ ppm).$^{[35c]}$
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**Figure 2-9.** $^1$H NMR spectrum of 17 in benzene-$d_6$ at 298 K.

**Figure 2-10.** Assignment of the $^{13}$C nuclei chemical shifts for the N-CH$_3$ and SiCH$_2$N moieties of compound 17 from $^1$H-$^{13}$C({$^1$H}) HMQC NMR spectrum in CD$_2$Cl$_2$ at 298 K.

Crystals of 17 suitable for single-crystal X-ray diffraction analysis were obtained in concentrated toluene solutions at $-20$ °C (Figure 2-11). It crystallizes in the orthorhombic space group $P2_12_12_1$. It is noteworthy that the nickel center exhibits a somewhat distorted square planar coordination geometry with the sum of the angles around nickel of 365.03°. The short distances of Br1 to the H15 and H24 atoms (2.884 and 2.990 Å, respectively) of the $i$Pr groups indicate strong intramolecular hydrogen bonding interactions, which is likely to be
the reason for the drastically downfield shifted resonance signal for the methine protons in the $^1$H NMR spectrum (*vide supra*). This also rationalizes the slight distortion of the nickel configuration from the square planar coordination geometry. The Ni1–Si1 distance of 2.1553(8) Å is similar to those in the pincer-type bis(NH2Si)NiII [2,6-(OSi:$^1$L1)$_2$-3,5-tBuC$_6$H]NiBr complex (2.1737(7) Å),$^{[35c]}$ whereas it is longer than those in the NHSi supported Ni$^0$(η$_6$-arene) complexes (2.0369(6)-2.0936(10) Å) which have a somewhat stronger Ni$\rightarrow$Si(II) π back-donation.$^{[44a, 96]}$ The substantially longer Ni1–Br2 distance (2.4437(6) Å) in comparison to that of Ni1–Br1 (2.3538(5) Å) might be attributed to a stronger *trans* effect of the NHSi ligand compared to that of the NHC moiety.

**Figure 2-11.** Molecular structure of compound 17. Thermal ellipsoids are drawn at 50% probability level; all hydrogen atoms (except H15 and H24) and solvent molecules (toluene) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–Si1 2.1553(8), Ni1–C33 1.885(3), Ni1–Br1 2.3538(5), Ni1–Br2 2.4437(6), Si1–N1 1.804(2), Si1–N2 1.813(2), C1–C2 1.499(4), C2–C3 1.387(4), C3–C4 1.400(4), C4–C5 1.495(4), Br1–H15 2.884, Br1–H24 2.990; C33–Ni1–Si1 82.40(9), C33–Ni1–Br1 160.12(9), Si1–Ni1–Br1 85.97(3), C33–Ni1–Br2 101.79(9), Si1–Ni1–Br2 158.83(3), Br1–Ni1–Br2 94.87(2).

### 3.2.1.2 Reduction of 17 to nickel(0) complexes in the presence of various exogenous ligands

Compound 17 represents the first transition metal complex stabilized by a chelating NHSi-NHC ligand, so it would be interesting to investigate its reduction to isolable Ni(0) complexes. The desired debromination of 17 with two molar equivalents of KC$_8$ in the presence of PMe$_3$ as an exogenous ligand was carried out in THF. Unexpectedly, after a reaction time of 3 hours at room temperature, only the new silyl-NHC monobromo Ni(II)
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Complex [L²Si(CH₂)NHC]Ni(Br)(PMe₃) 18 could be isolated in 76% yield (Scheme 2-8a). Complex 18 was formed through the dehydrobromination of 17. It is noteworthy that a similar dehydrobromination occurred in the preparation of L²SiBr₂, which is the dibromo precursor for synthesizing L²Si:[¹⁹] After a prolonged reaction time at room temperature (4 hours), the reduction resulted in the formation of the unprecedented hydrolysilyl-NHC Ni⁰ [η²(Si−H)][L²Si(H)(CH₂)NHC]Ni(PMe₃)₂ complex 19 featuring an agostic Si−H→Ni interaction, which could be isolated in 68% yield as a light-yellow solid (Scheme 2-8a). The mechanism for the formation of 19 is unclear but might proceed via the Ni(I) species [L²Si(CH₂)NHC]Ni¹(PMe₃) 18a, generated by the one-electron reduction of 18. However, the Ni(I) species 18a is expected to be highly reactive, and can abstract a hydrogen atom from the environment (THF or other sources) affording a hydrido-silyl-NHC Ni(II) species [L²Si(CH₂)NHC]Ni²(H)(PMe₃) 18b. [¹⁶⁸, ⁹⁷] The latter undergoes reductive elimination of the Si−H moiety, yielding the Ni(0) complex 19 bearing an agostic Si−H→Ni interaction (Scheme 2-8b).

Scheme 2-8. (a) Reduction of 17 with KC₈ in the presence of PMe₃ affording complexes 18 and 19, respectively, and the equilibrium between 19 and 19a owing to the
coordination/dissociation of one PMe$_3$ ligand; (b) a proposed pathway for the formation of the Ni(0) complex 19 through the reduction of the Ni(II) complex 18 with KC$_8$.

Compound 18 was isolated as red crystals in a concentrated n-hexane solution at 0 °C; it exhibits good solubility in n-hexane, benzene and toluene. Akin to complex 17, owing to the intramolecular hydrogen bonding interaction between the bromide atom and the methine hydrogen atoms, two lowfield shifted proton resonance signals ($\delta = 4.52$ and 5.44 ppm) for iPr groups are observed in the $^1$H NMR spectrum in benzene-d$_6$. In contrast to complex 17, the proton resonance signals of the SiCH$_2$N fragment are shown as two doublet signals at $\delta = 2.87$ and 3.00 ppm with a coupling constant of $^2J = 13.6$ Hz indicating the chemical inequivalence of these two hydrogen atoms owing to the chiral nature of the nickel center bearing four different substituents. The protons of PMe$_3$ resonate at $\delta = 1.64$ ppm as a doublet ($^2J_{H,P} = 8.0$ Hz), and the corresponding $^{31}$P resonance signal is observed at $\delta = -14.9$ ppm in the $^{31}$P{$^1$H} NMR spectrum. Due to the coupling with one $^{31}$P nucleus, the $^{29}$Si resonance signal reveals as a doublet at $\delta = 12.2$ ppm ($^2J_{Si,P} = 45.9$ Hz) in the $^{29}$Si{$^1$H} NMR spectrum, which is downfield shifted in comparison to that of complex 17 ($\delta = 8.3$ ppm). Complex 18 is the first example of any nickel complex containing a chelating silyl-NHC ligand. It is noteworthy that silyl donors functionalized NHC cobalt(II) and iron(II) complexes have recently been reported by Deng and coworkers.[98]

![Figure 2-12](image)

**Figure 2-12.** Molecular structures of complexes 18 (left) and 19 (right). Thermal ellipsoids are drawn at 50% probability level; all hydrogen atoms (except those at C1 and Si1) are omitted for clarity. Selected bond lengths (Å) and angles (°): for 18: Ni1–Si1 2.2273(4), Ni1–P1 2.2052(4), Ni1–Br1 2.4263(3), Ni1–C33 1.8975(14), Si1–N1 1.7703(12), Si1–N2 1.7618(12), C1–C2 1.360(2), C2–C3 1.454(2), C3–C4 1.353(2), C4–C5 1.496(2);
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P1–Ni1–Si1 101.164(15), P1–Ni1–Br1 90.595(13), Si1–Ni1–Br1 149.969(15), C33–Ni1–P1 163.67(4), C33–Ni1–Si1 80.27(4), C33–Ni1–Br1 96.07(4). For 19: Ni1–Si1 2.2012(5), Ni1–P1 2.2352(5), Ni1–P2 2.2214(5), Ni1–C33 1.9161(16), Ni1–H1 1.485(19), Si1–H1 1.738(19), Si1–N1 1.8010(13), Si1–N2 1.7903(14), C1–C2 1.355(2), C2–C3 1.459(2), C3–C4 1.350(2), C4–C5 1.503(2); C33–Ni1–Si1 85.65(5), C33–Ni1–P2 99.41(5), Si1–Ni1–P2 122.58(2), C33–Ni1–P1 114.87(5), Si1–Ni1–P1 126.778(19), P1–Ni1–P2 102.75(2), Si1–Ni1–H1 51.9(8), Ni1–Si1–H1 42.3(6).

The molecular structure of complex 18 is portrayed in Figure 2-12. It crystallizes in the monoclinic space group $P2_1/\text{c}$. The C1–C2 bond (1.360(2) Å) is significantly shorter than C4–C5 bond (1.496(2) Å), indicating its C=C bond character. The Ni1–Si1 bond (2.2273(4) Å) is slightly longer than the Si(II)→Ni dative bond (2.1553(8) Å) of 17, but comparable to those of the silyl-nickel complexes (2,4,6-Me$_3$C$_6$H$_2$B(o-Ph$_2$PC$_6$H$_4$)$_2$($\mu$-H)NiE (E = SiH$_2$Ph, 2.2379(4) Å; SiHPh$_2$, 2.2479(7) Å).[99]

**Figure 2-13.** $^{31}$P{\textsuperscript{1}H} (left) and $^{29}$Si{\textsuperscript{1}H} (right) NMR spectra of complex 19 in toluene-d$_8$ at 298 K.

The NMR spectra of complex 19 in toluene-d$_8$ at room temperature are rather complex and consistent with the coexistence of two species (19 and 19a) in solutions owing to the coordination and dissociation of one of the PMe$_3$ ligands (Scheme 2-8a). This is exemplified by one sharp (δ = −18.8 ppm) and two broad resonances (δ = −27.9 and −31.3 ppm) for the PMe$_3$ groups in the $^{31}$P{\textsuperscript{1}H} NMR spectrum in toluene-d$_8$, of which belong to 19a and 19, respectively (Figure 2-13). In analogy, the $^{29}$Si{\textsuperscript{1}H} NMR spectrum reveals one doublet signal (δ = −19.2 ppm, $^{2}$J$_{Si,P}$ = 8.8 Hz) for 19a and a broad signal around δ = 2.5 ppm for 19 (Figure 2-13). The variable temperature NMR spectroscopic studies show that the two broad
$^{31}$P resonance signals for 19 are converted into two doublet signals with a coupling constant of $^{2}J_{P,P} = 35.4$ Hz when the sample is cooled down to $-20 \, ^\circ$C, this indicates that the two PMe$_3$ ligands of 19 are chemically inequivalent (Figure 2-14a). Correspondingly, the proton resonance signal for the Si–H group of 19 becomes a quartet (doublet of doublets) at $-80 \, ^\circ$C owing to the coupling with two chemically inequivalent PMe$_3$ groups (Figure 2-14b). Meanwhile, the broad $^{29}$Si resonance signal of 19 becomes a triplet signal at $-80 \, ^\circ$C most probably owing to a similar coupling constant between the $^{29}$Si and two chemically different $^{31}$P nuclei ($^{2}J_{Si,P} = 71.5$ Hz) (Figure 2-14c).

a)

![Diagram of 19 and 19a at different temperatures](image)

b)

$^1$H NMR at $-80 \, ^\circ$C

![Diagram of Si–H resonance signal](image)
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c) $^{29}\text{Si} \{^1\text{H}\}$ NMR at -80 °C

**Figure 2-14.** (a) $^{31}\text{P} \{^1\text{H}\}$ of complex 19 in toluene-d$_8$ at variable temperatures; (b) $^1\text{H}$ NMR spectrum of complex 19 in toluene-d$_8$ at -80 °C; (c) $^{29}\text{Si} \{^1\text{H}\}$ NMR spectrum of complex 19 in toluene-d$_8$ at -80 °C.

The Si–H signal of 19 is observed at $\delta = -7.8$ ppm in the $^1\text{H}$ NMR spectrum with $^{29}\text{Si}$ satellites ($^1J_{\text{Si, H}} = 87.5$ Hz), which is substantially upfield shifted when compared to that of the $\eta^2$(Si–H)Ni(0)(PPh$_3$) complex ($\delta = -2.9$ ppm)$^{[100]}$. This might be due to the strong electron-donating property of the ligand 16. The $^1J_{\text{Si, H}}$ coupling constant of 87.5 Hz is much larger than the typical values for silyl-hydrido-metal complexes (< 20 Hz) formed via oxidative addition of Si–H bonds to transition metal centers. Moreover, the large value of the minimum $T_1$ (1319 ms) for the Si–H proton determined by the $T_1$ measurements at 298 K and 400 MHz clearly indicates a $\eta^2$(Si–H) coordination mode to the nickel center of 19.$^{[101]}$ The stretching vibration mode of the Si–H bond is observed at $\nu = 1746$ cm$^{-1}$ in the IR spectrum, which is in the range of the values for related $\sigma$-silane transition metal complexes ($\nu = 1650$-1800 cm$^{-1}$)$^{[102]}$. The Si1–H1 bond length (1.738(19) Å) of 19 (Figure 2-12) is also in the range of those reported for related $\eta^2$(Si–H) transition metal complexes (1.70-1.90 Å). Based on these information, complex 19 represent a $\eta^2$(Si–H)Ni(0) complex with an agostic Si–H→Ni(0) bonding interaction.
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Scheme 2-9. Reduction of 17 to yield the Ni(0) complexes 20 and 21 with DMPE and CO as exogenous ligands, respectively.

In an attempt to isolate a chelate NHSi-NHC ligand stabilized Ni(0) complex, the chelate diphosphine ligand DMPE and CO were utilized as additional supporting ligands. Accordingly, the reduction of 17 with KC₈ was carried out in THF in the presence of one molar equivalent of DMPE. In contrast to the case with PMe₃ as an exogenous ligand, the reaction afforded the desired Ni(0) complex \([\text{L}^2\text{Si:(CH₂)NHC}]\text{Ni}(0)(\text{dmpe})\) 20 in 43% yield as dark-green crystals (Scheme 2-9). This shows that the chelate NHSi-NHC ligand 16a is also capable of stabilizing Ni(0) species. The \(^{31}\text{P}\{^1\text{H}\}\) resonance of 20 is observed as a singlet signal at \(\delta = 15.8\) ppm with \(^{29}\text{Si}\) satellites \(\left(2J_{\text{Si,P}} = 30.9\right)\) Hz in benzene-\(d_6\). Correspondingly, a triplet signal \(\delta = 60.0\) ppm, \(2J_{\text{Si,P}} = 30.9\) Hz) is observed in the \(^{29}\text{Si}\{^1\text{H}\}\) NMR spectrum owing to the coupling with two chemically equivalent \(^{31}\text{P}\) nuclei of the DMPE ligand.

Figure 2-15. Molecular structures of complexes 20 (left) and 21 (right). Thermal ellipsoids are drawn at 50% probability level; all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): for 20: Ni1–Si1 2.1740(18), Ni1–C33 1.918(7), Ni1–P1 2.1571(17), Ni1–P2 2.156(2), Si1–N1 1.881(5), Si1–N2 1.910(5), C1–C2 1.496(8), C2–C3
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1.403(8), C3–C4 1.401(9), C4–C5 1.517(8); P1–Ni1–Si1 126.19(8), P2–Ni1–Si1 122.04(8), P2–Ni1–P1 89.93(8), C33–Ni1–Si1 85.76(19), C33–Ni1–P1 114.04(18), C33–Ni1–P2 122.4(2). For 21: Ni1–Si1 2.2131(13), Ni1–C33 1.947(4), Ni1–C37 1.759(5), Ni1–C38 1.762(5), Si1–N1 1.859(4), Si1–N2 1.875(4), C1–C2 1.500(6), C2–C3 1.397(6), C3–C4 1.391(7), C4–C5 1.506(6); C33–Ni1–Si1 85.15(13), C37–Ni1–C38 113.2(2), C37–Ni1–C33 114.4(2), C38–Ni1–C33 112.3(2), C37–Ni1–Si1 111.54(16).

The molecular structure of 20 was unambiguously determined by single-crystal X-ray diffraction analysis (Figure 2-15). The Ni center features a tetrahedral geometry, and the Ni–Si bond (2.1740(18) Å) is slightly shorter than those in the bis(NHSi)-Ni(0) [L\(^1\)Si:(μ-O):SiL\(^1\)]Ni(cod) complex (2.1908(7) and 2.1969(7) Å).\[^{53a}\] The DFT calculations revealed a significant π back-donation from the Ni center to both Si and carbon centers as indicated by the highest occupied molecular orbital (HOMO). In addition, a π-type bonding orbital (HOMO-1) is present and this orbital appears to be delocalized over the Si–Ni–C framework of compound 20 (Figure 2-16). In order to understand the electron-donating property of the chelate NHSi-NHC ligand 16a, the Ni(0) dicarbonyl [L\(^3\)Si:(CH\(_2\))NHC]Ni(CO)\(_2\) complex 21 was synthesized.

\[\text{Figure 2-16.} \text{ Selected molecular orbitals of complex 20 (6-31G(d) for } H, C, N, \text{ Si and P atoms, LANL2DZ for Ni).}^{[95]}\]

Reduction of 17 with two molar equivalents of K(BHEt\(_3\)) under a CO atmosphere afforded complex 21 as brown crystals in 60% yield (Scheme 2-9).\[^{103}\] The \(^{13}\)C resonances for the CO and carbene-carbon are observed at \(δ = 198.8\) and 206.2 ppm, respectively, in the \(^{13}\)C\(^{1}H\) NMR spectrum in THF-d\(_8\), which are comparable to those of (NHC\(^{Cy}\))\(_2\)Ni(CO)\(_2\) (\(δ = 198.3\) and 205.2 ppm, respectively; NHC\(^{Cy}\) = (CHNCy)\(_2\)C; Cy = cyclohexyl).\[^{104}\] The \(^{29}\)Si nucleus resonates at \(δ = 66.8\) ppm in the \(^{29}\)Si\(^{1}H\) NMR spectrum, which is downfield shifted when
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compared to that of 20 ($\delta = 60.0$ ppm). This is owing to the stronger $\pi$-acidity of CO than that of phosphine ligands, which results in decreasing the $\pi$ back-donation from the Ni center to the silicon and NHC carbon centers. This consequently leads to longer Ni1–Si1 (2.2131(13) Å) and Ni1–C33 (1.947(4) Å) bond lengths of 21 (Figure 2-15) in comparison to those in 20 (2.1740(18) and 1.918(7) Å, respectively). The absorption bands for the CO groups of 21 are observed at $\nu = 1952$ and 1887 cm$^{-1}$ in the infra-red spectrum, which are blue-shifted in comparison to those observed for [(dmpm)Ni(CO)$_2$]$_2$ ($\nu = 1991$ and 1927 cm$^{-1}$, dmpm = bis(dimethylphosphino)methane)$^{[105]}$ and (NHC$_{\text{Mes}}$)$_2$Ni(CO)$_2$ ($\nu = 2050$ and 1877 cm$^{-1}$, NHC$_{\text{Mes}}$ = (CHNMes)$_2$C:, Mes = 2,4,6-Me$_3$C$_6$H$_2$).$^{[104]}$ This suggests that the NHSi-NHC ligand 16a is a stronger $\sigma$ donor than two phosp

3.2.1.3 Catalytic performance of 17 for Kumada-Corriu type cross-coupling reactions

Metal-catalyzed C–C formation is one of the most straightforward and versatile methods in organic synthesis.$^{[106]}$ In 1972, Kumada et al. and Corriu et al. independently reported the cross-coupling reaction of Grignard reagents with aryl and alkenyl halides in the presence of catalytic amounts of nickel(II) reagents.$^{[107]}$ The catalytic cycle is believed to involve oxidative addition of the organic halides to the Ni(0) center, which is generated through the reduction of nickel(II) precursors with Grignard reagents, affording the Ni(II) species A. The latter further undergoes transmetallation with one molar equivalent of Grignard reagents to yield species B, from which the cross-coupling product is formed via reductive elimination with concomitant regeneration of the active catalyst (Scheme 2-7). These cross-coupling reactions proceed smoothly with a variety of organometallic reagents as nucleophiles; however, the coupling partners are generally limited to aryl and alkenyl halides and pseudohalides. The utilization of alkyl halides, triflates, or tosylates usually leads to unsatisfactory results mainly due to the slow oxidative addition of the substrates to transition metal catalysts and the facile $\beta$-hydride elimination from the alkylmetal intermediates (such as species A and B in Scheme 2-10).$^{[108]}$
Scheme 2-10. A possible catalytic mechanism for nickel-catalyzed Kumada-Corriu type cross-coupling reaction.

Very recently, Kambe and coworkers reported that the cross-coupling reactions of alkyl bromides and tosylates with Grignard reagents gave almost quantitative yields at 0 °C in the presence of NiCl₂ (1-3 mmol%) and a butadiene (10-100 mol%). In the absence of a butadiene, reduction and/or elimination of the electrophiles were mainly observed.[109]

The postulated mechanism of the reaction is depicted in Scheme 2-11.[109] The actual catalyst results from the reduction of NiCl₂ with R₃MgX and subsequent reaction of the formed Ni(0) species with two molar equivalents of 1,3-butadiene. This catalyst is unreactive towards R₄X but reacts with R₃MgX to form the anionic nickel(II) complex C. Subsequent alkylation with R₄X affords the nickel(IV) intermediate D, which further undergoes reductive elimination yielding the cross-coupling product with regeneration of the active catalyst.
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Scheme 2-11. Mechanism postulated by Kambe and coworkers for the nickel-catalyzed Kumada-Corriu type cross-coupling reaction.

In order to highlight the influences of the mixed NHSi-NHC ligand 16a on the reactivity of the nickel center, the catalytic performance of 17 in Kumada-Corriu type cross-coupling reaction was tested (Scheme 2-12). It was found that complex 17 could efficiently effect the cross-coupling reactions of 4-Me-C₆H₄-MgCl with aromatic halides (yields: >99%) bearing Me, tBu, CF₃ and Me₂N groups at para positions, respectively. Moreover, the effect of halide leaving group was studied, showing excellent yields with I, Br, Cl. (22a-e, >99%). With 2,4,6-Me₃C₆H₂Br as the substrate, a significant decrease in the yield was observed which was likely to be a result of the steric hindrance from the mesityl group (22g, 29%).

Interestingly, the precatalysts 17 was also capable of catalyzing the cross-coupling reactions of the heterocyclic bromides with 4-Me-C₆H₄-MgCl with yields of >99% (22h) and 58% (22i). Strikingly, the 86% yield for the sp³−sp² C-C bond formation with the sp³ hybridized carbon source 1-octyl bromide and 4-Me-C₆H₄-MgCl as the substrates was still afforded (22j), whereas no cross-coupling product was detected when the oxo bridged bis-(NHSi)-Ni(0) [L¹Si:(μ-O):SiL¹]Ni(cod) complex was used as the precatalyst. When tBuMgCl was employed as the Grignard reagent, the coupling reaction with 4-MeO-C₆H₄Br gave 31% yield along with 69% of hydrodehalogenation product (22k). Overall, complex 17 shows good performance for Kumada-Corriu type cross-coupling reactions and moreover
highlights the potential of the NHSi-NHC supported transition metal complexes in homogeneous catalysis.

Scheme 2-12. Catalytic performance of 17 for Kumada-Corriu type cross-coupling reactions.
3.2.2 From thio- and selenosilanoic acids to dinuclear copper(I) complexes featuring an intermolecular Si=E→Cu(I)–O–Si (E = S, Se) interaction

Using well-defined organic complexes containing M–O–Si moieties as structural models for silica-supported metal/metal oxide pre-catalysts has proved to be a facile method to unravel the structure of a precatalyst as well as the mechanism of a catalytic reaction. For example, the globular 56-membered copper(I) siloxane containing a core made up of Cu–O–Si moieties (Scheme 2-13), which is soluble in organic solvents, could be readily prepared by the reaction of the silanetriol (Ar(SiMe3)NSi(OH)3, Ar = 2,6-iPr2C6H3) with (MesCu)4 (Mes = 2,4,6-Me3C6H2). This copper siloxane cluster is active for the Ullmann-Goldberg-type C–N coupling reactions and can serve as a structural and functional model for silica-supported copper (pre)catalysts. In order to better understand the structure-reactivity relationships of Cu–O–Si systems for various Cu-based chemical transformations, the synthesis of other types of Cu–O–Si containing compounds as structural and functional models for silica-supported copper materials is highly desired.

Scheme 2-13. Selected examples of silanols and the globular 56-membered copper(I) siloxane.

Organic silanols that have been reported to form well defined M–O–Si type compounds include silanediols, disiloxane-1,3-diols, silanetriols, trisiloxane-diol and silsequioxane-triols
As possible intermediates involved in silica synthesis through hydrolysis of a suitable silicon(IV) starting material under acidic conditions, silicic acids, SiO<sub>x</sub>(OH)<sub>4-2x</sub>, have not received much attention as precursors for the selective synthesis of M–O–Si containing compounds owing to their elusive nature. Likewise, organic silanoic acids RSi(=O)OH, the silicon analogues of carboxylic acids, represent elusive species which could only been studied at liquid nitrogen temperatures because of the presence of the highly polarized Si=O subunit which can undergo facile isomerisation or intermolecular head-to-tail polymerisation.

Recently, we reported the first example of a Lewis base stabilized thiosilanoic acid L<sup>3</sup>Si(=S)OH(dmap) (L<sup>3</sup> = CH[C(Me)NAr]<sub>2</sub>, Ar = 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, dmap = 4-dimethylaminopyridine) by the reaction of H<sub>2</sub>S with the silanone adduct L<sup>2</sup>Si(=O)(dmap) (L<sup>2</sup> = CH[C(Me)(C=CH<sub>2</sub>)](NAr<sub>2</sub>), Ar = 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). The silanone adduct could be prepared by oxidation of the Lewis base stabilized NHSi L<sup>2</sup>Si:(dmap) with N<sub>2</sub>O.

Herein, the facile synthesis of the first isolable selenosilanoic acid-base adduct LSi(=Se)OH(dmap) is reported. The metalation reactions of L<sub>3</sub>Si(=S)OH(dmap) and LSi(=Se)OH(dmap) with (MesCu)<sub>4</sub> furnish the novel dimeric LSi(=E)OCu complexes (E = S) and (E = Se) featuring unprecedented intermolecular Si=E→Cu–O–Si coordination modes. Moreover, both complexes are efficient precatalysts for aziridination of styrene with PhI=N(Ts) (Ts = tosyl).

### 3.2.2.1 Synthesis of a novel selenosilanoic acid-base adduct

The thiosilanoic acid-base adduct L<sup>3</sup>Si(=S)OH(dmap) was readily accessible by the reaction of the base stabilized silanone L<sup>2</sup>Si(=O)(dmap) with H<sub>2</sub>S at ambient temperature (Scheme 2-14). Considering the toxicity of H<sub>2</sub>Se, dilithium selenide was used as a selenium source to synthesize the selenium congener of L<sub>3</sub>Si(=S)OH(dmap). Dilithium selenide can be facilely obtained by the reaction of elemental selenium with two molar equivalents of lithium triethylhydridoborate in THF at room temperature. Treatment of the as-prepared dilithium selenide with one molar equivalent of L<sup>2</sup>Si(=O)(dmap) in THF from −78°C to room temperature, followed by protonation with two molar equivalents of trimethylammonium chloride, led to a clear yellow solution, from which compound L<sup>3</sup>Si(=Se)OH(dmap) could be isolated as yellow crystals in 75% yield. The formation of L<sup>3</sup>Si(=Se)OH(dmap) might firstly undergo 1,2-addition of Li<sub>2</sub>Se to the Si=O bond of L<sup>2</sup>Si(=O)(dmap) to afford the dilithium complex L<sup>3</sup>Si(=Se)(dmap), which is further protonated by trimethylammonium chloride resulting in the formation of L<sup>3</sup>Si(=Se)OH(dmap) with concomitant elimination of two molar equivalents of LiCl and Me<sub>3</sub>N.
The species 25b is likely unstable and further undergoes 1,5-hydride migration affording the selenosilanoic acid 25.

![Scheme 2-14](image)

**Scheme 2-14.** Synthetic routes to the thiosilanoic acid-base adduct 23 (reported procedure)\(^{[113]}\) and selenosilanoic acid-base adduct 25 with H\(_2\)S and *in situ* prepared Li\(_2\)Se as chalcogen sources, respectively.

Compound 25 is thermally stable, and it has a very similar solubility as complex 23. It is soluble in toluene, THF, chloroform and dichloromethane, marginally soluble in benzene but insoluble in *n*-hexane. The compound was fully characterized by multinuclear \(\left\{^1\text{H}, ^{13}\text{C}\left\{^1\text{H}\right\}, ^{29}\text{Si}\left\{^1\text{H}\right\}, ^{77}\text{Se}\left\{^1\text{H}\right\}\right\}\) NMR spectroscopy, elemental analysis, mass spectrometry, IR spectroscopy, as well as single-crystal X-ray diffraction analysis.

The molecular peak of [25 + H]\(^+\) is revealed at *m/z* 665.3138 in the high resolution electrospray ionization mass spectrum (calcd. *m/z* 665.3154). In the \(^1\text{H}\) NMR spectrum in CDCl\(_3\), the chemical shift of the ring proton at the \(\gamma\)-position of the \(\beta\)-diketiminato ligand is observed at \(\delta = 5.73\) ppm, which is comparable to that observed for 23 (\(\delta = 5.71\) ppm). The proton of the OH group resonates at \(\delta = 6.42\) ppm and the signal is superimposed with the resonance signals of the protons of the pyridine moiety of DMAP. The \(^{29}\text{Si}\left\{^1\text{H}\right\}\) resonance signal appears at \(\delta = -25.5\) ppm as a singlet, which is slightly downfield shifted when compared to that of 23 (\(\delta = -30.0\) ppm). The \(^{77}\text{Se}\left\{^1\text{H}\right\}\) NMR spectrum exhibits a singlet at \(\delta = -545.2\) ppm, which is upfield shifted compared to those of the related selenosilanoic silylester diastereomers (\(\delta = -384.8\) and \(-401.3\) ppm).\(^{[115]}\)
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**Figure 2-17.** Molecular structure of compound 25 with 50% probability level for the core structure. Hydrogen atoms (except H1) and the n-hexane molecules are omitted for the sake of clarity. Selected bond lengths (Å) and angels (°): O(1)–Si(1) 1.619(2), O(1)–H(1) 0.73(4), Se(1)–Si(1) 2.1348(7), Si(1)–N(1) 1.816(2), Si(1)–N(2) 1.823(2); Si(1)–O(1)–H(1) 120(3), O(1)–Si(1)–N(1) 102.40(10), O(1)–Si(1)–N(2) 102.63(10), N(1)–Si(1)–N(2) 96.87(10), O(1)–Si(1)–Se(1) 120.13(9), N(1)–Si(1)–Se(1) 116.11(7), N(2)–Si(1)–Se(1) 115.28(7).

The molecular structure of compound 25 is depicted in Figure 2-17. It crystallizes in the triclinic space group P-1. The structural motif of 25 is analogous to that of 23, in which the DMAP moiety is bounded to the selenosilanoic acid moiety through an O–H⋯N hydrogen bonding interaction. The Si1–O1 bond length of 1.619(2) Å is comparable to that of 23 (1.620 (2) Å), and the Si(1)–Se(1) bond distance of 2.1348(7) Å is close to the Si=Se distance of a related selenosilanoic silyl ester (2.117(1) Å).[115] As expected, the other metric parameters of 25 are akin to those of complex 23.

3.2.2.2 Synthesis of dinuclear copper(I) complexes 26 and 27

In order to isolate the copper(I) complexes bearing Si(=E)–O–Cu (E = S and Se) moieties, (MesCu)₄ (Mes = 2,4,6-Me₃C₆H₂) was utilized as a copper(I) source to react with the silanoic acids 23 and 25. (MesCu)₄ is known to serve as a smooth reagent for preparing Cu(I) complexes through deprotonation of amines and silanols with concomitant elimination of mesitylene.[84b,116] The reaction of 1/4 molar equivalent of (MesCu)₄ with 23 and 25, in THF from −20 °C to room temperature afforded the dinuclear copper(I) [L²Si(=E)OCu]₂ complexes (26: E = S; 27: E = Se), respectively, as light yellow crystals in good yields (76% and 82%, respectively; Scheme 2-15). They represent the first examples of copper(I) complexes bearing to a Si(=E)–O (E = S, Se) motif.
Results and Discussion

Scheme 2-15. Syntheses of the dinuclear Cu(I) complexes 26 and 27.

Single crystals of 26 and 27 suitable for X-ray diffraction analysis could be obtained from concentrated toluene solutions at 0 °C. The structural analyses revealed that 26 and 27 are isostructural (Figure 2-18). The complexes possess C_2 symmetry and consist of a planar eight-membered Si_2O_2E_2Cu_2 ring with two trans-oriented β-diketiminato ligands L^3. The Cu centers are linearly coordinated by an oxygen atom and a chalcogen atom of the neighbouring Si=E subunit.

Figure 2-18. Molecular structures of compounds 26 (left) and 27 (right). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): 26: Si1–O1 1.568 (2), Si1–S1 2.0609 (9), Si1–N1 1.816(2), Si1–N2 1.810(2), Cu1–O1A 1.8404 (19), Cu1–S1 2.1299 (8), Cu1···Cu1A 2.8135 (7); O1–Si1–S1 120.98 (8), O1A–Cu1–S1 170.62 (6), Si1–O1–Cu1A 130.06(11), Si1–S1–Cu1 99.28 (4).

27: Cu1–Se1 2.2531(5), Cu1–O1A 1.844(2), Cu1···Cu1A 2.9271(8), Si1–O1 1.567(2), Si1–N2 1.817(3), Si1–N1 1.824(3), Si1–Se1 2.2011(9); O1A–Cu1–Se1 172.07(7), O1–Si1–N2 108.67(13), O1–Si1–N1 106.31(13), N2–Si1–N1 97.19(13), O1–Si1–Se1 120.89(10), N2–Si1–Se1 109.54(9), N1–Si1–Se1 111.61(9), Si1–Se1–Cu1 93.49(3), Si1–O1–Cu1A 137.07(14). Operation symmetry for all atoms labelled with “A”: –x+3/2, –y+1/2, –z (26); –x+2, –y, –z (27).
In complex 26, the Cu(1)···Cu(1A) distance of 2.8135 (7) Å suggests a weak d^{10}···d^{10} interaction in this molecule.\textsuperscript{[117]} A slightly longer Cu(1)···Cu(1A) bond distance (2.9271(8) Å) is observed in complex 27. This is likely due to the longer Si–Se distance (2.2011(9) Å) in comparison to that of the Si–S bond (2.0609 (9) Å) of 26 owing to the larger atomic radius of selenium vs. sulfur. The Si(1)–O(1) distance of 1.568 (2) Å in 26 is significantly shorter than that in 23 (1.620 (2) Å), whereas the Si(1)–S(1) bond length (2.0609 (9) Å) is longer than that of 23 (1.993 (1) Å), suggesting a carboxylate-like \pi-conjugation in the SiSO moiety;\textsuperscript{[118]} a similar phenomenon is also observed for complex 27.

a)

\[ \text{ppm (t1) } 5.550 \quad 5.500 \quad 5.450 \]

b)

\[ \text{ppm (t1) } -55.0 \quad -50.0 \quad -45.0 \quad -40.0 \quad -35.0 \quad -30.0 \quad -25.0 \quad -20.0 \]
Figure 2-19. $^1$H (a), $^{29}$Si{$^1$H} (b) and $^1$H-DOSY (c) NMR spectra of complex 26 in CDCl$_3$ solutions at 298 K.

The compositions of 26 and 27 were unambiguously confirmed by multinuclear NMR spectroscopy, elemental analysis and IR spectroscopy. The solubility of 26 and 27 are similar to those of the starting materials 23 and 25. Unexpectedly, two sets of resonances for the $\beta$-diketiminato ligand $L^3$ of 26 are observed in the $^1$H and $^{13}$C{$^1$H} NMR spectra in CDCl$_3$ with a ratio of 1:0.62 as indicated by the integrals of the resonance signals of the ring proton at the $\gamma$-position of $L^3$ at $\delta =$ 5.55 and 5.49 ppm, respectively (a similar behavior is also observed for 27). Similarly, the $^{29}$Si{$^1$H} NMR spectrum also reveals two somewhat close resonance signals at $\delta =$ –38.0 and –39.1 ppm (Figure 2-19). The two sets of resonance signals clearly suggest the presence of two stereoisomers of 26 (indicated as 26a and 26b) in chloroform-d$_1$ solutions. Indeed, this is substantiated by the results obtained from diffusion ordered spectroscopic (DOSY) measurement, revealing identical diffusion coefficients for these two species (Figure 2-19) and thus the same molecular size and composition for these two isomers. In other words, dissociation of 26 forming mononuclear copper(I) species in chloroform-d$_1$ solutions can be excluded.
Results and Discussion

Figure 2-20. $^1$H NMR spectra of 26 in CDCl$_3$ solutions at varied temperatures.

In order to gain more structural information of complexes 26 and 27, $^1$H NMR measurements at variable temperatures were carried out, and the results indicate that the two stereoisomers can be interconverted. Cooling the sample of 26 in CDCl$_3$ solutions to 230 K changes the ratio of signal sets of 26a and 26b from 1:0.62 at ambient temperature to 1:0.42 (Figure 2-20). In the solid state $^{29}$Si{$^1$H} NMR spectrum of 26 in crystalline form, only one resonance signal at $\delta = -41.6$ ppm could be observed, whereas the spectrum recorded with the fine powder of 26 in amorphous form exhibits two signals ($\delta = -41.6$ ppm and $-38.7$ ppm), suggesting 26a holds a structure as shown in Figure 2-18 with two ligands L$^3$ in the trans-position. It is possible that the other stereoisomer 26b preserves the $C_2$ symmetry, but the two ligands L$^3$ are now cis-oriented. However, this is ruled out by the results of DFT calculations (B3LYP/6-31G(d)/LANL2DZ(Cu) level),[95] which revealed that the proposed cis isomer is energetically unfavorable. Whereas the DFT calculations suggest a structure bearing a twisted Si$_2$O$_2$S$_2$Cu$_2$ core also with $C_2$ symmetry as a possible stereoisomer, which is only 5.5 kJ·mol$^{-1}$ less stable than 26a (Figure 2-21). And this is likely to be the structure of species 26b.
Results and Discussion

Figure 2-21. Optimized structure of the proposed stereoisomer 26b. Hydrogen atoms are omitted for the sake of clarity.

3.2.2.3 Catalytic performances of 26 and 27 for aziridination reaction

Metal-catalyzed olefin aziridination is a rather interesting reaction not only because it is analogous to the olefin epoxidation and cyclopropanation reactions but also the formed aziridines serve as important starting materials for organic synthesis.\[^{119}\] For instance, aziridines can react with various nucleophiles to undergo ring-opening reactions due to the ring strain. In the aziridination reaction, a nitrène group is transferred to the C=C bond of an olefin forming aziridines; copper(I) complexes have demonstrated to be the most effective catalysts for aziridination reactions.\[^{120}\]

The mechanistic studies showed that the reaction goes through the copper(I)-nitrène intermediate, which is formed through the reaction of the copper(I) catalysts with a nitrène source. Further nitrène group transfer from the copper(I)-nitrène species furnishes the aziridines and regenerates the active catalysts (Scheme 2-16).\[^{121}\]

![Scheme 2-16. A proposed mechanism for copper(I)-catalyzed aziridination reaction.](image-url)
In a preliminary study the catalytic ability of complexes 19 and 20 in the aziridination reaction has been evaluated. The catalytic reactions were carried out by using styrene and PhI=N(Ts) (Ts = tosyl) as an olefin and a nitrene source, respectively, in the presence of 2.5 mol% of 26 or 27 in CH$_2$Cl$_2$ at ambient temperature. The resulting yields of the N-tosyl-2-phenylaziridine product [85% (26) and 87% (27)] are similar with the reported results (Scheme 2-17). It is generally considered that the Cu(I)-nitrene species as shown in scheme 2-16 is the active component for the aziridination reaction.$^{[120c]}$ Thus, it is reasonable to assume that the dimeric Cu(I) complexes react initially with PhI=N(Ts) to form the corresponding mononuclear Cu(I)-nitrene intermediates with concomitant elimination of PhI (confirmed by GC-MS), which are capable of facile nitrene-transfer to the C=C bond of styrene affording the anticipated product.

Scheme 2-17. Aziridination reaction of styrene and PhI=N(Ts) (Ts = tosyl) catalyzed by the dinuclear copper(I) complexes 26 and 27.
3.3 CO₂ reduction to methanol mediated by an N-heterocyclic germylene hydride and syntheses of aluminum(I)- and gallium(I)-hydride complexes

3.3.1 CO₂ reduction to methanol mediated by an N-heterocyclic germylene-hydride

In the first chapter, the reduction of CO₂ to CO with silyl-copper(I) complexes, facilely obtained through the Cu–X (X = O, H) bond activation of copper(I) reagents with NHSi₇, has been discussed. In 2009, Roesky and coworkers reported that the N-heterocyclic germylene hydride (L₃GeH) was capable of activating CO₂ affording the germylene-formate L₃GeOCH(=O) complex 29° (L₃ = CH(MeC=NAr₂)₂, Ar = 2,6-iPr₂C₆H₃). Later on, the authors also showed that the germylene-formate could be converted into formic acid and methanol with LiNH₂•BH₃ and NH₃•BH₃ as a hydride source, respectively, after hydrolysis with water. Moreover, a possible mechanism for the formation of methanol was proposed based on NMR spectroscopic investigation; however, no intermediates were isolated in the study. Very recently, a computational study by Sakaki and coworkers showed that L₃GeH could also act as a catalyst for CO₂ hydrosilylation to F₃SiOCH(=O) with HSiF₃ as the hydride source. Until now, there is no solid evidence elucidating the mechanism of CO₂ reduction to methanol mediated by an N-heterocyclic germylene hydride, and there are only two examples of germylene-hydride complexes bearing β-diketiminato ligands that can activate CO₂. Thus, it seems desirable to apply more ligands with various scaffolds to stabilize the highly active germylene hydride species and investigate their capacity for CO₂ activation.

Recently, we have successfully utilized the 2-iminocyclohexylidenebenzylamine L⁵CyH (L⁵Cy = cyclo-C₆H₉-1-NAr-2-C(Ph)NAr, Ar = 2,6-iPr₂C₆H₃) to stabilize several N-heterocyclic germylene species. Herein, L⁵CyH is further applied as a supporting ligand to stabilize a novel germylene-hydride L⁵CyGeH, which is further utilized for CO₂ activation affording the germylene-formate L⁵CyGeOCH(=O) 29. The formate 29 and the previously reported formate species L₃GeOCH(=O) 29° can be further hydrogenated to methanol with AlH₃•NMe₃ as a hydride source after hydrolysis with water. Moreover, the mechanism for CO₂ reduction to methanol mediated by an N-heterocyclic germylene hydride with AlH₃•NMe₃ as the hydride source was elucidated based on the model reaction of L⁵AlH₂ with L₃GeOCH(=O) 29°.
3.3.1.1 Synthesis of a novel germlylene-hydride and its application in CO₂ activation

The synthesis of the L\textsuperscript{Cy}H stabilized germlylene hydride complex was firstly carried out. Akin to the preparation of LGeH\textsuperscript{[58c]}, L\textsuperscript{Cy}GeCl\textsuperscript{[123]} was treated with one molar equivalent of K[BH(sBu)]\textsubscript{3} in toluene at −78 °C and the reaction mixture was allowed to slowly warm up to room temperature. Unexpectedly, after a reaction time of 12 hours at ambient temperature, the anticipated germlylene hydride L\textsuperscript{Cy}GeH could not be isolated. Instead, L\textsuperscript{Cy}(H)Ge (28) was obtained as the single product in 84% yield (Scheme 2-18).

\textbf{Scheme 2-18.} Synthesis of the compound 28 via the fragile Ge(II) hydride.

However, when the reaction process was monitored by \textsuperscript{1}H NMR spectroscopy, after 3 hours at room temperature, the characteristic resonance signal for Ge(II)–H could indeed be observed at $\delta = 7.96$ ppm which is comparable to that of L\textsuperscript{3}GeH ($\delta = 8.08$ ppm).\textsuperscript{[62a]} This indicates that L\textsuperscript{Cy}GeH is indeed formed during the reaction, but it is labile and ultimately undergoes a 1,3-hydrogen transfer from the Ge(II) center to the backbone of the ligand affording the tautomeric diamidogermlylene 28 bearing a hydrogenated ligand scaffold as the thermodynamic product. A similar reaction mode was reported by Jones et al. when they attempted to utilize $^{\text{tBu}}$NacnacH ($^{\text{tBu}}$Nacnac = CH($^{\text{tBu}}$CNAr)\textsubscript{2}, Ar = 2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) and $^{\text{tBu}}$MesNacnacH ligands ($^{\text{tBu}}$MesNacnac = CH($^{\text{tBu}}$CNMes)\textsubscript{2}, Mes = 2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{3}) to stabilize germlylene hydride species. In both cases the only isolable products are the diamidogermlylene complexes with 1,3-hydride migration from the Ge(II) center to the backbone of L\textsuperscript{Cy} ligands.\textsuperscript{[62c, 124]} Nevertheless, complex 28 was tested for CO\textsubscript{2} activation, but no reaction occurred even at elevated temperatures in toluene or benzene.
Results and Discussion

Scheme 2-19. Activation of CO₂ with in situ formed Ge(II) hydride to afford the Ge(II) formate complex 29.

Although L⁺CyGeH is only a kinetic product, it might still be useful for CO₂ activation under suitable conditions, such as low temperatures. Therefore, L⁺CyGeCl was reacted with K[BH(sBu)₃] in toluene at -5 °C for 12 hours under a N₂ atmosphere, and then the atmosphere was changed with CO₂ through a freeze-pump-thaw cycle, and the reaction mixture was further stirred for another five hours. From the reaction mixture, after workup, the germylene formate L⁺CyGeOCH(=O) compound 29 could indeed be isolated as light yellow crystals in 77% yield (Scheme 2-19). This result also indicates that the formation of 28 indeed goes through the elusive germylene hydride L⁺CyGeH.

Both compounds 28 and 29 are yellowish solids, and are thermally robust (Mp. 178 °C (28); 165 °C (29)) without any decomposition when stored under a dry N₂ atmosphere at room temperature for several months. They are soluble in toluene, benzene and THF, and slightly soluble in n-hexane. They were fully characterized by NMR spectroscopy (¹H, ¹³C{¹H}), mass spectrometry, elemental analyses as well as single-crystal X-ray diffraction analyses. The resonance signal for the γ-H proton (PhCHNAr) in complex 28 is observed at δ = 4.75 ppm as a singlet signal in the ¹H NMR spectrum in benzene-d₆ at room temperature. The corresponding ¹³C nucleus resonates at δ = 74.8 ppm in the ¹³C{¹H} NMR spectrum. In the APCI-HR-MS spectrum, the signal for the molecular ion peak of 28 is found at m/z 595.3082 (cacl'd: m/z 595.3102), whereas the molecular ion peak for compound 29 could not be observed, but the signal for the molecule fragment corresponding to loss of the formate group is revealed at m/z 593.2936 (cacl'd: m/z 593.2946). The resonance signal for the proton of the formate group in 29 is shown at δ = 8.78 ppm in the ¹H NMR spectrum, which is comparable to that of the formate group in L²GeOCH(=O) (δ = 8.4 ppm). The corresponding ¹³C resonance signal is revealed at δ = 164.4 ppm in the ¹³C{¹H} NMR spectrum. The molecular structures of complexes 28 and 29 are shown in Figure 2-22.
Results and Discussion

Figure 2-22. Molecular structures of compounds 28 (left) and 29 (right). Thermal ellipsoids are drawn in 50% probability level; the Dipp groups are depicted in wireframe style. Disorders at C36 and C38 of compound 29 and hydrogen atoms (except those at C19 of compound 28 and C37 of compound 29) are omitted for clarity. Selected bond lengths (Å) and angels (°): 28: Ge1–N1: 1.8250(19), Ge1–N2 1.867(2), N1–C19 1.482(3), N2–C13 1.419(3), C13–C14 1.346(3), C14–C19 1.513 (3); N1–Ge1–N2 95.89(9), N2–C13–C14 123.0(2), C13–C14–C19 125.8(2), C14–C19–N1 113.99(19). 29: Ge1–O1 1.958(2), Ge1–N1 1.976(2), Ge1–N2 1.988(2), C1–C2 1.507(4), C2–C3 1.411(4), C3–C4 1.399(4), C2–N1 1.338(4), C4–N2 1.341(3), C37–O1 1.288(4), C37–O2 1.213(4); O1–Ge1–N1 89.38(8), O1–Ge1–N2 90.40(8), N1–Ge1–N2 90.19(9), O2–C37–O1 127.3(3).

Complex 28 crystallizes in the triclinic space group P1, which is a chiral crystal system. The germanium center is coordinated by two nitrogen atoms (N1 and N2). The distances of Ge1 to N1 and N2 are 1.8250(19) Å and 1.867(2) Å, respectively. They are comparable to those in L^{Cy'}Ge (L^{Cy'} = cyclo-C_6H_7-1-NAr-2-C(Ph)NAr, Ar = 2,6-iPr_2C_6H_3) which bears a dianionic ligand L^{Cy'} (1.861 and 1.843 Å). [123] The C14–C19 (1.513 (3) Å) and C13–C14 (1.346(3) Å) bond distances indicate the single and double bond character, respectively. This is in consistent with the structure depicted in Scheme 2-18 for 28. Compound 29 crystallizes in the monoclinic space group P2_1/c. The tricoordinate germanium atom bears an oxygen and two nitrogen atoms in its immediate coordinate environment and the sum of bond angles around it is 269.97°. These are indicative of a distorted trigonal-pyramidal geometry around the germanium atom and the presence of a lone pair of electrons at the germanium center. The Ge1 center deviates from the plane defined by N1–C2–C3–C4–N2 by 0.534 Å. The distances of Ge1–N1, Ge1–N2 (1.976(2) and 1.988(2) Å, respectively) and Ge1–O1 (1.958(2)
Å) are consistent with those observed in L\textsuperscript{3}GeOCH(=O) (Ge–N: 1.969(2) and 1.968(2) Å, Ge–O: 1.9339(18) Å).\textsuperscript{[58e]}

3.3.1.2 Conversion of the germylene formates into methanol and the mechanistic investigation

Roesky and coworkers demonstrated that the germylene formate L\textsuperscript{3}GeOCH(=O) (29') could be converted to formic acid and methanol with LiNH\textsubscript{2}•BH\textsubscript{3} and NH\textsubscript{3}•BH\textsubscript{3} as the respective hydride sources.\textsuperscript{[63]} However, the detailed mechanism for the latter process is still not well-understood although a possible mechanism was proposed only based on the NMR spectroscopic studies. Very recently, the computational studies by Sakaki and coworkers revealed that L\textsuperscript{3}GeH is capable of acting as a catalyst in CO\textsubscript{2} hydrosilylation when a suitable silane is applied as the hydride source.\textsuperscript{[122]} Inspired by these results, I was interested in introducing an alane as a hydride transfer source for further conversion of the germylene formats 29 and 29' into methanol and studying the mechanism of this process.

\textbf{Figure 2-23.} \textsuperscript{1}H NMR spectra of the reaction of 29' with three molar equivalents of NMe\textsubscript{3}•AlH\textsubscript{3} for 60 min (top) and 29' in benzene-d\textsubscript{6} (bottom).

Therefore, the trimethylamine-alane adduct Me\textsubscript{3}N•AlH\textsubscript{3} was chosen as a hydride source. Accordingly, Me\textsubscript{3}N•AlH\textsubscript{3} was treated with 1/3 molar equivalent of 29' or 29 in toluene at room temperature. The \textsuperscript{1}H NMR spectra in benzene-d\textsubscript{6} showed that both of the reactions
Results and Discussion

proceeded smoothly regenerating the corresponding germylene hydrides in almost quantitatively yields within one hour at room temperature (see Figure 2-23 for the $^1$H NMR spectra for the former reaction). After stirring for two hours in toluene, the reactions were quenched with D$_2$O at 0 °C. The yields of CH$_3$OD were determined as 46% ($29'$) and 42% ($29$) by $^1$H NMR spectroscopy with 1,4-dioxane as an internal standard. And except Me$_3$N, no other water soluble species was observed.

Schematic 2-20. The model reaction of $29'$ with L$^3$AlH$_2$ afforded new compounds 30 and 31.

Encouraged by these results, I further tried to elucidate the stepwise process for conversion of the germylene formate into methanol with Me$_3$N•AlH$_3$ as the hydride source. For this purpose, L$^3$AlH$_2$ was employed as a milder hydride delivery agent to react with $29'$. Through the reaction of $29'$ with one molar equivalent of L$^3$AlH$_2$, the formate group of $29'$ was further reduced affording the striking compound 30 as an OCH$_2$O bridged heterobimetallic complex (Scheme 2-20). The resonance for the protons at the OCH$_2$O group is observed at $\delta = 4.48$ ppm as a singlet singal in the $^1$H NMR spectrum in CDCl$_3$. The $\gamma$-H protons of the $\beta$-diketiminato ligands resonate at $\delta = 4.90$ and 5.02 ppm, respectively. The integral ratio for these three signals is 2:1:1, which is in accordance with the structure of 30 as depicted in Scheme 2-20. Hence, the reduction of the formate group to the OCH$_2$O group represents the second step for CO$_2$ reduction mediated by an N-heterocyclic germylene hydride. Moreover, complex 30 represents the first example of any complex bearing both Ge(II) and Al(III) centers.
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There is still one free Al–H bond in compound 30, and the yellow solution of 30 in THF gradually turned to red when left at room temperature, this indicates that complex 30 is likely thermally fragile. In fact, if compound 30 was treated at 60 °C in benzene-d$_6$ for 3 hours, it could be converted to L$_3$GeH and a new species as indicated by the $^1$H NMR spectroscopy. The latter compound turned out to be [L$_3$Al(OCH$_2$O)]$_2$ complex 31, which could be isolated as a colorless crystalline product in 60% yield. The proton signals for the OCH$_2$O group and γ-H hydrides of the β-diketiminato ligands of 31 are observed at δ = 4.74 and 5.00 ppm, respectively, with an integral ratio of 4:2. The investigation of the thermal stability of 30 suggests that L$_3$GeH is regenerated in this step. Unfortunately, the attempts to cleave the O–CH$_2$O bond of 31 with various hydride sources were unsuccessful, probably due to the steric crowding resulting from two bulky β-diketiminato ligands in 31.

![Molecular structures of compounds 30 and 31](image_url)

**Figure 2-24.** Molecular structures of compounds 30 (left) and 31 (right). Thermal ellipsoids are drawn in 50% probability level; the Dipp groups are depicted in wireframe style. Disorders at the core part GeOCH$_2$OAl of compound 30 and hydrogen atoms (except those at C30 and Al1 in 30, C30 and C30A in 31) are omitted for clarity. Operation symmetry for all atoms labelled with “A”: –x+1/2,–y+1/2,–z+2 (30); –x+1/2,–y+1/2,–z+1 (31). Selected bond lengths (Å) and angels (°): 30: Ge1–O1 1.826(5), Ge1–N1 2.0191(14), Ge1–N2 2.0324(14), C50–O1 1.398(5), Al1–O2 1.833(3), Al1–N1A 1.9037(17), Al1–N2A 1.9191(17); O1–Ge1–N1 96.62(14), O1–Ge1–N2 99.05(14), N1–Ge1–N2 89.14(6). 31: Al1–O(1) 1.7123(11), Al1–O2 1.7239(11), Al1–N2A 1.8963(13), Al1–N1 1.8979(13); O1–Al1–O2 114.22(6), O1–Al1–N2 114.11(6), O2–Al1–N2 107.98(6), O1–Al1–N1 108.58(6), O2–Al1–N1 113.27(6), N2–Al1–N1 97.59(6).

The molecular structures of compounds 30 and 31 are shown in Figure 2-24. They crystallize in the monoclinic space group C2/c. In complex 30, the Ge1 atom has a trigonal pyramidal geometry and the Al1 center features a tetrahedral coordination, and the metal
atoms are bridged by the OCH₂O group. The Ge1–O1 bond length (1.854(4) Å) is shorter than that of the starting material 29' (1.9339(18) Å),[58e] whereas it is comparable to that of L₃GeOiPr (1.821(2) Å).[127] The Al1–O2 bond distance (1.807(3) Å) is akin to those in [[L₃AlMe(μ-O)AlMe₂]]₂ (av. 1.8493 Å).[128] Compound 31 is a binuclear aluminum complex with a (AlOCH₂O)₂ core structure. The Al–N (1.8979(13) and 1.8963(13) Å) and Al–O (1.7123(11) and 1.7239(11) Å) bond lengths are similar to those in LAl[OB(3-MeC₆H₄)]₂(μ-O) (Al–N: 1.872(2) and 1.862(2) Å; Al–O: 1.7362(17) and 1.7418(17) Å).[129]

3.3.1.3 Proposed mechanism for CO₂ reduction to methanol mediated by an N-heterocyclic germylene hydride

Based on the isolation of complexes 30 and 31 from the model reaction of L³AlH₂ with 29', the stepwise process for the conversion of 29 or 29' with Me₃N•AlH₃ into methanol upon hydrolysis with water can be explained as follows (Scheme 2-21): complex 29' is hydrogenated to form the complex L³GeOCH₂OAlH₂•NMe₃ with the conversion of the formate group into the OCH₂O group, and the subsequent hydride transfer from a Me₃N•AlH₃ molecule to the Ge(II) center regenerates the germylene hydride L³GeH. Concomitantly, Me₃N•AlH₂OCH₂OAlH₂•NMe₃ is formed which is continuously converted into Me₃N•AlH₂–OMe and Me₃N•AlH₂OH₂Al•NMe₃ with cleavage of the O–CH₂O bond. Hydrolysis of Me₃N•AlH₂–OMe with D₂O yields CH₃OD as the C₁ product.

![Scheme 2-21](attachment:image.png)

**Scheme 2-21.** Plausible reaction mechanism for germylene-hydride mediated CO₂ reduction to CH₃OD with Me₃N•AlH₃ as the hydride source.
3.3.2 An elusive hydridoaluminum(I) complex for facile C–H and C–O bond activation of ethers and access to its isolable hydridogallium-(I) Analogue

Since divalent Group 14 element hydrides have exhibited excellent properties in small molecule activations and homogeneous catalysis, e.g. CO\textsubscript{2} activation mediated by N-heterocyclic germylene hydrides as discussed in previous part, it would be interesting to extent the chemistry to Group 13 elements. However, in comparison to the flourishing chemistry of divalent Group 14 (semi)metal-hydrides, the field for monovalent Group 13 elements is far less developed\textsuperscript{130}. The stabilization ‘free’ Al(I)-hydride and Ga(I)-hydride species have been spectroscopically studied by matrix isolation techniques at low temperatures through the reaction of elemental aluminum and gallium, respectively, with dihydrogen under UV light irradiation\textsuperscript{64}. These species are highly reactive and can react readily with another molar equivalent of dihydrogen forming the corresponding metal trihydrides at elevated temperatures. However, isolable monovalent Group 13 (semi)metal-hydride complexes are exceptionally scarce. The only existing examples so far reported are (CAAC)\textsubscript{2}BH A (CAAC = cyclic (alkyl)(amino) carbene),\textsuperscript{65} the mixed carbene ligands stabilized hydridoboron(I) B\textsuperscript{66} and (tmeda)Ga(H)[Cr(CO)\textsubscript{5}] C (tmeda = N,N’-tetramethylethylenediamine)\textsuperscript{67} reported by Bertrand et al. and Fischer et al., respectively (Scheme 2-22). The hydridoboron(I) moieties in A and B are stabilized by two neutral carbene ligands, whereas the Ga(I)–H in C is stabilized by TMEDA and a Cr(CO)\textsubscript{5} moiety acting as an electron donor and acceptor, respectively. Additionally, Robinson et al. reported the NHC-stabilized diborene complex D which can be described as a dimer of (NHC)BH\textsuperscript{68}.
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Considering this early stage in the development of Group 13 metal(I)-hydride chemistry, it would be highly demanding to investigate more on this chemistry in order to garner more structural and reactivity properties. Recently, in our group we have demonstrated that the chelate bisNHC (bis-(N-Ar-imidazole-2-ylidene)methylene, Ar = 2,6-iPr₂C₆H₃) is capable of stabilizing low-valent metal complexes, and the respective germylone,[12] silylone,[11] (dicoordinate germanium(0) and silicon(0) compounds that feature two lone-pair electrons at the respective element centers),[13] as well as the Fe(0)-arene complexes[131] have been prepared. Moreover, Ingleson et al.[132] and Meyer et al.,[133] have reported several Fe(II) complexes supported by this ligand, and very recently, Hofmann and coworkers showed that the bisNHC ligand can also stabilize Ni(0) and Pd(0) species.[70] Inspired by these results, I was interested in obtaining the hydridoaluminum(I) and hydridogallium(I) complexes employing the bisNHC ligand.

Herein, the synthesis of the elusive [bisNHC]Al(H):→[Fe(CO)₄] complex 34a and its isolable Ga(I) analogue [bisNHC]Ga(H):→[Fe(CO)₄] 39, which show distinctly different reactivities, is discussed. Compound 34a enables unexpectedly facile C–H and C–O bond activation of tetrahydrofuran (THF) and tetrahydropyran (THP), whereas complex 39 is inert towards cyclic ethers and can be isolated in high yield. The THF and THP molecules are deprotonated by 34a at the α-carbon positions to yield bisNHC-Al(2-cyclo-OC₄H₇)[Fe(CO)₄] 34 and bisNHC-Al(2-cyclo-OC₅H₉)[Fe(CO)₄] 35, respectively, with concomitant elimination of dihydrogen. This represents the first example of deprotonation of a sp³ C–H bond with a low-valent main group hydride complex. Moreover, compound 34a can also cleave the C–O
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bond, with concomitant ring opening of THF, affording bisNHC-Al(OnBu)[Fe(CO)_4] as the sole product when a Lewis acid BR_3 (R = Et or sBu) is present. The reaction mechanisms for both C–H and C–O bond activations were elucidated by density functional theory (DFT) calculations.

3.3.2.1 Unexpected C–H and C–O bonds activation of cycloethers with the hydridoaluminum(I) complex

Treatment of bisNHC (bis-(N-Ar-imidazole-2-ylidene)methylene, Ar = 2,6-iPr_2C_6H_3) with one molar equivalent of AlBr_3 at −20 °C resulted in the formation of [bisNHC-AlBr_2]^+Br^- 32 as an off-white solid in high yield (92%) (Scheme 2-23). It represents the first example of any aluminum trihalide complex stabilized by a chelate bis-N-heterocyclic carbene ligand. It is noteworthy that the reaction of the ethylene bridged bis-N-heterocyclic carbene with AlCl_3 only afforded the bis-imidazolium salt as reported by Jones et al.,[134] and the mono-NHC stabilized AlX_3 (X = Cl, I) has been reported by Roesky and coworkers.[135] Very recently, a tetracarbene supported Al(III) complex has also been reported.[136]

![Scheme 2-23. Synthesis of complex [bisNHC-AlBr_2]^+Br^- 32.](image)

Single crystals of 32 suitable for single-crystal X-ray diffraction analysis were obtained by slow diffusion of n-hexane to a concentrated solution of 32 in CH_2Cl_2 at room temperature, and the molecular structure is depicted in Figure 2-25. It shows that 32 is an ion pair complex with a bromide as the counter-anion. The aluminum center features a tetrahedral geometry with the coordination to two carbon atoms from the bisNHC ligand and two bromide atoms. The Al–C bond distances (2.018(5) and 2.027 (5) Å) are similar to that in (IPr)AlI_3 (2.031(2) Å; IPr = :C(ArNCH)_2, Ar = 2,6-iPr_2C_6H_3).[135b] In the asymmetric unit, another molecule of [bisNHC-AlBr_2]^+[AlBr_4]^- (32a) with AlBr_4^- as the counter-anion is co-crystallized with 32, the molecular structure of complex 32a is also shown in Figure 2-25. The formation of 32a is likely due to the slight excess of AlBr_3 in the reaction, and if bisNHC was used in a slight
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excess amount (1.05 molar equivalents with respect to AlBr₃), compound 32 could be exclusively isolated. In consistent with the ionic nature, compound 32 is soluble in CH₂Cl₂ and acetonitrile, and it is marginally soluble in non-polar solvents, such as toluene, diethyl ether and n-hexane. The ¹H NMR spectrum in CD₂Cl₂ reveals two doublet resonance signals (δ = 1.05 and 1.18 ppm) and one septet signal (δ = 2.36 ppm) for the 2-propyl groups, indicating $C_2v$ symmetry of the molecule in solution, and it is consistent with the structure in the solid state. The protons of the bridging methylene group resonate at δ = 7.83 ppm as a singlet, and the corresponding ¹³C signal is observed at δ = 59.9 ppm in the ¹³C{¹H} NMR spectrum.

Figure 2-25. Molecular structures of complexes 32 (left) and 32a (right) in the solid state. Thermal ellipsoids are drawn at 50% probability level, all the hydrogen atoms and the solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (°) for 32: Al1–C3 2.027(5), Al1–C7 2.018(5), Al1–Br1 2.2708(15), Al1–Br2 2.2611(15); C3–Al1–C7 93.7(2), C3–Al1–Br2 116.96(15), C3–Al1–Br1 109.63(14), C7–Al1–Br2 114.05(15), C7–Al1–Br1 108.83(15), Br1–Al1–Br2 112.13(6).

With compound 32 as a starting material, the reduction of it to bisNHC-aluminum(I) species with various reducing agents was further studied. However, the attempts to reduce complex 32 with either KC₈ or sodium naphthalenide afforded only intractable product mixtures. It turned out that K₂Fe(CO)₄ was a suitable reducing agent for this purpose. Accordingly, the reduction of 32 with one molar equivalent of K₂Fe(CO)₄ was carried out in THF from −50 °C to room temperature, resulting in the formation of bisNHC-Al(Br)[Fe(CO)₄] 33 which could be isolated as colourless crystals in moderate yield (72%) (Scheme 2-24). Compound 33 is the first example of a stable Al(I) complex bearing an NHC ligand.²⁰,¹³⁷

Compound 33 is soluble in THF and CH$_2$Cl$_2$, but has low solubility in toluene and other aliphatic solvents. Due to the lower symmetry of complex 33 compared to that of 32, which has C$_{2v}$ symmetry, four doublet resonance signals ($\delta = 0.95, 1.01, 1.22$ and $1.32$ ppm) and two septet signals ($\delta = 2.50$ and $3.00$ ppm) for the 2-propyl groups are observed in the $^1$H NMR spectrum in THF-d$_8$. In the infra-red spectrum, the stretching frequencies for the carbonyl groups are revealed at $\nu = 1982, 1897, 1859, 1819$ cm$^{-1}$, and are blue-shifted compared to those in Cp*Al[Fe(CO)$_4$] ($\nu = 2024, 1948, 1903$ cm$^{-1}$; Cp* = pentamethylcyclopentadienyl),$^{[138]}$ suggesting a stronger electron donating capacity of the bisNHCAl:(Br) moiety in 33. This is likely attributed to the strong $\sigma$-donating ability of the bisNHC ligand. The solid state structure of complex 33 is depicted in Figure 2-26 which crystallizes in the monoclinic space group $P2_1/c$. The Al center exhibits a tetrahedral geometry with the coordination to two carbon centers of the bisNHC ligand, bromide and iron atoms. The iron center exhibits a trigonal bipyramidal geometry with the bisNHC-Al moiety in an apical position. The Al–C (2.045(4) and 2.048(4) Å) bond distances are comparable to that in IPr-AlI$_3$ (2.031(2) Å),$^{[135b]}$ and slightly longer than those in the starting material 32 (2.018(5) and 2.027 (5) Å). The Al–Fe bond distance is longer than that in Cp*Al-Fe(CO)$_4$ (2.231 (3) Å).$^{[138]}$
**Figure 2-26.** Molecular structure of complex 33. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and the solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Al1−C3 2.045(4), Al1−C7 2.048(4), Al1−Br1 2.3173(11), Al1−Fe1 2.4062(11); C3−Al1−C7 88.73(14), C3−Al1−Br1 104.80(10), C7−Al1−Br1 103.84(11), C3−Al1−Fe1 112.57(10), C7−Al1−Fe1 113.54(11), Br1−Al1−Fe1 126.54(5).

With compound 33 as an Al(I) source, I further targeted the synthesis of the corresponding hydridoaluminum(I) complex. Hence, potassium hydride (KH) was utilized firstly as a hydride source. The reaction of KH with 33 was carried out in THF at room temperature for 48 hours (Scheme 2-25). However, the expected salt metathesis reaction did not yield the desired Al(I)-hydrido complex 34a, instead the bisNHCAl(2-cyclo-OC₄H₇)[Fe(CO)₄] complex 34 was isolated bearing a THF moiety deprotonated at the α-carbon position attached to the aluminum center. A plausible explanation for the formation of 34 could be that the desired bisNHC-Al(H)[Fe(CO)₄] 34a is formed at the beginning as an elusive species (reactive intermediate) which metalates a THF molecule at the α-carbon position affording complex 34, with concomitant elimination of dihydrogen. The formation of dihydrogen was additionally confirmed by ¹H NMR spectroscopy: A resonance signal at δ = 4.53 ppm is observed, corresponding to H₂, from the reaction of 33 with KH at room temperature in THF-d₈ in a sealed NMR tube. The formation of H₂ instead of the anticipated HD can be explained by the degree of deuteration of THF-d₈ = 99.5% D. In addition, the C–D bond is stronger than the C–H bond. In this case, it is more favourable to deprotonate the C–H bond (isotope effect). Moreover, the detailed mechanism was further elucidated by DFT calculations (*vide infra*).
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Scheme 2-25. C–H and C–O bonds activation mediated by the elusive hydrido-Al(I)→Fe complex 34a.

The composition of complex 34 was determined by the combination of NMR spectroscopic and X-ray crystallographic studies. The molecular structure of 34 is portrayed in Figure 2-27. It reveals that the α-metalated THF moiety is attached to the Al(I) center through α-carbon and stays intact at ambient temperature without any ring opening and/or bond cleavage. This is remarkable since the conventional α-metalation of THF with organolithium and organopotassium reagents normally initiates ring opening and cleavage of C–O and C–C bonds forming ethylene and the enolate of acetaldehyde at ambient temperature.[139] Very recently, Mulvey et al. developed a methodology based on bimetallic bases [(tmeda)Na(μ-TMP)(μ-CH₂SiMe₃)Zn(CH₂SiMe₃)] (TMP = 2, 2, 6, 6-tetramethylpiperidine) and [(THF)Li(TMP)(TMP)Al-(iBu)₂] for α-metalation of cyclic ethers and their analogues. The cyclic ether anions are cooperatively stabilized by the Na/Zn[140] or Li/Al[141] cations. In contrast to the reported bimetallic system, in complex 34, the THF anion is only stabilized by the Al center. Moreover, in the bimetallic base systems, the alkaline bases are crucial for the activation of the inert C–H bonds, since the organo-zinc or aluminum reagents themselves are not basic enough to deprotonate cyclic ethers and their analogues. It is also noteworthy
that a recent investigation by Mulvey et al. showed that the \( \alpha \)-metalation of THF with the bimetallic base LiTMP•Al(iBu)\(_3\) is a two-step process involving initial metalation of THF with LiTMP followed by trapping of the metalated species by the Al reagent.\(^{[142]}\) In contrast, no reaction between KH and THF was observed, indicating that the \( \alpha \)-metalation of THF occurs through the hydrido-Al(I) \( 34a \) directly.

**Figure 2-27.** Molecular structure of 34. Thermal ellipsoids are drawn at the 50\% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): A11–C3 2.060(5), A11–C7 2.059(4), A11–Fe1 2.4834(14), A11–C99 1.998(5); C99–A11–C7 110.2(2), C99–A11–C3 110.3(2), C7–A11–C3 87.48(17), C99–A11–Fe1 124.29(15), C7–A11–Fe1 109.68(12), C3–A11–Fe1 108.68(13).

As a result of the substitution of one hydrogen atom in the \( \alpha \)-C position of THF with an Al atom, the \( \alpha \)-C atom is bonded to four different atoms (Al, O, C and H atoms), rendering it chiral. The consequence of this induced chirality is the complete loss of symmetry of compound 34 in comparison to the starting materials 32 and 33. Thus, all the eight methyl groups in the isopropyl moieties are chemically inequivalent and eight doublet resonance signals are observed in the \( ^{1}H \) NMR spectrum in THF-\( d_8 \) solutions (\( \delta = 0.95, 0.97, 0.98, 1.04, 1.09, 1.13, 1.30 \) and 1.31 ppm). Moreover, two \( ^{13}C \) resonance signals for the carbene carbon are found in the \( ^{13}C\{^{1}H\} \) NMR spectrum (\( \delta = 177.0 \) and 177.4 ppm). The \( ^{13}C \) NMR chemical shifts for the AlCHO and OCH\(_2\) moieties are revealed at \( \delta = 69.1 \) and \( \delta = 74.7 \) ppm (broad, due to the coupling with the quadrupolar \( ^{27}Al \) nucleus), respectively.

Prompted by the facile \( \alpha \)-metalation of THF with the elusive hydridoaluminum(I) species \( 34a \), I further explored the \( \alpha \)-metalation of tetrahydropyran (THP), the six-membered ring homologue of THF. In analogy, THP was also readily \( \alpha \)-metalated affording the
corresponding (bisNHC)Al(I)(2-cyclo-C₅H₅O)[Fe(CO)₄] 35 in moderate yield by the reaction of 33 with an excess amount (two molar equivalents) of KH in THP at 55 °C for 48 hours (Scheme 2-25). An elevated temperature is necessary due to the low solubilities of 33 and KH in THP. Due to the chirality of the α-carbon of the THP anion attached to the Al(I) center, complex 35 exhibits similar features as 34 in terms of the NMR chemical shifts in the ¹H and ¹³C{¹H} NMR spectra in THF-d₈. For instance, the protons of the methine groups are observed as four septet resonance signals (δ = 2.10, 2.26, 3.28 and 3.61 ppm), and the carbene carbon nuclei (NCN) are revealed as two close resonance signals in the ¹³C{¹H} NMR spectrum (δ = 177.1 and 177.3 ppm). In the high resolution mass spectrum, the signal of the molecular peak could not be observed, whereas the molecular fragment corresponding to loss of the THP moiety and one CO is revealed at m/z 637.2475 (calcd. m/z 637.2416). This result demonstrates that 34a is also capable of α-metalation of THP, and it represents the first example of a low-valent main group (semi)metal hydrido complex that can activate the relatively inert sp³ C–H bond of cyclic ethers, hitherto the domain of transition metal complexes.[143]

In order to get a better understanding of the mechanism for the α-C–H activation of THF with 34a forming 34, DFT calculations were carried out at the B97-D/def2-TZVP(THF)//B97-D/6-31G* [Al,Fe def2-TZVP] level of theory (Figure 2-28). The calculations reveal that the first step is the coordination of the THF molecule to the Al center in 34a affording the intermediate INT1 bearing a five-coordinate aluminum center, which is succeeded by the H–H interaction of the Al–H and C–H moieties yielding a five-membered ring transition state TS1 with an associated free energy of +29.2 kcal mol⁻¹. TS1 is rather high considering the reaction conditions. However, taking into account the margin of error associated with DFT methods, this mechanism is still feasible. TS1 is followed by the H₂ elimination step, also observed experimentally (vide supra), to generate the zwitterionic species P1 which immediately rearranges, without activation barrier, affording the product (−4.3 kcal mol⁻¹).
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Figure 2-28. Reaction mechanism for the formation of 34 and H₂, starting from 34a and THF, derived from DFT calculations at the B97-D/def2-TZVP(THF)/B97-D/6-31G* [Al,Fe def2-TZVP] level of theory. * The determination of P1 and P2 is somewhat complicated. Both are not intermediates in the sense that tight optimization does not yield such these structures. However, we include them in the energy profile since after the elimination of H₂ species P1 remains and then isomerizes to P2. [95]

Interestingly, in contrast to the case of KH as the hydride source, when K(BHR₃) (R = Et or sBu) was applied as the hydride source to react with 33 in THF at room temperature, the reaction afforded the THF ring opened product bisNHC-Al(O₃Bu)[Fe(CO)₄] 36 in 62% yield with cleavage of the C–O bond in THF (Scheme 2-25). In order to confirm that the O₃Bu group in the product originates from the C–O bond cleavage of a THF molecule, the reaction was carried out in THF-d₈, and as expected, all the proton signals corresponding to the O₃Bu moiety were vanished when compared to the ¹H NMR spectrum of compound 36 synthesized in non-deuterated THF. The composition of 36 was determined by NMR (¹H and ¹³C{¹H}) spectroscopy, elemental analysis and IR spectroscopy. Unfortunately, the attempts to obtain the single-crystals of complex 36 under various conditions were unsuccessful; this is probably owing to the flexibility of the O₃Bu group which hinders the crystallization process. The proton signals for the O₃Bu group are observed at δ = 0.49-0.55 ppm as a multiplet signal (7 H) and δ = 2.74 ppm as a triplet signal (2 H) in the ¹H NMR spectrum in THF-d₈. The corresponding ¹³C nuclei chemical shifts can be determined in the ¹³C{¹H}, HMQC and DEPT-135 NMR spectra (δ = 14.7, 19.4, 37.3, 61.6 ppm). It is noteworthy that cleavage of the C–O bond of THF to form ring opened products has also been observed with transition metal hydrido complexes [144] and a ‘frustrated Lewis pair’ [145].
Further DFT calculations suggest that the Al(I)–H bond in 34a is activated by the Lewis acid BEt3, formed in situ from the reaction of K[BHEt3] with 33, through ‘frustrated Lewis pair’ like interaction affording INT1_BEt3 (Figure 2-29). The interaction of the Al center with a THF molecule further weakens the Al–H bond leading to the transition state TS1_BEt3 (+16.4 kcal mol⁻¹), the rate-determining barrier of the overall reaction (+19.6 kcal mol⁻¹), which prompts the Al–H bond dissociation to form the ionic species INT2_BEt3 (−10.8 kcal mol⁻¹). Further hydride transfer from the HBEt3 anion to the THF moiety triggers the C–O bond cleavage leading to the highly stable product 36 (−59.4 kcal/mol).

\[
\begin{align*}
\text{B}97\text{-D/def2-TZVP(THF)//B97-D/6-31G* [Al,Fe def2-TZVP]} \text{ level of theory.}^{[95]} \\
\end{align*}
\]

### 3.3.2.2 Synthesis of an isolable hydridogallium(I) complex

In order to obtain an isolable monovalent Group 13 metal hydrido analogue of 34a, I further tried to prepare the bisNHC-hydrido-Ga(I)→Fe(CO)₄ complex 39. Owing to the larger electronegativity of gallium vs. aluminum, the Ga–H bond exhibits a higher covalent character than that of the corresponding Al–H bond; this should lead to a higher stability of complex 39 vs. 34a. Actually, the isolable complex 39 could indeed be accessible through a similar synthetic protocol as applied for the preparation of the elusive complex 34a. Accordingly, the starting material [bisNHCGaCl₂]+Cl⁻ 37 was synthesized by the reaction of bisNHC with one molar equivalent of GaCl₃ in toluene at room temperature. Compound 37 was isolated as an off-white solid in 90% yield in a similar manner as complex 32. Complex 37 was readily reduced by K₂[Fe(CO)₄] in THF at ambient temperature resulting in the first bisNHC-stabilized chloro-Ga(I) complex bisNHC-Ga(Cl)[Fe(CO)₄] 38 (Scheme 2-26).^{[146]}
The compositions of 37 and 38 were further elucidated by single-crystal X-ray diffraction analyses, elemental analyses, IR spectroscopy as well as NMR (\(^1\)H and \(^{13}\)C\(^{1}\)H) spectroscopy for 37. Compound 38 is extremely insoluble in organic solvents, so it has not been characterized by solution NMR spectroscopy.

![Scheme 2-26. Syntheses of complexes 37-39.](image)

The solubility of compound 37 is similar to that of complex 32. The \(^1\)H NMR spectrum indicates a high symmetry (C\(_{2v}\)) of 37 in CD\(_2\)Cl\(_2\). For instance, the protons at the 2-propyl groups are revealed as two doublet resonance signals (\(\delta = 1.06\) and 1.17 ppm) for the methyl groups and one septet (\(\delta = 2.35\) ppm) for the methine moieties. The crystal structure analyses of complexes 37 and 38 are shown in Figure 2-30. The structure motifs of 37 and 38 are akin to those of 32 and 33, respectively. In compound 37, the Ga atom exhibits a tetrahedral configuration, and the Ga–C bond distances of 2.000(4) and 2.006(3) Å are close to those in mono-NHC stabilized Ga(III) complexes.\(^{[147]}\) The Ga atom in 38 is tetrahedrally coordinated by two carbon and one chloride atoms, along with a Fe(CO)\(_4\) moiety; the coordination environment of the Ga center is also comparable to those observed for Ga(I) complexes stabilized by one neutral bidentate nitrogen containing ligand.\(^{[67, 148]}\)

![Figure 2-30. Molecular structure of 37 (left) and 38 (right).](image)

Selected bond lengths...
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(Å) and angles (°): 37: Ga1–C3 2.000(4), Ga1–C7 2.006(3), Ga1–Cl1 2.1431(10), Ga1–Cl2 2.1584(10); C3–Ga1–C7 93.61(15), C3–Ga1–Cl1 114.63(10), C7–Ga1–Cl1 115.20(11), C3–Ga1–Cl2 109.25(10), C7–Ga1–Cl2 109.52(10), Cl1–Ga1–Cl2 113.00(5). 38: Ga1–C3 2.0827(18), Ga1–C7 2.0829(18), Ga1–Cl1 2.2463(5), Ga1–Fe1 2.3539(4); C3–Ga1–C7 89.94(7), C3–Ga1–Cl1 102.30(5), C7–Ga1–Cl1 97.38(5), C3–Ga1–Fe1 119.27(5), C7–Ga1–Fe1 126.10(5), Cl1–Ga1–Fe1 116.349(16).

The chloride/hydride exchange of 38 with one molar equivalent of K[BHR₃] (R = Et or sBu) in THF at room temperature facilely afforded the expected hydrido-Ga(I)→Fe complex 39, bisNHC-Ga(H)[Fe(CO)₄], stabilized by the bisNHC and the Fe(CO)₄ moieties. Complex 39 was isolated in high yield as colorless crystals from concentrated THF solutions at 0 °C. Remarkably, compound 39 does not react with THF or THP even at elevated temperatures which is contrary to its aluminum analogue. It was fully characterized by NMR and IR spectroscopy, elemental analysis as well as single-crystal X-ray diffraction. It has a relatively low solubility in THF, but much better than the starting material 38, and is also marginally soluble in toluene and n-hexane. The proton signal for Ga−H is revealed at δ = 4.58 ppm in the ¹H NMR spectrum in THF-d₈, which is comparable to those of L₃GaH₂ (δ = 4.53 ppm; L³ = CH(CMeNAr)₂, Ar = 2,6-iPr₂C₆H₃)[¹⁴⁹] and (tmeda)Ga(H)[Cr(CO)₅] (δ = 5.03 ppm).[⁶⁷]

Single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution in THF at 0 °C, and the structure is portrayed in Figure 2-31. It crystallizes in the monoclinic space group P₂₁/c, and the Ga center is tetrahedrally coordinated by the C3, C7, Fe1 and H3 atoms. The Ga1–Fe1 bond distance is slightly longer than that in the starting material bisNHC-Ga(Cl)[Fe(CO)₄] 38.

**Figure 2-31.** Molecular structure of 39. Thermal ellipsoids are drawn at the 50% probability level; all hydrogen atoms (except Ga–H) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga1–C3 2.084(5), Ga1–C7 2.093(6), Ga1–Fe1 2.4010(12), Ga1–H3 1.84(6);
C3–Ga1–C7 88.3(2), C3–Ga1–Fe1 116.72(16), C7–Ga1–Fe1 121.41(16), C3–Ga1–H3 103(2), C7–Ga1–H3 103(2), Fe1–Ga1–H3 119(2).

In order to have a rational understanding for the formation and stability of the Ga(I)-hydrido complex 39, which is inert towards THF, in contrast to its aluminum analogue 34a, DFT calculations were carried out in probing the hypothetical C–O bond activation of THF with 39 (Figure 2-32). The overall reaction to form the C–O bond cleavage product bisNHC-Ga(OnBu)[Fe(CO)]4 is indeed thermodynamically favorable with an exergonic energy of –27.7 kcal mol\(^{-1}\) with respect to that of the starting materials (note that this is 31.7 kcal mol\(^{-1}\) higher than in the case of the aluminum analogue (vide supra)). However, the free energy of activation of the rate determining step is very high (+34.3 kcal mol\(^{-1}\)) compared to the aluminum case, at only +19.6 kcal mol\(^{-1}\), suggesting notably higher kinetic stability of 39 towards the C–O bond activation of THF. These findings hence rationalize the inertness of 39 with respect to C–O bond activation of cyclic ethers, in accordance with the experimental findings. In addition, the C–H bond activation process analogous to the observed reaction of 34a was also investigated (Figure 2-33). The activation barrier affording TS1_Ga is extremely high (+84.2 kcal mol\(^{-1}\)) and the product is also much less stable than the reactants (+47.5 kcal mol\(^{-1}\)), therefore this reaction cannot proceed, again fits with the experimental findings.

![Figure 2-32](image-url)  
**Figure 2-32.** Mechanism for hypothetical C–O bond cleavage of THF with 39 derived from DFT calculations at the B97-D/def2-TZVP(THF)//B97-D/6-31G* [Ga,Fe def2-TZVP] level of theory.\[^{[95]}\]
Figure 2-33. Mechanism for hypothetical C–H bond cleavage of THF with 39 derived from DFT calculations at the B97-D/def2-TZVP(THF)/B97-D/6-31G* [Ga,Fe def2-TZVP] level of theory. * The determination of P3 and P4 is somewhat complicated. Both are not intermediates in the sense that tight optimization does not yield these structures. However we include them in the energy figure since after the elimination of H2 species P3 remains and then isomerizes to P4.[95]
4. SUMMARY AND CONCLUSION

This work mainly focused on the application of monovalent Group 13 metal and divalent silicon and germanium compounds in small molecule activations as well as supporting ligands for transition metal coordination chemistry, and using the obtained transition metal complexes as precatalysts for organic transformations.

The reactivities of the $N$-heterocyclic silylenes (NHSis) $L^1(X)Si$: ($X = Cl, OrBu, NMe_2$), $L^1Si:(O):SiL^1$ ($L^1 = PhC(NtBu)_2$) and $L^2Si$: ($L^2 = CH(C=CH_2)(CM)(NAr)_2$, $Ar = 2,6$-iPr$_2$C$_6$H$_3$) towards copper(I) reagents were investigated. The compounds $L^2Si(H)(CH_2)NHC$ and $L^3Si(=E)OH(dmap)$ ($L^3 = CH(MeCNAr)_2$, $Ar = 2,6$-iPr$_2$C$_6$H$_3$; $dmap = 4$-dimethylaminopyridine; $E = S$ and $Se$) were applied as supporting ligands for nickel(II) and copper(I) ions, respectively. Moreover, the reactivities as well as the catalytic properties of the emerging metal complexes were studied (Figure 3-1).

Figure 3-1. The reactivities of NHSis, $L^3Si(=E)OH(dmap)$ ($E = S$ and $Se$) and $L^2Si(H)(CH_2)NHC$ towards copper(I) and nickel(II) reagents, respectively, and the application of the obtained metal complexes in small molecule activations as well as in homogeneous catalysis.
As an important realm of low-valent main group chemistry, the chemistry of germylene-hydride, aluminium(I)-hydride and gallium(I)-hydride was investigated. The activations of CO$_2$ and $\alpha$-C–H bonds of cyclic ethers with the former two complexes exhibit the reactivities of the Ge(II)–H and Al(I)–H bonds, respectively. In contrast, the analogous Ga(I)-hydride complex is inert towards cyclic ethers (Figure 3-2).

**Figure 3-2.** Syntheses and reactivities of germylene-hydride, aluminium(I)- and gallium-hydride complexes.

The reactions of the amidinato-substituted NHSis $L^1$XSi: (X = Cl, OrBu, NMe$_2$) with [tmCUDA(CH$_3$CN)]OTf afforded the second examples of NHSi copper(I) complexes $[L^1$XSi:→Cu(tmeda)][OTf] (2: X = Cl, 3: X = OrBu, 4: X = NMe$_2$) featuring a Si:→Cu(I) interaction. Moreover, the reaction of the oxo-bridged bis(NHSi) ligand $L^1$Si:(O):Si$L^1$ with [Cu(CH$_3$CN)$_4$]OTf yielded the dinuclear NHSi copper(I) complex 6 featuring a metallacyclic dication (Scheme 3-1). The solid-state structure analyses revealed that the OTf counter anions and the complex cations of 2 and 6 have strong interactions with relatively short O⋯Cu distances, whereas they have much weaker interactions in complexes 3 and 4. These results indicate that the substituents at the silylene centers can not only change the donor properties of the NHSi ligands, but also can influence the interaction of the complex cations and counter anions of the NHSi metal complexes in the solid state structures.
Scheme 3-1. Coordination of $L^1(X)Si:SiL^1_1$ and $L^1Si:(O):SiL^1_1$ to copper(I) centers affording the second examples of NHSi copper(I) complexes.

In contrast to the reactions of the amidinato ligand supported NHSis with copper(I) reagents which led to the formation of NHSi copper(I) complexes, the zwitterionic NHSi $L^2Si:7$ is capable of activating the Cu–O and Cu–H bonds of (IPr)CuX ($X = OtBu, OH, H, OC_6F_5$) to afford the silyl copper(I) complexes $L^2Si(X)Cu(IPr)$ (8: $X = OtBu$; 9: $X = OH$; 10: $X = H$; 11: $X = OC_6F_5$) bearing various functional groups at the silicon centers. These silyl copper(I) complexes were capable of reducing CO$_2$ to CO forming the corresponding siloxy copper(I) complexes 12-15 (Scheme 3-2). The reaction kinetic studies showed that of the complexes 8 and 9 exhibited higher activities in CO$_2$ reduction to CO compared to 10 and 11. The comparison of the activities in CO$_2$ reduction and the nucleophilicities of the silyl groups of 8-11 indicates that the silyl copper(I) complex, which contains a more nucleophilic silicon center, has a higher activity in CO$_2$ reduction to CO. These results can provide useful insights for designing more efficient CO$_2$ reduction catalysts.

Scheme 3-2. Insertion of the Si(II) atom of $L^2Si:$ into the Cu–O and Cu–H bonds of (IPr)CuX affording the silyl copper(I) complexes and CO$_2$ reduction to CO by these silyl copper(I) complexes.
The first mixed NHSi-NHC chelate ligand was realized in the dibromo nickel(II) complex \( \text{L}^3\text{Si}(\text{CH}_2)(\text{NHC})\text{NiBr}_2 \) 17 through the Ni(II)-mediated tautomerization of the \( N \)-heterocyclic hydrosilylcarbene \( \text{L}^2(\text{H})\text{Si}(\text{CH}_2)\text{NHC} \) 16 via hydride migration from the silicon atom to the exocyclic methylene carbon center (Scheme 3-3).

**Scheme 3-3.** Synthesis of the first NHSi-NHC Ni(II) complex 17, and reduction of 17 with KC\(_8\) in the presence of PMe\(_3\) affording complexes 18 and 19.

The reduction of 17 with KC\(_8\) in the presence of PMe\(_3\) afforded the silyl-NHC bromo Ni(II) complex \[ \text{L}^3\text{Si}(\text{CH}_2)\text{NHC}]\text{Ni}(\text{Br})(\text{PMe}_3) \) 18 and the \[ \eta^2-(\text{Si}–\text{H})][\text{L}^2\text{Si}(\text{H})(\text{CH}_2)\text{NHC}]-\text{Ni}(\text{PMe}_3)_2 \] complex 19 depending on the reaction time (Scheme 3-3). When DMPE (dmpe = 1,2-bis(dimethylphosphino)ethane) was employed as an auxiliary ligand, the analogous reduction smoothly furnished the desired Ni(0) complex \([\text{L}^3\text{Si}(\text{CH}_2)\text{NHC}]\text{Ni}(\text{dmpe}) \) 20 (Scheme 3-4).

**Scheme 3-4.** Reductions of 17 to afford the first NHSi-NHC Ni(0) complexes 20 and 21.
The dicarbonyl Ni(0) complex \([L^3 \text{Si(CH}_2\text{NHC})\text{Ni(CO)}_2]\text{21}\) was obtained through the reduction of \textbf{17} with two molar equivalents of K(BHEt\textsubscript{3}) in a CO atmosphere (Scheme 3-4), and the substantially low IR stretching frequencies of \textbf{21} in comparison to its analogues bearing two phosphine or two NHC ligands suggest that the chelate NHSi-NHC ligand is a stronger \(\sigma\)-donor than two phosphine or NHC ligands. Remarkably, complex \textbf{17} serves as a highly efficient precatalyst for Kumada-Corriu-type sp\textsuperscript{2}-sp\textsuperscript{2} and sp\textsuperscript{2}-sp\textsuperscript{3} C–C formation reactions, highlighting the potential of the mixed NHSi-NHC chelating ligand supported transition metal complexes in homogeneous catalysis.

By utilizing dilithium selenide as a selenium source, the first isolable selenosilanoic acid-base adduct \(L^3\text{Si(}=\text{Se})\text{OH(dmap)}\text{25}\) could be synthesized. Complex \textbf{25} is a heavier homologue of the previously reported thiosilanoic acid-base adduct \(L^3\text{Si(}=\text{S})\text{OH(dmap)}\text{23}\). The complexes \textbf{23} and \textbf{25} can react with 1/4 molar equivalent of (MesCu\textsubscript{4}) to form the dinuclear copper(I) complexes \([L^3\text{Si(}=\text{S})\text{OCu}]_2\text{26}\) and \([L^3\text{Si(}=\text{Se})\text{OCu}]_2\text{27}\), respectively, bearing an intermolecular Si–O–Cu←E=Si interaction (E = S, Se) (Scheme 3-5). Both complexes \textbf{26} and \textbf{27} exhibit excellent performance for copper(I)-catalyzed aziridinaiton reaction of styrene with TsN=IPh (Ts = tosyl).

\textbf{Scheme 3-5.} Syntheses of the dinuclear copper(I) complexes \textbf{26} and \textbf{27}.

A novel \(N\)-heterocyclic germylene-hydride mediated CO\textsubscript{2} reduction to methanol with \text{Me\textsubscript{3}N•AlH\textsubscript{3}} as a hydride source could be achieved. The hydride exchange reaction of \(L^\text{Cy}\text{GeCl}\) with K[BH\textsubscript{3}(\text{tBu})\textsubscript{3}] furnished the new germylene-hydride \(L^\text{Cy}\text{GeH}\). However, the latter is highly reactive, and readily undergoes the hydride migration from the Ge(II) center to the backbone of the ligand, affording the \(N\)-heterocyclic germylene \((L^\text{Cy}\text{H})\text{Ge}\text{28}\). Nevertheless, the fragile germylene-hydride could be generated \textit{in situ} and utilized to activate CO\textsubscript{2} to afford a novel germylene-formate \(L^\text{Cy}\text{GeOCH(}=\text{O})\text{29}\) (Scheme 3-6).
Complex 29 and the previously reported L$_3$GeOCH(=O) 29$^*$ were smoothly hydrogenated to yield methanol when Me$_3$N•AlH$_3$ was employed as the hydride source upon workup with water, and the respective germylene hydrides were concomitantly regenerated in the process. Based on the model reaction of L$_3$GeOCH(=O) 29$^*$ with the mild hydride delivery agent L$^3$AlH$_2$, a plausible mechanism for the N-heterocyclic germylene hydride mediated CO$_2$ reduction to methanol was suggested with the isolation of L$_3$GeOCH$_2$OAl(H)L$_3$ 30 and (L$_3$AlOCH$_2$O)$_2$ 31 (Scheme 3-7). These studies shed new light on the understanding of low-valent main group metal hydrides mediated CO$_2$ reductions.

**Scheme 3-6.** Syntheses of complexes 28 and 29.

**Scheme 3-7.** A plausible reaction mechanism for the N-heterocyclic germylene hydride mediated CO$_2$ reduction to CH$_3$OD with Me$_3$N•AlH$_3$ as the hydride source.

In comparison to the chemistry of divalent Group 14 element hydrides, the field of monovalent Group 13 (semi)metal hydrides is far less developed. The syntheses of the Al(I)-
monohydride and Ga(I)-monohydride complexes with a chelate bis-N-heterocyclic carbene ligand (bisNHC, bis-(N-Ar-imidazole-2-ylidene)methylene, Ar = 2,6-iPr₂C₆H₃) were also vigorously investigated. The expected bisNHC-Al(H)[Fe(CO)₄] complex 34a, generated through the reaction of bisNHC-Al(Br)[Fe(CO)₄] 33 with KH, turned out to be kinetically labile, and can activate the α-C–H bond of THF or THP (tetrahydropyran) affording bisNHC-Al(2-cyclo-OC₄H₇)[Fe(CO)₄] 34 and bisNHC-Al(2-cyclo-OC₄H₇)[Fe(CO)₄] 35, respectively. Remarkably, when K(BHR₃) (R = Et or sBu) was applied as the hydride source, the analogous reaction in THF afforded complex bisNHC-Al(OnBu)[Fe(CO)₄] 36 as the sole product via the C–O bond cleavage and ring opening of THF (Scheme 3-8). The mechanisms for these novel C–H and C–O bond activations mediated by the elusive hydridoaluminum(I) complex 34a were further elucidated by density functional theory (DFT) calculations.

Scheme 3-8. Unexpected α-C–H and C–O bond activations of THF and THP with the elusive Al(I)-hydride 34a.

In contrast to the aluminum case, the analogous hydridogallium(I) bisNHC-Ga(H)[Fe(CO)₄] complex 39 could be isolated in high yield through the reaction of bisNHC-Ga(Cl)[Fe(CO)₄] 38 with one molar equivalent of K[BHR₃] (R = Et, sBu) in THF at room temperature (Scheme 3-9). The isolation of 39 and its inertness toward cyclic ethers might be attributed to the higher electronegativity of gallium vs. aluminum, which leads to a stronger Ga–H bond. The stronger Ga(I)–H bond, in turn, hampers the α-C–H metalation or C–O bond cleavage of cyclic ethers. This hypothesis was also supported by DFT calculations.
In conclusion, this doctoral work has extended the scope of low-valent main group chemistry especially that of the N-heterocyclic silylene (NHSi) and monovalent Group 13 metal hydride chemistry. The reactivities of NHSis and their derivatives towards copper(I) and Ni(II) reagents have been intensively investigated; some of the obtained complexes were employed for CO$_2$ activations and as precatalysts for organic transformations. The chemistry of germylene-hydride, aluminum(I)- and gallium(I)-hydride has also been studied. Remarkably, this work demonstrated for the first time that low-valent main group (semi)metal hydride complexes (eg. the Al(I)-hydride complex in this work) could activate the inert sp$^3$ C–H bonds, which is a domain of transition metal chemistry; this work sheds new light on heavier main group element complexes which can mediate desired organic transformations.
5. EXPERIMENTAL SECTION

5.1 General consideration

All experiment and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in nitrogen filled glovebox. The glassware used in all manipulations was dried at 150 °C prior to use, cooled to ambient temperature under high vacuum, and flushed with N₂. The handling of solid samples and the preparation of samples for spectroscopic measurements were carried out inside a glovebox, where the O₂ and H₂O levels were normally kept below 1 ppm.

All solvents were purified using conventional procedures and freshly distilled under N₂ atmosphere prior to use. They were stored in Schlenk flasks containing activated molecule-sieves. Benzene, toluene, n-hexane were purified by distillation from Na/benzophenone. Et₂O and THF were initially pre-dried over KOH, and then distilled from Na/benzophenone. CH₂Cl₂ and chloroform were dried by stirring over CaH₂ at ambient temperature.

5.2 Analytical methods

NMR Measurements: NMR samples of air and/or moisture sensitive compounds were all prepared under inert atmosphere and sealed off in a NMR tube in vacuo for measurement. The deuterated solvents were dried by stirring over Na mirror (benzene-d₆, toluene-d₈ and THF-d₈) or CaH₂ (CD₂Cl₂ and CDCl₃), distilled under N₂ atmosphere and stored in Schlenk flasks containing activated molecule-sieves. The ¹H- and ¹³C-NMR spectra were recorded on ARX 200 (¹H, 200 MHz; ¹³C, 50 MHz) and ARX 400 (¹H, 400 MHz; ¹³C, 100.46 MHz) spectrometers from the Bruker Company. The ²⁹Si{¹H} and ²⁹Si{INEPT} NMR spectra were recorded only on ARX 400 (²⁹Si, 79.49 MHz) spectrometer. ¹H and ¹³C{¹H} NMR spectra were referenced to residual solvent signals as internal standards (benzene-d₆, δH = 7.15 ppm and δC = 128.0 ppm; CDCl₃ δH = 7.27 ppm and δC = 77.0 ppm; THF-d₈, δH = 1.73 ppm and δC = 25.3 ppm; CD₂Cl₂, δH = 5.32 ppm and δC = 53.8 ppm; toluene-d₈, δH = 2.08 ppm and δC = 20.4 ppm. Heteronuclear spectra were calibrated as follows: ³¹P{¹H}: external 85% H₃PO₄, ²⁹Si{¹H}: SiMe₄. Whereby in each case an 1-mm glass capillary tube containing the standard substance was placed in the appropriate solvent in a 5 mm NMR tube and the spectrum recorded. Unambiguous signal assignments were made by employing a combination of 2D
NMR H,C-HMQC (Heteronuclear Multiple-Quantum Correlation) and DEPT (Distortionless Enhancement by Polarization Transfer) experiments. The abbreviations used to denote the multiplicity of the signals are as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad.

**Infra-red spectroscopy** IR spectra (4000-400 cm\(^{-1}\)) were recorded on a Perkin-Elmer Spectra 100 FT-IR spectrometer, bands were reported in wave-numbers (cm\(^{-1}\)). Samples of solids were measured as KBr pellets. Air or moisture sensitive samples were prepared in the glovebox, and measured immediately. The spectra were processed using the program OMNIC and the abbreviations associated with the absorptions quoted are: vs = very strong; s = strong, m = medium; w = weak, br = broad, the intensities of which were assigned on the basis of visual inspection.

**Mass Spectrometry** Mass spectra were performed at the Chemistry institute of Technical University Berlin. EI spectra were recorded on a 311A Arian MAT/AMD spectrometer. ESI mass spectra were recorded on a Thermo Scientific Orbitrap LTQ XL spectrometer. Solid samples were prepared in glove box and the solution of samples was prepared 15 min before the measurement under N\(_2\) atmosphere. Mass spectra are presented in the standard form, m/z (percent intensity relative to the base peak).

**Elemental analysis** The C, H, N, and S analyses of all compounds were carried out on a Thermo Finnigan Flash EA 1112 Series instrument. Air or moisture sensitive samples were prepared in “tin-boats” in the glove box. Samples with halogen were filled in the “silver-boats” for better measuring accuracy.

**Melting Point determinations** A BSGT Apotec II instrument was used for the determination of melting points. Samples were prepared in glass capillary tubes under N\(_2\) atmosphere. The melting point was determined while the melded examples had the same color like the solid before. Without melting of samples the color change was observed, was determined as decomposition temperature.

**Single crystal X-ray structure determinations:** Crystals, suitable to the single crystal X-ray structure analysis, were put on a glass capillary with perfluorinated oil and measured in a cold nitrogen stream. The data of all measurements were collected with an Oxford Diffraction Xcalibur S Saphire diffractometer at 150 K (MoK\(_\alpha\) radiation, \(\lambda = 0.71073\ \text{Å}\)) or an Oxford Diffraction Supernova, Single source at offset, Atlas at 150 K (Cu-K\(_\alpha\)-radiation, \(\lambda = 1.5418\ \text{Å}\)). The structures were solved by direct methods. Refinements were carried out with the
SHELXL-97 software package. All thermal displacement parameters were refined anisotropically for non-H atoms and isotropically for H atoms. All refinements were made by full matrix least-square on $F^2$. In all cases, the graphical representation of the molecular structures was carried out using Ortep32 version 3v2. The details for the individual structure solutions included in this dissertation are available in the appendix.

5.3 Starting materials

Commercially available starting materials were used as received. The following important precursors were prepared according to literature procedures:

- $L^1(\text{Cl})\text{Si}^-$, \cite{72}
- $L^1(\text{OrBu})\text{Si}^-$ and $L^1(\text{NMe}_2)\text{Si}^-$, \cite{34a}
- $[\text{Cu(tmeda})(\text{CH}_3\text{CN})][\text{OTf}]$, \cite{73}
- $L^1\text{Si}(\mu-O)\text{Si}^-L^1$, \cite{53a}
- $[\text{Cu(THF)}(\text{CN})_2]$\text{OTf}$^-$, \cite{76}
- $L^2\text{Si(THF)}(\text{CH}_2)\text{NHC}^-$, \cite{24}
- $L^2\text{Si}^-$, \cite{19}
- (IPr)$\text{Cu(OTf)}$ and (IPr)$\text{CuH}$, \cite{83}
- (IPr)$\text{CuOH}$, \cite{85}
- $L^2\text{Si(OH)(dmap)}$ and $L^3\text{Si(S=O)(dmap)}$, \cite{113}
- (MesCu)$_4$, \cite{150}
- GeCl$_2$•1,4-dioxane, \cite{151}
- $L^\text{CyGeCl}$, \cite{123}
- $L^2\text{GeH}$ and $L^2\text{GeOCH(OH)}$, \cite{58e}
- $L^3\text{AlH}_2$, \cite{126}
- bis-(N-Dipp-imidazole-2-ylidene)methylene (bisNHC), \cite{132a}
- $K_2\text{Fe(CO)}_4$, \cite{152}. 


5.4 Synthesis and characterization of all the new compounds

5.4.1 Synthesis of \([\text{L}^1\text{ClSi:} \rightarrow \text{Cu(tmeda)}][\text{OTf}]\) (2)

L\(^1\)SiCl (0.147 g, 0.5 mmol) and \([\text{tmedaCu(CH}_3\text{CN)}][\text{OTf}]\) (0.185 g, 0.5 mmol) were placed in a Schlenk flask in the glovebox, and toluene (30 mL) was transferred to the flask via cannula under stirring at -78 °C. Then the mixture was allowed to warm up to room temperature with stirring. After stirring for 12 hours at room temperature, the obtained clear colorless solution was concentrated to ca. 5 mL and filtered. The filtrate was left at 0 °C for 24 hours to afford a colorless crystalline product of 2. The product was collected by decantation of the supernatant and the obtained solid was dried in vacuo for several hours. Yield: 0.26 g, 0.4 mmol (80%).

\(^1\)H NMR (200.1 MHz, CD\(_2\)Cl\(_2\), 298 K, ppm): \(\delta = 1.20\) (s, 18 H, \(t\text{Bu-}H\)), 2.61 (br, 12 H, N(CH\(_3\))\(_2\)), 2.65 (br, 4 H, NCH\(_2\)CH\(_2\)N), 7.12-7.25 (m, 1 H, Ph-\(H\)), 7.40-7.67 (m, 4 H, Ph-\(H\)).

\(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CD\(_2\)Cl\(_2\), 298 K, ppm): \(\delta = 31.2\) (tBu-CH\(_3\)), 48.4 (N(CH\(_3\))\(_2\)), 55.0 (tBu-C), 58.3 (NCH\(_2\)CH\(_2\)N), 122.9 (CF\(_3\)), \(^1\)J\(_{C-F} = 321\) Hz) 128.5, 128.8, 129.31, 130.8, 129.9 (Ph-CH), 131.4 (Ph-C), 174.9 (NCN).

\(^{19}\)F\{\(^1\)H\} NMR (188.3 MHz, CD\(_2\)Cl\(_2\), 298 K, ppm): \(\delta = -78.7\).

\(^{29}\)Si\{\(^1\)H\} NMR (79 MHz, CD\(_2\)Cl\(_2\), 298 K, ppm): \(\delta = 32.9\).

Elemental analysis: for [C\(_{29}\)H\(_{35}\)ClCuF\(_3\)N\(_4\)O\(_3\)SSi·1/3 toluene] (determined from \(^1\)H NMR spectroscopy)] Calcd: C, 44.66; H, 6.42; N, 8.56; S, 4.90. Found: C, 43.96; H, 6.49; N, 8.91; S, 4.57.
5.4.2 Synthesis of $[L^1(\text{OtBu})\text{Si}:\rightarrow \text{Cu(tmeda)}][\text{OTf}]$ (3)

This compound was synthesized in the similar procedure as compound 2. Yield: 0.24 g, 0.36 mmol (72%).

$^1\text{H NMR}$ (200.1 MHz, CD$_2$Cl$_2$, 298 K, ppm): $\delta = 1.23$ (s, 18 H, NtBu-$H$), 1.51 (s, 9 H, OtBu-$H$), 2.67 (br, 12 H, N(CH$_3$)$_2$), 2.73 (br, 4 H, NCH$_2$CH$_2$N), 7.32-7.36 (m, 1 H, Ph-$H$), 7.49-7.66 (m, 4 H, Ph-$H$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, CD$_2$Cl$_2$, 298 K, ppm): $\delta = 31.3$ (NtBu-CH$_3$), 32.2 (OtBu-CH$_3$), 48.1 (N(CH$_3$)$_2$) 53.8 (NtBu-C), 57.9 (NCH$_2$CH$_2$N), 74.5 (OtBu-C), 124.3 (CF$_3$, $^1\text{J}_{C-F} = 321$ Hz), 127.2, 128.3, 128.4, 128.7, 130.8 (Ph-CH$_2$), 131.0 (Ph-C), 172.9 (NCN).

$^{19}\text{F}\{^1\text{H}\}$ NMR (188.3 MHz, CD$_2$Cl$_2$, 298 K, ppm): $\delta = -78.8$.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, CD$_2$Cl$_2$, 298 K, ppm): $\delta = 5.4$.

Elemental analysis: for [C$_{26}$H$_{48}$CuF$_3$N$_4$O$_4$SSi]: Calcd: C, 47.22; H, 7.32; N, 8.47; S, 4.85. Found: C, 47.25; H, 7.22; N, 8.33; S, 4.40.

5.4.3 Synthesis of $[L^1(\text{NMe})\text{Si}:\rightarrow \text{Cu(tmeda)}][\text{OTf}]$ (4)

This compound was synthesized in the similar procedure as compound 2. Yield: 0.21 g, 0.33 mmol (66%).

$^1\text{H NMR}$ (200.1 MHz, CD$_2$Cl$_2$, 298 K, ppm): $\delta = 1.11$ (s, 18 H, tBu-$H$), 2.57
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(br, 12 H, N(CH₃)₂) 2.62 (br, 6 H, NMe₂-H), 2.64 (br, 4 H, NCH₂CH₂N), 7.23-7.30 (m, 1 H, Ph-H), 7.38-7.56 (m, 4 H, Ph-H).

¹³C{¹H} NMR (50.3 MHz, CD₂Cl₂, 298 K, ppm): δ = 31.0 (tBu-CH₃), 47.8 (N(CH₃)₂), 53.3 (NMe₂-C), 57.8 (NCH₂CH₂N), 124.2 (CF₃), 127.0, 128.4, 128.5, 129.1, 130.7 (Ph-CH), 131.2 (Ph-C), 170.9 (NCN).

¹⁹F{¹H} NMR (188.3 MHz, CD₂Cl₂, 298 K, ppm): δ = -78.8.

²⁹Si{¹H} NMR (79 MHz, CD₂Cl₂, 298 K, ppm): δ = 18.3.

Elemental analysis for [C₂₄H₄₅CuF₃N₅O₃SiS]: Calcd: C, 45.59; H, 7.17; N, 11.08; S, 5.07. Found: C, 45.79; H, 6.95; N, 10.49; S, 4.81.

5.4.4 Synthesis of [Cu₂{η¹, η¹-L¹Si:(O):SiL¹}₂][OTf]₂ (6)

:Si(L¹)(μ₂-O)(L¹)Si: (0.267 g, 0.5 mmol) and [Cu(CH₃CN)₄][OTf] (0.188 g, 0.5 mmol) were placed in a Schlenk flask in the glovebox. Toluene (40 mL) was transferred to the flask via cannula under stirring at -78 °C. The mixture was allowed to warm up to room temperature gradually and stirred for another 12 hours. Then the solution was filtered, the filtrate was concentrated to ca. 5 mL and left at -20 °C for 3 days affording colorless crystalline product of 6. The product was collected by decantation and the obtained solid was dried in vacuo for several hours. The crystals of 6 suitable for single crystal X-ray diffraction analysis were obtained by recrystallization in THF and n-hexane (v:v, 2:1) at room temperature. Yield: 0.39 g, 0.26 mmol (52%).

¹H NMR (200.1 MHz, CD₂Cl₂, 298 K, ppm): δ = 1.24 (s, 36 H, tBu-H, [Cu₂{η¹, η¹-L¹Si(μ₂-O)SiL¹}₂][OTf]ⁿ), 1.27 (s, 36 H, tBu-H, [Cu₂{η¹, η¹-L¹Si(μ₂-O)SiL¹}₂][OTf]ⁿ), 7.39-7.69 (m, 20 H, Ph-H).
Experimental Section

\[ \text{[Cu}_2\{\eta^1, \eta^1-\text{L}^1\text{Si(\mu}_2\text{-O})\text{SiL}^1\}_2\} \]

\(^{13}\text{C}\{^1\text{H}\} \text{ NMR}\) (50.3 MHz, CD\(_2\)Cl\(_2\), 298 K, ppm): \(\delta = 31.7\) [br s, tBu-CH\(_3\)], [Cu\(_2\)\{\eta^1, \eta^1-\text{L}^1\text{Si(\mu}_2\text{-O})\text{SiL}^1\}_2\}]^{2+}\ldots(\text{OTf})_n\), 32.0, (s, tBu-CH\(_3\), [Cu\(_2\)\{\eta^1, \eta^1-\text{L}^1\text{Si(\mu}_2\text{-O})\text{SiL}^1\}_2\}]^{2+}\). (N(CH\(_3\))\(_3\)), [Cu\(_2\)\{\eta^1, \eta^1-\text{L}^1\text{Si(\mu}_2\text{-O})\text{SiL}^1\}_2\}]^{2+}\), 54.2 (N\(_\text{C}(\text{HCH}))\(_3\)), [Cu\(_2\)\{\eta^1, \eta^1-\text{L}^1\text{Si(\mu}_2\text{-O})\text{SiL}^1\}_2\}]^{2+}\), 125.6, 127.0, 128.5, 128.8, 128.9, 129.1, 129.3, 129.5, 130.0, 131.3, 131.5 (all s, Ph-C), [Cu\(_2\)\{\eta^1, \eta^1-\text{L}^1\text{Si(\mu}_2\text{-O})\text{SiL}^1\}_2\}]^{2+}\ldots(\text{OTf})_n.\) The carbon signals for CF\(_3\) is not observed in the \(^{13}\text{C}\) NMR spectrum.

\(^{19}\text{F}\{^1\text{H}\} \text{ NMR}\) (188.3 MHz, CD\(_2\)Cl\(_2\), 298 K, ppm): \(\delta = -77.1\).

\(^{29}\text{Si}\{^1\text{H}\} \text{ NMR}\) (79 MHz, CD\(_2\)Cl\(_2\), 298 K, ppm): \(\delta = 3.26\) (s, [Cu\(_2\)\{\eta^1, \eta^1-\text{L}^1\text{Si(\mu}_2\text{-O})\text{SiL}^1\}_2\}]^{2+}\), 7.73 (br, [Cu\(_2\)\{\eta^1, \eta^1-\text{L}^1\text{Si(\mu}_2\text{-O})\text{SiL}^1\}_2\}]^{2+}\ldots(\text{OTf})_n).\)

Elemental analysis for [C\(_{62}\)H\(_92\)Cu\(_2\)F\(_6\)N\(_8\)O\(_8\)S\(_2\)Si\(_4\)]: Calcd: C, 49.81; H, 6.20; N, 7.50; S, 4.29. Found: C, 50.11; H, 6.49; N, 7.43; S, 3.97.

5.4.5 Synthesis of L\(^2\)Si(OrBu)Cu(IPr) (8)

The NHSi 7 (0.223 g, 0.5 mmol) and (IPr)CuOrBu (0.262 g, 0.5 mmol) were placed in a Schlenk flask in the glovebox. Toluene (30 mL) was transferred to the flask under stirring via cannula at \(-20^\circ\text{C}\) and a light yellow solution was formed. Then it was allowed to warm up to room temperature and stirred for another 12 hours. The solution was concentrated to \(ca.\) 5 mL and filtered. The filtrate was left at room temperature for 24 hours affording a colorless crystalline product of 8. The product was collected by decantation of the supernatant and the obtained solid was washed with \(n\)-hexane (2 mL), and then dried \textit{in vacuo} for several hours. Yield: 0.38 g, 0.39 mmol, 78%. Mp. 254 \(^\circ\text{C}\) (decomposed with color changing to brown).
**Experimental Section**

**1H NMR**

(200.1 MHz, THF-$d_8$, 298 K, ppm): $\delta = 0.20$ (s, 9 H, $t$Bu-$H$), 0.84 (d, 3 H, $^3J_{H-H} = 6.8$ Hz, (CH$_3$)$_2$CH), 0.99 (d, 3 H, $^3J_{H-H} = 6.8$ Hz, (CH$_3$)$_2$CH), 1.03(d, 3 H, $^3J_{H-H} = 6.8$ Hz, (CH$_3$)$_2$CH), 1.04 (d, 6 H, $^3J_{H-H} = 6.6$ Hz, (CH$_3$)$_2$CH), 1.11 (d, 6 H, $^3J_{H-H} = 6.6$ Hz, (CH$_3$)$_2$CH), 1.14 (d, 6 H, $^3J_{H-H} = 6.6$ Hz, (CH$_3$)$_2$CH), 1.20-1.40 (d and d, 9 H, (CH$_3$)$_2$CH), 1.27 (d, 6 H, $^3J_{H-H} = 6.6$ Hz, (CH$_3$)$_2$CH), 1.30 (d, 6 H, $^3J_{H-H} = 6.8$ Hz, (CH$_3$)$_2$CH), 1.38 (s, 3 H, $\alpha$-CH$_3$), 2.44 (d, 1 H, $^2J_{H-H} = 1.2$ Hz, C=CH$_2$), 2.82 (sept, 2 H, $^3J_{H-H} = 6.8$ Hz, (CH$_3$)$_2$CH), 3.16 (sept, 2 H, $^3J_{H-H} = 6.8$ Hz, (CH$_3$)$_2$CH), 3.18 (d, 1 H, $^2J_{H-H} = 1.2$ Hz, C=CH$_2$), 3.38 (sept, 2 H, $^3J_{H-H} = 6.8$ Hz, (CH$_3$)$_2$CH), 3.91 (sept, 2 H, $^3J_{H-H} = 6.8$ Hz, (CH$_3$)$_2$CH), 4.81 (s, 1 H, $\gamma$-H), 6.86-6.99 (m, 6 H, Ar-$H$), 7.29-7.45 (m, 6 H, Ar-$H$), 7.49 (s, 2 H, CH=CH$_2$).

**13C{1H} NMR**

(50.3 MHz, THF-$d_8$, 298 K, ppm): $\delta = 19.8$ ( $\alpha$-CH$_3$), 20.1, 20.7, 21.2, 21.4, 22.0, 23.9, 24.0, 24.3, ((CH$_3$)$_2$CH) 25.8 ((CH$_3$)$_2$CH), 26.0 ((CH$_3$)$_2$CH), 26.2((CH$_3$)$_2$CH), 26.3, 26.6, 26.7((CH$_3$)$_2$CH), 27.2, 30.6 (OC(CH$_3$)$_3$), 67.2 (OC(CH$_3$)$_3$), 77.6 (C=CH$_2$), 98.6 ($\gamma$-C), 120.3, 120.4, 120.5, 121.6, 122.2 (CH=CH), 122.6, 122.7, 123.2, 123.5, 127.9, (Ar-CH) 134.4, 138.3, 138.5, 138.6, 143.6, 146.2, 146.7, 147.4, 148.3, 148.6, (Ar-C + ArNC) 185.7 (NCN).

**29Si{1H} NMR**

(79.6 MHz, THF-$d_8$, 298 K, ppm): $\delta = -9.4$.

**APCI-HR-MS** for [C$_{60}$H$_{86}$CuN$_4$OSi]$^+$ ($m/z$): Calcd: 969.5861; Found: $m/z$ 969.5866.

**Elemental analysis**

calcd for C$_{60}$H$_{85}$CuN$_4$OSi (%): C, 74.29; N, 5.78; H, 8.83; Found: C, 74.35; N, 5.92; H, 8.79.

**IR (KBr, cm$^{-1}$):**

$\nu = 457$ (w), 501 (w), 542 (w), 574 (w), 594 (w), 677 (w), 736 (w), 758 (m), 774 (s), 909 (w), 936 (w), 975 (m), 990 (m), 1043 (s), 1109 (w), 1178 (w), 1202 (w), 1253 (m), 1309 (w), 1322 (m), 1357 (s), 1385 (s), 1441 (m), 1460 (m), 2865 (m), 2939 (m), 2967 (s).
5.4.6 Synthesis of $L^2\text{Si(OH)}\text{Cu(IPr)}$ (9)

This compound was synthesized in a similar procedure as compound 8. Yield: 0.35 g, 0.38 mmol, 76%. Mp. 271 °C (decomposed with color changing to brown).

$^1$H NMR (200.1 MHz, THF-d$_8$, 298 K, ppm): $\delta$ = 0.75 (d, 3 H, $^3J_{H-H} = 6.6$ Hz, (CH$_3$)$_2$CH), 0.77 (d, 3 H, $^3J_{H-H} = 6.8$ Hz, (CH$_3$)$_2$CH), 0.86 (d, 12 H, $^3J_{H-H} = 7.0$ Hz, (CH$_3$)$_2$CH), 0.95 (d, 6 H, $^3J_{H-H} = 7.0$ Hz, (CH$_3$)$_2$CH), 0.97 (d, 6 H, $^3J_{H-H} = 6.6$ Hz, (CH$_3$)$_2$CH), 0.98 (d, 12 H, $^3J_{H-H} = 7.0$ Hz, (CH$_3$)$_2$CH), 1.07 (d, 3 H, $^3J_{H-H} = 6.6$ Hz, (CH$_3$)$_2$CH), 1.10 (d, 3 H, $^3J_{H-H} = 6.6$ Hz, (CH$_3$)$_2$CH), 1.20 (s, 3 H, $\alpha$-CH$_3$), 2.13 (s, 1 H, C=CH$_2$), 2.37 (sept, 4 H, $^3J_{H-H} = 6.6$ Hz, (CH$_3$)$_2$CH), 2.99 (s, 1 H, C=CH$_2$), 3.12 (s, 1 H, Si–OH), 3.48 (sept, 4 H, $^3J_{H-H} = 6.8$ Hz, (CH$_3$)$_2$CH), 4.80 (s, 1H, $\gamma$-H), 6.78-7.43 (m, 14 H, Ar-H and C=CH$_2$).

$^{13}$C{$^1$H} NMR (50.3 MHz, THF-d$_8$, 298 K, ppm): $\delta$ = 23.0 ($\alpha$-CH$_3$), 23.8, 24.1, 24.2, 24.5, 24.8, 25.0, 25.7, 26.8, ((CH$_3$)$_2$CH) 28.0, 28.1, ((CH$_3$)$_2$CH) 28.2, 28.9, 29.1, 29.2, 29.3, 29.4, ((CH$_3$)$_2$CH) 78.0 (C=CH$_2$), 101.5 ($\gamma$-C), 123.4, 123.9, 124.1, 124.4, 124.7, (Ar-CH) 124.8 (CH=CH$_2$), 126.1, 126.6, (Ar-CH) 130.6, 136.2, 141.5, 142.9, 142.9, 145.8, 145.9, 147.7, 148.6, 149.5, 150.0, 151.6, (Ar-C + ArNC) 183.4 (NCN).

$^{29}$Si{$^1$H} NMR (79.6 MHz, THF-d$_8$, 298 K, ppm): $\delta$ = –11.9.

HR-ESI-MS calcd. for [C$_{56}$H$_{78}$CuN$_4$OSi]$^+$: m/z 913.5241; found: m/z 913.5238.

Elemental analysis calcd for C$_{63}$H$_{85}$CuN$_4$OSi (9•Toluene) (%): C, 75.22; N, 5.57; H, 8.52; found: C, 75.44; N, 5.59; H, 8.71.

IR (KBr, cm$^{-1}$): $v =$ 723 (w), 755 (s), 802 (s), 856 (w), 907 (w), 935 (w), 1033 (w), 1062 (w), 1097 (w), 1179 (w), 1207 (w), 1245 (m), 1318 (m), 1363 (w).
(m), 1378 (s), 1553 (s), 1632 (s), 2863 (m), 2920 (m), 2961 (s), 3025 (w), 3066 (w), 3117 (w), 3151 (w), 3430 (br) (–OH).

5.4.7 Synthesis of L^2Si(H)Cu(IPr) (10)

(IPr)CuOtBu (0.524 g, 1 mmol) was placed in a Schlenk flask in the glovebox. Toluene (30 mL) was added to form a colorless solution, and the solution was cooled to –78 °C with acetone-dry ice bath. (EtO)₃SiH (0.181 g, 0.19 mL, 1.1 mmol) was added to this solution under vigorous stirring, and the solution immediately turned to bright yellow. The mixture was allowed to stir at –78 °C for 6 hours with exclusion of light. After that, the solution of silylene 7 (0.448 g, 1 mmol) in toluene (20 mL) was transferred to the yellow mixture under stirring at –78 °C via cannula. The mixture was allowed to warm up to room temperature slowly and stirred for another 12 hours under darkness. All volatiles were removed in vacuo affording a blackish residue, which was washed with n-hexane (50 mL). The remaining solid was extracted into toluene (30 mL), and filtered. The filtrate was concentrated to ca. 5 mL and left at 0 °C overnight yielding compound 10 as a colorless crystalline product. The product was collected by removal of the mother liquor via a syringe and washed with n-hexane (2 mL), then dried in vacuo for several hours. Yield: 0.61 g, 0.68 mmol, 68%. Mp. 242 °C (decomposed with color changing to black).

^1H NMR (200.1 MHz, THF-d₈, 298 K, ppm): δ = 0.69 (d, 3 H, CH(CH₃)₂), 3J_H-H = 6.8 Hz), 0.79-1.34 (m, 45 H, CH(CH₃)₂), 1.22 (s, 3 H, α-CH₃), 2.25 (s, 1 H, C=CH₂), 2.37 (sept, 4 H, 3J_H-H = 6.8 Hz, CH(CH₃)₂), 3.11 (sept, 2 H, 3J_H-H = 6.8 Hz, CH(CH₃)₂), 3.13 (s, 1 H, C=CH₂), 3.40 (sept, 1 H, 3J_H-H = 6.8 Hz, CH(CH₃)₂), 3.59 (sept, 1 H, 3J_H-H = 6.8 Hz, CH(CH₃)₂), 4.87 (s, 1 H, γ-H), 5.46 (s, 1 H, Si-H), 6.98-7.18 (m, 12 H, Ar-H and CH=CH in IPr), 7.39-7.47 (m, 2 H, Ar-H).

^13C{^1H} NMR (50.3 Hz, THF-d₈, 298 K, ppm): δ = 22.8 (α-CH₃), 23.0, 23.9, 24.0, 24.8, 25.3, (CH(CH₃)₂) 25.6 (CH(CH₃)₂), 25.8, 27.9, 28.2, 28.4,
Experimental Section

28.9, 29.1, (CH(CH₃)₂) 29.3, 29.4 (CH(CH₃)₂), 79.1 (C=CH₂), 102.3 (γ-C), 123.4, 123.5, 123.8, 124.2, (Ar-CH) 124.8 (CH=CH), 124.9, 125.0, 125.9, 126.0, 126.4, 128.7, 129.5, 130.7, (Ar-CH) 136.2, 138.2, 143.6, 143.7, 144.6, 145.8, 145.9, 146.8, 147.7, 149.8, 150.4, 152.9, (Ar-C + ArNC) 183.0 (N-CN).

29Si(INEPT) NMR (39.8 MHz, THF-d₈, 298 K, ppm): δ = –4.7.

APCI-HR-MS: calcld. for [C₅₆H₇₈CuN₄Si]⁺: m/z 897.5286; found: m/z 897.5270.

Elemental analysis calcld for C₅₆H₇₇CuN₄Si (%): C, 73.91; N, 6.24; H, 8.64; found: C, 73.82; N, 6.08; H, 8.82.

IR (KBr, cm⁻¹): ν = 590 (w), 691 (w), 726 (w), 758 (m), 789 (s), 903 (w), 938 (w), 973 (w), 1033 (m), 1106 (w), 1176 (w), 1211 (w), 1245 (m), 1321 (m), 1356 (s), 1382 (s), 1439 (m), 1464 (s), 1616 (s), 1957 (m) (Si–H), 2863 (w), 2923 (m), 2968 (s).

5.4.8 Synthesis of L²Si(OC₄F₅)Cu(IPr) (11)

This compound was synthesized in a similar procedure as compound 8. Yield: 0.40 g, 0.37 mmol, 74%.

1H NMR (200.1 MHz, THF-d₈, 298 K, ppm): δ = 0.23 (d, 3 H, J_H-H= 6.8 Hz, CH(CH₃)₂), 0.70 (d, 3 H, J_H-H= 6.8 Hz, CH(CH₃)₂), 0.79-0.81 (m, 9 H, CH(CH₃)₂), 0.84 (d, 3 H, J_H-H= 6.4 Hz, CH(CH₃)₂), 0.90 (d, 6 H, J_H-H= 6.8 Hz, CH(CH₃)₂), 0.95-0.99 (m, 9 H, CH(CH₃)₂), 1.03-1.09 (m, 15 H, CH(CH₃)₂), 1.23 (s, 3 H, CH₂C=N), 2.37 (s, 1 H, CH₂=C), 2.44 (sept, 2 H, J_H-H= 6.8 Hz, CH(CH₃)₂), 2.51 (sept, 2 H, J_H-H= 6.8 Hz, CH(CH₃)₂), 3.17 (sept, 1 H, J_H-H= 6.8 Hz, CH(CH₃)₂), 3.17 (sept, 1 H, J_H-H= 6.8 Hz, CH(CH₃)₂), 3.27 (sept, 1 H, J_H-H= 6.8 Hz, CH(CH₃)₂), 3.29 2.37 (s, 1 H, CH₂=C), 3.42 (sept, 1 H, J_H-H= 6.8 Hz, CH(CH₃)₂), 3.60 (sept, 1 H, J_H-H= 6.8 Hz, CH(CH₃)₂).
Experimental Section

110 Hz, CH(CH_3)_2), 5.21 (s, 1 H, γ-H), 6.77-6.83 (dd, 2 H, Ar-H), 6.96 (d, 2 H, Ar-H), 7.06-7.21 (m, 6 H, Ar-H), 7.23 (s, 2 H, CH=CH), 7.43 (t, 2 H, Ar-H).

^{13}C\{^1H\} NMR

(100.2 Hz, THF-d_8, 298 K, ppm): δ = 21.7 (α-CH_3), 22.5, 22.7, 23.3, 23.4, 24.0, 24.5, 24.9, 25.1, 25.2, 25.7, 26.2, 27.0, 27.3, 28.1, 28.5 (CH(CH_3)_2), 81.9 (C=CH_2), 106.9 (γ-C), 123.4, 123.5, 124.0, 124.2, 124.4, 124.5, 124.7, 125.0, 125.6, 126.2, 127.9, 128.7, (Ar-CH), 129.7 (CH=CH), 135.2, 139.7, 140.5, 140.7, 144.3, 144.4, 146.7, 147.5, 148.1, 148.2, 149.4 (Ar-C), 181.2 (NCN).

^{29}Si\{^1H\} NMR

(79.6 MHz, THF-d_8, 298 K, ppm): δ = -10.9.

APCI-HR-MS: calcd. for [C_62H_{77}CuF_5N_4OSi]^+: m/z 1079.5077; found: m/z 1079.5024.

5.4.9 Synthesis of L^2Si(OtBu)OCu(IPr) (12)

Compound 8 (0.502 g, 0.5 mmol) was placed in a Schlenk flask in the glovebox. Toluene (30 mL) was added forming a clear colorless solution under N_2 atmosphere, then the atmosphere was changed to CO_2 (1 atm) through one freeze-thaw-pump cycle. After stirred for 30 min under CO_2 atmosphere, the solution was concentrated to ca. 2 mL and left at –20 °C for 24 h affording a colorless crystalline product of compound 12. The product was collected by removal of the mother liquor via a syringe and washed with n-hexane (2 mL), then dried in vacuo for several hours. Yield: 0.42 g, 0.43 mmol, 86%. Mp: 282 °C (decomposed with color changing to black).

^{1}H NMR

(200.1 MHz, benzene-d_6, 298 K, ppm): δ = 0.64 (s, 9 H, OC(CH_3)_3), 0.90 (d, 6 H, J_H-H= 6.8 Hz, CH(CH_3)_2), 0.91 (d, 6 H, J_H-H= 6.8 Hz, CH(CH_3)_2), 1.10 (d, 6 H, J_H-H= 6.8 Hz, CH(CH_3)_2), 1.14 (d, 3 H, J_H-H= 6.8 Hz, CH(CH_3)_2), 1.30 (d, 12 H, J_H-H= 6.8 Hz, CH(CH_3)_2), 1.31 (d, 6 H, J_H-H= 6.8 Hz, CH(CH_3)_2), 1.45 (d, 3


**Experimental Section**

H, $^3J_{H-H} =$ 6.8 Hz, CH(CH$_3$)$_2$, 1.46 (d, 3 H, $^3J_{H-H} =$ 6.8 Hz, CH(CH$_3$)$_2$), 1.51 (d, 3 H, $^3J_{H-H} =$ 6.8 Hz, CH(CH$_3$)$_2$), 1.55 (s, 3 H, $\alpha$-CH$_3$), 2.82 (sept, 4 H, $^3J_{H-H} =$ 6.8 Hz, C=CH$_2$), 3.76 (s, 1 H, C=CH$_2$), 3.81-4.05 (m (sept + sept), 4 H, C=CH$_2$), 5.20 (s, 1 H, $\gamma$-H), 6.37 (s, 2 H, CH=CH), 6.97-7.26 (m, 12 H, Ar-H).

$^{13}$C {$^1$H} NMR (50.3 MHz, benzene-d$_6$, 298 K, ppm): $\delta$ = 22.2 ($\alpha$-CH$_3$), 23.0, 23.1, 24.0, 24.5, 24.7, 24.9, 25.2, 25.7, 25.8, (CH(CH$_3$)$_2$) 27.0, 27.2, 28.3, (CH(CH$_3$)$_2$) 28.5 28.6 (CH(CH$_3$)$_2$), 31.6 (OC(CH$_3$)$_3$), 71.1 (OC(CH$_3$)$_3$), 80.5 (C=CH$_2$), 102.2 ($\gamma$-C), 123.0 (Ar-CH), 123.1 (CH=CH), 123.2, 123.4, 123.6, 124.5, 126.0, 126.1, 128.0, 130.1, (Ar-CH) 135.4, 140.0, 140.1, 142.1, 144.7, 144.8, 148.3, 148.7, 149.4, 149.7, 152.0, (Ar-C + ArNC) 182.8 (NCN).

$^{29}$Si {$^1$H} NMR (79.6 MHz, benzene-d$_6$, 298 K, ppm): $\delta$ = −80.7.

ESI-HR-MS calcd. for [C$_{60}$H$_{86}$CuN$_4$O$_2$Si]: $m/z$ 985.5811; found: $m/z$ 985.5790.

Elemental analysis calcd for C$_{60}$H$_{85}$CuN$_4$O$_2$Si (%): C, 73.09; N, 5.68; H, 8.69; found: C, 72.98; N, 5.60; H, 8.97.

IR (KBr, cm$^{-1}$): $\nu$ = 739 (w), 755 (m), 796 (m), 932 (w), 976 (w), 1052 (s), 1084 (m), 1109 (w), 1207 (w), 1255 (w), 1325 (w), 1363 (w), 1382 (s), 1435 (m), 1467 (s), 1625 (s), 2866 (w), 2927 (m), 2965 (s).

**5.4.10 Synthesis of L$^2$Si(OH)OCu(IPr) (13)**

![Chemical structure of L$^2$Si(OH)OCu(IPr) (13)]

This compound was synthesized in a similar procedure under the same condition as compound 12. The crystal suitable for X-ray diffraction analysis was obtained by slow diffusion of n-hexane into concentrated solution of 13 in CH$_2$Cl$_2$ at room temperature. Yield: 0.37 g, 0.40 mmol, 80%.
**Experimental Section**

**1H NMR**

(400 MHz, benzene-d₆, 298 K, ppm): δ = 0.88 (d, 6 H, 3J_H-H = 6.8 Hz, CH(CH₃)₂), 0.94-1.02 (m, 24 H, CH(CH₃)₂), 1.14 (d, 3 H, 3J_H-H = 6.8 Hz, CH(CH₃)₂), 1.25-1.30 (m, 9 H, CH(CH₃)₂), 1.42 (s, 1 H, SiOH), 1.46 (d, 3H, 3J_H-H = 6.8 Hz, CH(CH₃)₂), 1.49 (d, 3 H, 3J_H-H = 6.8 Hz, CH(CH₃)₂), 1.54 (s, 3 H, α-CH₃), 2.21 (sept, 4 H, 3J_H-H = 6.8Hz, CH(CH₃)₂), 3.15 (s, 1 H, C=CH₂), 3.76 (sept, 2 H, 3J_H-H = 6.8 Hz, CH(CH₃)₂), 3.84 (s, 1 H, C=CH₂), 3.89 (sept, 2 H, 3J_H-H = 6.8 Hz, CH(CH₃)₂), 5.34 (s, 1 H, γ-H), 6.07 (s, 2 H, CH=CH), 6.96-7.25 (m, 12 H, Ar-H).

**13C{1H} NMR**

(100 MHz, benzene-d₆, 298 K, ppm): δ = 22.2 (α-CH₃), 23.7, 23.8, 24.6, 24.8, 24.9, 25.0, 25.1, 25.5, 25.6, 25.9, 26.3, 26.8, 27.8, 28.2, 28.3, 28.4, 28.7, (CH(CH₃)₂) 80.8 (C=CH₂), 101.5 (γ-C), 122.4 (CH=CH), 123.3, 123.5, 123.9, 124.1, 124.1, 124.3, 125.7, 126.3, 126.3, 130.5, (Ar-CH) 134.8, 137.9, 138.8, 142.1, 142.8, 145.4, 145.5, 148.6, 149.0, 149.3, 149.6, 151.8, (Ar-C + ArNC) 182.1 (NCN).

**29Si{1H} NMR**

(79.6 MHz, benzene-d₆, 298 K, ppm): δ = –71.4.

**APCI-HR-MS**

calcd for [C₅₆H₇₈CuN₄O₂Si]⁺: m/z 929.5185; found: m/z 929.5182.

**Elemental analysis**

calcd for C₅₆H₇₇CuN₄O₂Si (%): C, 72.33; H, 8.35; N, 6.03; found: C, 72.56; H, 8.48; N, 5.88.

**IR (KBr, cm⁻¹):**

ν = 475 (w), 562 (w), 756 (s), 802 (s), 935 (w), 1005 (w), 1060 (m), 1103 (m), 1118 (m), 1178 (w), 1204 (w), 1257 (m), 1323 (m), 1352 (m), 1378 (s), 1442 (m), 1468 (s), 1540 (m), 1630 (s), 2866 (m), 2926 (s), 2964 (vs), 3065 (w), 3682 (br) (OH).
5.4.11 Synthesis of \( \text{L}_2\text{Si(H)OCu(IPr)} (14) \)

This compound was synthesized in a similar procedure under the same condition as compound 12. Yield: 0.35 g, 0.38 mmol, 76%. Mp. 245 °C (decomposed with color changing to brown).

\( ^1\text{H NMR} \) (200.1 MHz, benzene-\( \text{d}_6 \), 298 K, ppm): \( \delta = 0.87 \) (d, 9 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 0.92 (d, 6 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 0.93 (d, 6 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 0.94 (d, 6 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 0.97 (d, 3 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 1.03 (d, 3 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 1.16 (d, 3 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 1.19 (d, 3 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 1.21 (d, 3 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 1.36 (d, 3 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 1.41 (d, 3 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 1.50 (s, 3 H, \( \alpha \)-CH(\( \text{CH}_3 \))), 2.19 (sept, 4 H, \( ^3 J_{\text{H-H}} = 6.8 \) Hz, CH(\( \text{CH}_3 \)\( _2 \)), 3.15 (s, 1 H, C=CH(\( \text{CH}_3 \))), 3.53-3.93 (m (sept + sept), 4 H, CH(\( \text{CH}_3 \)\( _2 \))), 3.83 (s, 1 H, C=CH(\( \text{CH}_3 \))), 5.08 (s, 1 H, Si-H, \( ^1 J(\text{Si, H}) = 125.6 \) Hz), 5.87 (s, 1 H, \( \gamma \)-H), 6.06 (s, 2 H, CH=CH), 6.92-7.24 (m, 12 H, Ar-H).

\( ^{13}\text{C}\{^1\text{H}\} \text{NMR} \) (50.3 MHz, benzene-\( \text{d}_6 \), 298 K, ppm): \( \delta = 21.7 \) (\( \alpha \)-C), 23.5, 23.6, 24.0, 24.4, 24.8, 25.2, 25.7, 25.8, 25.9, 26.3, (CH(\( \text{CH}_3 \)\( _2 \))) 27.8, 27.9, 28.4, (CH(\( \text{CH}_3 \)\( _2 \))) 80.9 (C=CH(\( \text{CH}_3 \))), 100.5 (\( \gamma \)-C), 122.1 (CH=CH), 122.9, 123.3, 123.5, 123.8, 123.9, 124.0, 126.0, 126.1, 128.0, 130.1, (Ar-CH) 134.5, 137.9, 138.2, 140.9, 145.0, 145.1, 148.0, 148.1, 149.5, 149.6, 150.7, (Ar-C + ArNC) 181.8 (NCN).

\( ^{29}\text{Si}\{\text{INEPT}\} \) (39.8 MHz, benzene-\( \text{d}_6 \), 298 K, ppm): \( \delta = -59.6 \).

APCI-HR-MS: calcd. for [\( \text{C}_{56}\text{H}_{78}\text{CuON}_4\text{Si} \)]\(^+\): \( m/z \) 913.5235; found: \( m/z \) 913.5217.

Elemental analysis calcd for \( \text{C}_{56}\text{H}_{77}\text{CuON}_4\text{Si} \) (%): C, 73.60; N, 6.13; H, 8.49; found: C, 74.33; N, 6.06; H, 8.50.
Experimental Section

IR (KBr, cm\(^{-1}\)): \(\nu = 698\) (w), 736 (w), 758 (m), 805 (s), 859 (w), 932 (w), 983 (w), 1055 (w), 1084 (m), 1116 (s), 1176 (w), 1204 (w), 1249 (m), 1328 (m), 1353 (w), 1388 (s), 1438 (m), 1461 (m), 1625 (s), 2122 (m) (Si-H), 2870 (w), 2927 (m), 2965 (s).

5.4.12 Synthesis of \([\text{L}^2\text{Si(OC}_6\text{F}_5)\text{OCu}(\text{IPr})\text{]}\) (15)

![Chemical Structure of \([\text{L}^2\text{Si(OC}_6\text{F}_5)\text{OCu}(\text{IPr})\text{]}\) (15)](attachment:chemical_structure.png)

This compound was synthesized in a similar procedure under the same condition as compound 12. Yield: 0.32 g, 0.29 mmol, 59%.

\(^1\)H NMR (400.2 MHz, benzene-d\(_6\)), 298 K, ppm): \(\delta = 0.33\) (d, 3 H, \(\text{^3}J_{\text{H-H}} = 5.9\) Hz, CH(CH\(_3\))\(_2\)), 0.77 (d, 3 H, \(\text{^3}J_{\text{H-H}} = 6.1\) Hz, CH(CH\(_3\))\(_2\)), 0.87 (d, 6 H, \(\text{^3}J_{\text{H-H}} = 6.1\) Hz, CH(CH\(_3\))\(_2\)), 0.95-1.07 (m, 15 H, CH(CH\(_3\))\(_2\)), 1.14(d, 3 H, \(\text{^3}J_{\text{H-H}} = 6.7\) Hz, CH(CH\(_3\))\(_2\)), 1.19 (d, 3 H, \(\text{^3}J_{\text{H-H}} = 6.4\) Hz, CH(CH\(_3\))\(_2\)), 1.21 (d, 3 H, \(\text{^3}J_{\text{H-H}} = 6.1\) Hz, CH(CH\(_3\))\(_2\)), 1.21-1.30 (m, 6 H, CH(CH\(_3\))\(_2\)), 1.36 (d, 3 H, \(\text{^3}J_{\text{H-H}} = 6.4\) Hz, CH(CH\(_3\))\(_2\)), 1.41 (d, 3 H, \(\text{^3}J_{\text{H-H}} = 6.1\) Hz, CH(CH\(_3\))\(_2\)), 1.46 (s, 3 H, \(\alpha\)-CH\(_3\)), 2.30 (sept, 2 H, \(\text{^3}J_{\text{H-H}} = 6.4\) Hz, CH(CH\(_3\))\(_2\)), 2.45 (sept, 2 H, \(\text{^3}J_{\text{H-H}} = 6.4\) Hz, CH(CH\(_3\))\(_2\)), 2.85-3.34 (m, 2 H, CH\(_2\)=C (1 H) + CH(CH\(_3\))\(_2\) (1 H)), 3.64 (sept, 1 H, \(\text{^3}J_{\text{H-H}} = 5.9\) Hz, CH(CH\(_3\))\(_2\)), 3.75 (sept, 1 H, \(\text{^3}J_{\text{H-H}} = 5.9\) Hz, CH(CH\(_3\))\(_2\)), 3.86 (sept, 1 H, \(\text{^3}J_{\text{H-H}} = 6.4\) Hz, CH(CH\(_3\))\(_2\)), 3.92 (s, 1 H, CH\(_2\)=C), 5.52 (s, 1 H, \(\gamma\)-H), 6.14 (s, 2 H, CH=CH), 7.01-7.03 (m, 3 H, Ar-H), 7.10-7.12 (m, 4 H, Ar-H), 7.19-7.29 (m, 5 H, Ar-H).

\(^{13}\)C\({\ (^1}\)H\}) NMR (100 MHz, benzene-d\(_6\)), 298 K, ppm): \(\delta = 21.1\) (\(\alpha\)-CH\(_3\)), 21.6, 23.1, 23.3, 23.4, 23.5, 23.6, 24.0, 24.1, 24.3, 24.4, 24.9, 25.0, 25.3, 25.5, 26.1, 27.3 (CH(CH\(_3\))\(_2\)), 27.8, 28.0, 28.1, 28.2, 28.3, 28.4, 28.5, 28.6 (CH(CH\(_3\))\(_2\)), 84.3 (CH\(_2\)=C), 107.2 (\(\gamma\)-C), 122.6 (CH=CH), 122.9, 123.2, 123.6, 123.9, 124.2, 124.4, 125.3, 126.1, 126.3, 128.2, 128.9, 130.0 (Ar-CH), 134.7, 137.5, 138.7, 141.8, 142.4, 144.6, 144.9, 145.3, 147.3, 148.2, 148.6, 148.7 150.1, (Ar-C (12 C)) + (CH\(_2\)=C,
Experimental Section

$^{13}$C NMR (125 MHz, CDCl$_3$, 298 K, ppm): $\delta$ = 161.2 (OC$_6$F$_5$-C), (the other $^{13}$C signals at OC$_6$F$_5$ were not observed in the $^{13}$C NMR spectrum), 181.4 (NCN).

$^{29}$Si$\{^1$H$\}$ NMR (79.6 MHz, benzene-d$_6$, 298 K, ppm): $\delta$ = -81.9.

APCI-HR-MS: calcd. for [C$_{62}$H$_{76}$CuF$_5$N$_4$O$_2$Si]$^+$: $m/z$ 1095.5026; found: $m/z$ 1095.4974.

5.4.13 Detection of CO formation by the reaction of $^{13}$CO$_2$ with 8

40 mg of 8 was placed in a NMR tube under a N$_2$ atmosphere, benzene-d$_6$ (0.7 mL) was added into the tube with a syringe at room temperature, and the atmosphere was changed to $^{13}$CO$_2$ through one freeze-thaw-pump cycle. Then the NMR tube was sealed, and after 30 min standing at ambient temperature the $^{13}$C NMR spectrum was recorded. The characteristic signal for $^{13}$CO could be observed at $\delta$=179 ppm in the spectrum.

5.4.14 Synthesis of [L$^3$Si:(CH$_2$)NHC]NiBr$_2$ (17)

![Structure of [L$^3$Si:(CH$_2$)NHC]NiBr$_2$ (17)](image)

The ligand 16 (0.29 g, 0.5 mmol) and NiBr$_2$(dme) (0.15 g, 0.5 mmol) were placed in a Schlenk flask, and toluene (50 mL) was transferred to the flask via cannula at room temperature. The resulting yellow suspension was stirred for 12 hours at 50 °C affording a dark red suspension. The supernatant was collected, and the residue was extracted twice with hot toluene (50 °C, 30 mL for each time). The combined solution was concentrated to ca. 5 mL, and left at −30 °C for 12 hours to yield compound 17 as a dark red crystalline solid. The product (0.33 g) was collected by removing the supernatant with syringe, and dried in vacuo for several hours. Yield: 0.33 g, 0.41 mmol, 82%.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K, ppm): $\delta$ = 1.03 (d, 6 H, $^3$J$_{H,H}$ = 6.4 Hz, CH(CH$_3$)$_2$), 1.05 (d, 6 H, $^3$J$_{H,H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 1.24 (d, 6 H, $^3$J$_{H,H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 1.57 (s, 3 H, $\alpha$-CH$_3$), 1.66 (s, 3 H, $\alpha$-CH$_3$), 1.77 (d, 6 H, $^3$J$_{H,H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 1.86 (s, 6 H, NHC-CH$_3$), 2.73 (s, 2 H, SiCH$_2$N), 2.95 (sept, 2 H, $^3$J$_{H,H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 3.64 (s, 3 H, NCH$_3$), 5.03 (sept, 2 H, $^3$J$_{H,H}$ = 6.4 Hz, CH(CH$_3$)$_2$).
5.4.15 Synthesis of $[L^2\text{Si(CH}_2\text{)}\text{NHC}]\text{Ni(Br)PMe}_3$ (18)

Compound 17 (0.15 g, 0.19 mmol) and KC₈ (0.056 g, 0.42 mmol) were placed in a Schlenk flask, and THF (30 mL) was transferred to the flask via cannula at −78 °C under stirring. PMe₃ (0.76 mL, 0.76 mmol, 1 M in hexane) was added via syringe, and the mixture was allowed to warm up to room temperature. After stirring for 3 hours, a red solution was formed, and the mixture was filtered affording a red filtrate. All the volatiles were removed in vacuo, and the residue was extracted with n-hexane (15 mL). The filtrate was concentrated to ca. 5 mL and left at 0 °C for 24 hours affording compound 18 as red crystals. The product was collected by removing the supernatant via a syringe, and dried in vacuo for several hours. Yield: 0.11 g, 0.14 mmol, 76%.

$^1\text{H NMR}$ (400 MHz, benzene-d₆, 298 K, ppm): $\delta = 0.83$ (s, 3 H, NHC-CH₃), 1.08 (s, 3 H, NHC-CH₃), 1.30 (d, 3 H, $^3J_{\text{H-H}} = 6.8$ Hz, CH(CH₃)₂), 1.36 (d, 3 H, $^3J_{\text{H-H}} = 6.4$ Hz, CH(CH₃)₂), 1.37 (d, 3 H, $^3J_{\text{H-H}} = 6.8$ Hz, CH(CH₃)₂).
117 Hz, CH(CH$_3$)$_2$, 1.40 (d, 3 H, $^3$J$_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 1.43 (d, 3 H, $^3$J$_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 1.48 (s, 3 H, $\alpha$-CH$_3$), 1.64 (d, 9 H, $^2$J$_{H-P}$ = 8.0 Hz, PMe$_3$-H), 1.70 (d, 3 H, $^3$J$_{H-H}$ = 6.4 Hz, CH(CH$_3$)$_2$), 1.71 (d, 3 H, $^3$J$_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 2.87 (d, 1 H, $^2$J$_{H-H}$ = 13.6 Hz, SiC$_2$H$_2$N), 3.00 (d, 1 H, $^2$J$_{H-H}$ = 13.6 Hz, SiC$_2$H$_2$N), 3.19 (s, 1 H, C=C$_a$H$^b$), 3.60 (sept, 1 H, $^3$J$_{H-H}$ = 6.8 Hz, C$_H$(CH$_3$)$_2$), 3.62 (s, 3 H, NC$_H$$_3$), 3.85 (s, 1 H, C=CH$^a$H$^b$), 4.52 (sept, 1 H, $^3$J$_{H-H}$ = 6.8 Hz, C$_H$(CH$_3$)$_2$), 5.35 (s, 1 H, $\gamma$-H), 5.44 (sept, 1 H, $^3$J$_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 6.96-7.05 (m, 3 H, Ar-H), 7.08-7.11 (m, 2 H, Ar-H), 7.17-7.19 (m, 1 H, Ar-H).

$^{13}$C{$^1$H} NMR (100.2 MHz, benzene-d$_6$, 298 K, ppm): $\delta$ = 8.6, 8.8 (NHC-CH$_3$), 19.5 (d, $^1$J$_{C-P}$ = 26.4 Hz, PMe$_3$-C), 23.1 ($\alpha$-CH$_3$), 24.5, 24.7, 26.3, 26.6, 27.2, 27.5, 27.6, 28.5 (CH(CH$_3$)$_2$), 28.8, 29.4, 29.6, 29.7 (CH(CH$_3$)$_2$), 37.4 (NCH$_3$), 38.5 (d, $^4$J$_{C-P}$ = 2.5 Hz, SiCH$_2$N), 86.6 (C=CH$_2$), 111.3 ($\gamma$-C), 122.4 (d, $^4$J$_{C-P}$ = 2.0 Hz, NHC-CCH$_3$), 124.6, 124.7, 125.2, 125.4, 127.0, 127.5 (Ar-CH), 127.1 (d, $^4$J$_{C-P}$ = 2.5 Hz, NHC-CCH$_3$), 137.6, 140.3, 142.0, 147.4, 147.6, 148.3, (Ar-C) 149.0, 149.1 (ArN=C), 175.8 (d, $^2$J$_{C-P}$ = 82.6 Hz, NCN).

$^{31}$P{$^1$H} NMR (161.9 MHz, benzene-d$_6$, 298 K, ppm): $\delta$ = −14.9.

$^{29}$Si{$^1$H} NMR (79.5 MHz, benzene-d$_6$, 298 K, ppm): $\delta$ = 12.2 (d, $^2$J$_{Si-P}$ = 45.9 Hz).

HR-APCI-MS for [C$_{36}$H$_{51}$BrN$_4$NiSi, M−PMe$_3$ + H]$^+$ (m/z): Cacld: 705.2493; Found: 705.2522.

Elemental analysis for [C$_{39}$H$_{60}$BrN$_4$NiPSi]:Cacld: C, 59.86; N, 7.16; H, 7.73. Found: C, 59.25; N, 6.80; H, 7.80.
5.4.16 Synthesis of $[\eta^2 (\text{Si–H})] L^2 \text{Si(H)(CH}_2\text{)}\text{NHC} \text{Ni(PMe}_3\text{)}_2$ (19)

Compound 17 (0.15 g, 0.19 mmol) and KC₈ (0.056 g, 0.42 mmol) were placed in a Schlenk flask, and THF (30 mL) was transferred to the flask via cannula at −78 °C under stirring. PMe₃ (0.76 mL, 0.76 mmol, 1 M in hexane) was added via syringe, and then the mixture was allowed to warm to room temperature. After stirring for 7 hours, an orange solution was formed, and the mixture was filtered to remove the precipitate affording an orange filtrate. The volatiles were removed in vacuo, and the residue was extracted with n-hexane (15 mL). The extraction was concentrated to ca. 5 mL and left at 0 °C for 24 hours, affording compound 19 as light yellow crystals. The product was collected by removing the supernatant with syringe, and dried in vacuo for several hours. Yield: 0.10 g, 0.13 mmol, 68%.

$^1$H NMR (400 MHz, benzene-d₆, 298 K, ppm): $\delta = −7.8$ (br, 1 H, (Si–H)Ni for 19 and 19a, $J_{\text{Si,H}} = 87$ Hz), 19: 0.62 (br, PMe₃-H, 19), 0.70 (d, $^3J_{\text{H,H}} = 6.7$ Hz, CH(CH₃)₂), 1.13 (d, $^3J_{\text{H,H}} = 6.7$ Hz, CH(CH₃)₂), 1.14 (s, NHC-CH₃, 19a), 1.22 (d, $^2J_{\text{H,H}} = 5.5$ Hz, PMe₃-H, 19a), 1.24 (d, $^3J_{\text{H,H}} = 7.0$ Hz, CH(CH₃)₂), 1.31 (d, $^3J_{\text{H,H}} = 7.0$ Hz, CH(CH₃)₂), 1.34 (d, $^3J_{\text{H,H}} = 6.6$ Hz, CH(CH₃)₂), 1.35 (d, $^3J_{\text{H,H}} = 6.6$ Hz, CH(CH₃)₂), 1.40 (d, $^3J_{\text{H,H}} = 6.8$ Hz, CH(CH₃)₂), 1.42 (d, $^3J_{\text{H,H}} = 6.8$ Hz, CH(CH₃)₂), 1.45 (s, NHC-CH₃, 19a), 1.49 (d, $^3J_{\text{H,H}} = 6.7$ Hz, CH(CH₃)₂), 1.55 (d, $^3J_{\text{H,H}} = 6.7$ Hz, CH(CH₃)₂), 1.56 (br, NHC-CH₃ + α-CH₃, 19), 1.58 (s, α-CH₃, 19a), 1.60 (d, $^3J_{\text{H,H}} = 6.7$ Hz, CH(CH₃)₂), 1.81 (s, NHC-CH₃, 19), 2.97 (s, N-CH₃, 19), 3.00 (sept, $^3J_{\text{H,H}} = 6.8$ Hz, CH(CH₃)₂, 19), 3.16 (s, C=CH₃Hb, 19a), 3.18 (s, N-CH₃, 19a), 3.33 (dd, $^2J_{\text{H,H}} = 14.7$ Hz, SiNCH₂, 19a), 3.37 (s, C=CH₃Hb, 19), 3.54 (sept, $^3J_{\text{H,H}} = 6.8$ Hz, CH(CH₃)₂, 19a), 3.65 (sept, $^3J_{\text{H,H}} = 6.7$ Hz, CH(CH₃)₂, 19), 3.75 (dd, $^2J_{\text{H,H}} = 13.5$ Hz, SiNCH₂, 19), 3.91 (sept, $^3J_{\text{H,H}} = 6.8$ Hz, CH(CH₃)₂, 19a), 3.96 (s,}
C=CH (a), 119.19 (s, C=CH (a)), 4.19 (s, C=CH (b), 19 and 19a), 4.19-4.25 (m, CH(CH3)2, 19 and 19a), 5.69 (br, γ-H, 19 and 19a), 7.01-7.06 (m, Ar-H, 19 and 19a), 7.14-7.31 (m, Ar-H, 19 and 19a).

13C{1H} NMR
(100.2 MHz, benzene-d6, 298 K, ppm): δ = 8.0, 8.4 (NHC-CH3, 19a), 9.0, 9.9 (NHC-CH3, 19a), 17.4 (CH3, 19a), 17.5 (CH3, 19), 17.8 (d, 1JCP = 18.0 Hz, PMe3-C, 19a), 22.7 (br, PMe3-C, 19), 22.7, 23.3, 23.9, 24.0, 24.1, 24.4, 24.9, 25.3, 25.5, 25.9, 26.9 (CH(CH3)2, 19 and 19a), 27.3, 27.6, 27.7, 27.8, 28.3, 28.6, 28.7, 29.1 (CH(CH3)2, 19 and 19a), 34.0 (N-C=CH, 19a), 34.1 (SiCH2N, 19a), 35.1 (N-CH3, 19a), 46.1 (br, SiCH2N, 19), 75.0 (CH2=C, 19a), 82.3 (CH2=C, 19), 108.2 (γ-C, 19 and 19a), 121.4, 121.9, 123.8, 124.0 (NHC-CCH3, 19 and 19a), 123.1, 123.3, 123.5, 123.9, 124.3, 124.4, 124.6, 125.1, 125.9, 126.0, 126.3, 127.9 (Ar-CH, 19 and 19a), 147.9, 148.2, 148.6, 148.7, 149.0, 149.6, 150.8, 160.7, 160.8 (Ar-C and CNAr, 19 and 19a), 195.8 (br, NCN, 19), 195.5 (d, 2JC,P = 11.7 Hz, NCN, 19a).

31P{1H} NMR
(161.9 MHz, toluene-d8, 298 K, ppm): δ = -20.6 (s, 19a), -30.1 (br), -32.8 (br) (19).

31P{1H} NMR
(161.9 MHz, toluene-d8, 194 K, ppm): δ = -18.8 (s, 19a), -27.9 (d, 2JPP = 35.3 Hz), -31.3 (d, 2JPP = 35.3 Hz) (19).

29Si{1H} NMR
(79.5 MHz, toluene-d8, 298 K, ppm): δ = -19.2 (d, 2JSi,P = 8.8 Hz, 19a), 2.5 (br, 19).

29Si{1H} NMR
(79.5 MHz, toluene-d8, 194 K, ppm): δ = -18.9 (d, 2JSi,P = 6.6 Hz, 19a), 3.3 (t, 2JSi,P = 71.5 Hz, 19).

IR (KBr, cm⁻¹):
v = 1746.

HR-APCI-MS
for [C39H62N4NiPSi, M-PMe3 + H]+ (m/z): Calcd: 703.3829; Found: 703.3824.

Elemental analysis
for [C42H70N4NiP2Si]: Calcd: C, 64.69; N, 7.19; H, 9.05. Found: C,
64.89; N, 7.69; H, 8.92.

5.4.17 Synthesis of \([L^3\text{Si:(CH}_2\text{)}\text{NHC}]\text{Ni(dmpe)}\) (20)

Compound 17 (0.15 g, 0.19 mmol) and KC₈ (0.056 g, 0.42 mmol) were placed in a Schlenk flask, and THF (30 mL) was transferred to the flask via cannula at −78 °C under stirring. dmpe (30 mg, 0.20 mmol) was added via syringe, and then the mixture was allowed to warm to room temperature. After stirring for 9 hours, a green solution was formed, and the mixture was filtered. The volatiles in the filtrate were removed in vacuo, and the residue was extracted with \(n\)-hexane (15 mL). The extraction was concentrated to ca. 5 mL and left at −20 °C for 24 hours, affording compound 20 as deep brown crystals.

\(^1\text{H NMR}\) (200.2 MHz, benzene-\(d_6\), 298 K, ppm): \(\delta = 0.44\) (m, 6 H, CH(CH₃)₂), 1.07-1.22 (m, 28 H, dmpe-\(H\) (16 H) + CH(CH₃)₂ (12 H)), 1.41 (d, 6 H, \(^3\)\(J_{\text{H,H}} = 6.8\) Hz, CH(CH₃)₂), 1.49 (s, 6 H, \(\alpha\)-CH₃), 1.69 (s, 3 H, NHC-CH₃), 1.99 (s, 3 H, NHC-CH₃), 3.15 (sept, 2 H, \(^3\)\(J_{\text{H,H}} = 6.8\) Hz, CH(CH₃)₂), 3.36 (s, 3 H, N-CH₃), 3.51 (s, 2 H, SiCH₂N), 3.54 (sept, 2 H, \(^3\)\(J_{\text{H,H}} = 6.8\) Hz, CH(CH₃)₂), 5.04 (s, 1 H, \(\gamma\)-H), 7.02-7.20 (m, 6 H, Ar-\(H\)).

\(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (100.2 MHz, benzene-\(d_6\), 298 K, ppm): \(\delta = 9.55, 10.25\) (NHC-CH₃), 22.0 (m, P(CH₃)₂, due to the coupling with \(^{31}\text{P}\) nuclei), 23.8 (CH(CH₃)₂), 24.4 (\(\alpha\)-CH₃), 24.6, 24.8 (CH(CH₃)₂), 28.6, 28.9 (CH(CH₃)₂), 33.5 (m, PCH₂, due to the coupling with \(^{31}\text{P}\) nuclei), 35.9 (N-CH₃), 45.7 (br, SiCH₂N), 101.4 (\(\gamma\)-C), 119.7, 121.8 (NHC-CCH₃), 123.2, 123.7, 124.2, 126.8 (Ar-CH), 142.4, 143.5, 144.1, 146.6 (Ar-C), 166.4 (Ar-CN), 206.3 (NCN).

\(^{31}\text{P}\{^1\text{H}\} \text{NMR}\) (161.9 MHz, benzene-\(d_6\), 298 K, ppm): \(\delta = 15.8\).
Experimental Section

\[ ^{29}\text{Si} \{ ^{1}\text{H} \} \text{NMR} \] (79.5 MHz, benzene-d_6, 298 K, ppm): \( \delta = 60.0 \) (t, \( ^{2}\text{J}_{\text{Si}, \text{p}} = 30.9 \) Hz).

HR-APCI-MS for [C_{42}H_{68}N_{4}NiP_{2}Si, M]^{+} (m/z): cacld: 776.4036; found: 776.4028.

5.4.18 Synthesis of [L^{3}\text{Si}:(\text{CH}_{2})\text{NHC}]\text{Ni(CO)}_{2} (21)

Compound 17 (100 mg, 0.13 mmol) was placed in a Schlenk flask, and THF (20 mL) was transferred to the flask via cannula under N\(_{2}\). The atmosphere was changed to CO through two freeze-pump-thaw cycles. Under CO atmosphere, two molar equivalents of K[BHEt\(_{3}\)] (0.26 mL, 1 M in THF, 0.26 mmol) was added to the mixture via syringe under vigorous stirring at \(-78^\circ\)C. Then the mixture was allowed to warm to \(-10^\circ\)C slowly, and stirred further for 4 hours. All the volatile was removed under reduced pressure at room temperature; the residue was extracted with toluene (15 mL), and filtered. The obtained filtrate was concentrated to ca. 2 mL and left at \(-30^\circ\)C for one week to give compound 21 as a dark brown solid. The product was collected by removed the mother liquor and dried in vacuo for several hours. The crystal suitable for single crystal X-ray diffraction analysis was obtained from concentrated solution in diethyl ether at \(-30^\circ\)C. Yield: 52 mg, 0.078 mmol, 60%.

\[ ^{1}\text{H} \text{NMR} \] (400 MHz, THF-d\(_{8}\), 298 K, ppm): \( \delta = 0.62 \) (d, 6 H, \( ^{3}\text{J}_{\text{H}, \text{H}} = 6.7 \) Hz, CH(CH\(_{3}\))\(_{2}\)), 1.11 (d, 6 H, \( ^{3}\text{J}_{\text{H}, \text{H}} = 6.8 \) Hz, CH(CH\(_{3}\))\(_{2}\)), 1.17 (d, 6 H, \( ^{3}\text{J}_{\text{H}, \text{H}} = 6.8 \) Hz, CH(CH\(_{3}\))\(_{2}\)), 1.90 (s, 6 H, \( \alpha\)-CH\(_{3}\)), 2.01 (s, 3 H, NHC-CH\(_{3}\)), 2.06 (s, 3 H, NHC-CH\(_{3}\)), 2.93 (sept, 2 H, \( ^{2}\text{J}_{\text{H}, \text{H}} = 6.8 \) Hz, CH(CH\(_{3}\))\(_{2}\)), 3.57 (overlap with the signals from THF-d\(_{8}\), 5 H, N-CH\(_{2}\)Si + N-CH\(_{3}\)), 3.67 (sept, 2 H, \( ^{3}\text{J}_{\text{H}, \text{H}} = 6.8 \) Hz, CH(CH\(_{3}\))\(_{2}\)), 5.60 (s, 1 H, \( \gamma\)-H), 7.05-7.07 (m, 2 H, Ar-CH\(_{3}\)), 7.11-7.21 (m, 4 H, Ar-CH\(_{3}\)).

\[ ^{13}\text{C} \{ ^{1}\text{H} \} \text{NMR} \] (100.2 MHz, THF-d\(_{8}\), 298 K, ppm): \( \delta = 9.4, 10.2 \) (NHC-CH\(_{3}\)), 24.2 (\( \alpha\)-CH\(_{3}\)), 24.3, 24.5, 24.9, 25.1 (CH(CH\(_{3}\))\(_{2}\)), 29.7, 30.2 (CH(CH\(_{3}\))\(_{2}\)), 36.5 (N-CH\(_{2}\)Si), 46.2 (N-CH\(_{3}\)), 101.7 (\( \gamma\)-C), 123.5, 124.1 (NHC-...
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CCH₃), 124.8, 125.3, 128.4 (Ar-CH), 141.2, 144.7, 146.0 (Ar-C), 170.6 (Ar-CN), 198.8 (CO), 206.2 (NCN).

²⁹Si{¹H} NMR (79.5 MHz, THF-d₈, 298 K, ppm): δ = 66.8.

HR-APCI-MS for [C₃⁷H₅₂N₄NiOSi, M–CO+H]⁺ (m/z): calcd: 655.3337; found: 655.3329.

IR (KBr, cm⁻¹): ν = 1952, 1887.

Elemental analysis for [C₄₂H₇₀N₄NiP₂Si]: Cacld: C, 66.57; N, 8.17; H, 7.94. Found: C, 66.89; N, 7.98; H, 7.63.

5.4.19 General Procedure for the Catalytic C–C Coupling Reactions

A Schlenk flask was charged with an appropriate amount of the precatalyst 17 (0.014 mmol, 2.0 mol%) and the corresponding aryl halide (0.72 mmol). The flask was repeatedly flushed with nitrogen and evacuated. THF (2.0 mL) was added followed by the corresponding Grignard reagent (1.08 mmol, 0.5 M in THF or 1.0 M in THF, respectively). The flask was sealed and heated to 70 °C for 24 h. The mixture was cooled, and dichloromethane and water were added. The aqueous layer was extracted with dichloromethane, and the collected organic layers were washed with water, brine and dried with Na₂SO₄. After filtration and removal of the solvent, the residue was dissolved in diethyl ether and purified by filtration through a short passage of silica gel. The analytical properties of the products are in agreement with literature data.

5.4.20 Synthesis of L₃Si(=Se)OH(dmap) (25)

Li(HBEt₃) (1 mL, 1 mmol, 1 M THF solution) was added dropwise to a suspension of Se (40mg, 0.5 mmol) in THF (20 mL) at −20 °C. This mixture was allowed to warm up to room temperature and stirred for another 12 hours. All volatiles were removed in vacuo, then THF (30 mL) and 24 (0.285 g, 0.5 mmol) was added at −20 °C. The mixture was stirred at room temperature for 12 hours and a yellow suspension was formed. The suspension was cooled to
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−78 °C and two molar equivalents of Me3N·HCl (95.6 mg, 1 mmol) were added, affording to a clear yellow solution after warming to room temperature. After 12 hours at ambient temperature, all volatiles were removed in vacuo and toluene (20 mL) was added to the solid residue. Filtration by cannula resulted in a yellow filtrate which was concentrated to ca. 5 mL, and n-hexane (3 mL) was added to the clear solution. After standing at 0 °C for 24 hours, a yellow crystalline product was separated from the yellow mother liquor by filtration, and dried in vacuo for three hours. Yield: 0.25 g (75%). Mp: 192-194 °C.

\[ \text{H NMR} \]
(400 MHz, CDCl3, 25 °C, ppm): \( \delta = 1.08 \) (d, 6 H, \( ^3J = 7.2 \) Hz, \( (CH_3)_2CH \)), 1.21 (d, 6 H, \( ^3J = 6.4 \) Hz, \( (CH_3)_2CH \)), 1.24 (d, 6 H, \( ^3J = 6.8 \) Hz, \( (CH_3)_2CH \)), 1.41 (d, 6 H, \( ^3J = 6.8 \) Hz, \( (CH_3)_2CH \)), 2.00 (s, 6 H, \( \alpha-CH_3 \)), 2.96 (s, 6 H, N(CH3)2), 3.27 (sept, 2 H, \( ^3J = 6.8 \) Hz, \( CH(CH_3)_2 \)), 3.44 (sept, 2 H, \( ^3J = 6.8 \) Hz, \( CH(CH_3)_2 \)), 5.73 (s, 1 H, \( \gamma-H \)), 6.42-6.44 (m, 3 H, Py-H and OH), 7.22-7.25 (m, 4 H, Ar-H), 7.32-7.36 (m, 2 H, Ar-H), 8.29-8.31 (m, 2 H, Py-H).

\[ ^{13}\text{C} \{^1\text{H}\} \text{ NMR} \]
(100 MHz, CDCl3, 25 °C, ppm): \( \delta = 23.7, 24.0, 24.1, 24.4 \) (CHMe2), 26.2 (NMe), 27.9 (CHMe2), 29.3 (CHMe2), 38.9 (NMe2), 100.8 (\( \gamma-C \)), 106.2, 124.5, 124.6, 128.6, 137.1, 144.3, 145.4, 149.2, 154.1, 170.0.

\[ ^{29}\text{Si} \{^1\text{H}\} \text{ NMR} \]
(79 Hz, CDCl3, 25 °C, ppm): \( \delta = -25.5 \).

ESI-MS

Elemental analysis
calcd for C36H52N4OSeSi (%): C, 65.13; H, 7.90; N, 8.44. Found: C, 65.28; H, 8.19; N, 7.95.

IR (KBr, cm\(^{-1}\)):
\( v = 536 \) (w), 585 (s), 654 (w), 761 (m), 799 (s), 897 (s), 1002 (s), 1028 (m), 1060 (w), 1103 (w), 1173 (w), 1228 (s), 1251 (m), 1320 (s), 1378 (vs), 1439 (s), 1462 (m), 1543 (vs), 1607 (vs) (C=N), 2866 (s), 2926 (s), 2958 (vs), 3059 (w), 3424 (m) (OH).
5.4.21 Synthesis of [L₃Si(=S)OCu]₂ (26)

To a mixture of (MesCu)₄ (0.106 g, 0.125 mmol) (Mes = 2,4,6-Me₃C₆H₂) and 23 (0.309 g, 0.5 mmol) was added THF (30 mL) at −20 °C, and a clear yellow solution formed instantly. It was left to warm to room temperature and stirred for another 12 hours. All volatiles were removed in vacuo, and the obtained residue was washed with n-hexane (5 mL) to remove dmap and then extracted with toluene (15 mL). The obtained yellow filtrate was concentrated to ca. 4 mL and left at –20 °C for 24 hours to afford yellow crystalline product, which was separated from the mother liquor by filtration and dried in vacuo for four hours. Yield: 0.21 g (76%). Mp: 320-323 °C (decomp.). There are two isomers that have equilibrium present in the solution, so two sets of signal for each moiety observed, and the ratio of isomers 26a and 26b is 1:0.62 according to the integral of γ-H of β-diketiminato ligand.

¹H NMR (CDCl₃, 25 °C, 400 MHz, ppm): isomer 26b: δ = 1.06 (d, 12 H, ³J = 6.8 Hz, CH(CH₃)₂), 1.13 (d, 24 H, ³J = 6.8 Hz, CH(CH₃)₂), 1.36 (d, 12 H, ³J = 6.8 Hz, CH(CH₃)₂), 1.89 (s, 12 H, α-CH₃), 3.10 (sept, 4 H, ³J = 6.8 Hz, CH(CH₃)₂), 3.42 (sept, 4 H, ³J = 6.8 Hz, CH(CH₃)₂), 5.55 (s, 2 H, γ-H), 7.19-7.42 (m, 12 H, Ar-H); isomer 26a: δ = 1.08 (d, 12 H, ³J = 6.8 Hz, CH(CH₃)₂), 1.12 (d, 24 H, ³J = 6.8 Hz, CH(CH₃)₂), 1.34 (d, 12 H, ³J = 6.8 Hz, CH(CH₃)₂), 1.86 (s, 12 H, α-CH₃), 3.26 (sept, 4 H, ³J = 6.8 Hz, CH(CH₃)₂), 3.48 (sept, 4 H, ³J = 6.8 Hz, CH(CH₃)₂), 5.49 (s, 2 H, γ-H), 7.19-7.42 (m, 12 H, Ar-H).

¹³C {¹H} NMR (CDCl₃, 25 °C, 50 MHz, ppm): δ = 23.6, 23.81, 24.2, 24.7, 24.8, 25.7, 26.2, 27.6, 28.0, 28.6, 29.2 (¹³C resonance signals for iPr and α-CH₃ groups in 26b and 26b), 100.0 (γ-C in 26a), 100.1 (γ-C in 26b), 124.0, 124.5, 124.6, 124.9, 127.9, 128.1, 136.7, 137.9, 144.8, 145.3, 146.3, 168.7, 168.8 (Ar-¹³C signals for 26a and 26b).

²⁹Si {¹H} NMR (CDCl₃, 25 °C, 79 MHz, ppm): δ = −39.1 (isomer 26b); −38.4
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(isomer 26a).

ESI-MS:  
m/z 1113.4071(2, [M + H]+), calcd: 1113.4088; 1051.4857 ([M – Cu + 2 H]+), calcd: 1051.4870.

Elemental analysis  
calcd for C_{58}H_{82}Cu_{2}N_{4}O_{2}S_{2}Si_{2}: C, 62.49; H, 7.41; N, 5.03; S, 5.75. Found: C, 62.98; H, 7.79; N, 5.72; S, 5.11.

IR (KBr, cm\(^{-1}\)):  
\(\nu = 504\) (w), 542 (w), 614 (vs), 660 (s), 721 (w), 756 (s), 802 (s), 901 (m), 932 (w), 1028 (s), 1057 (vs), 1106 (w), 1173 (w), 1248 (m), 1323 (vs), 1387 (vs), 1436 (s), 1468 (m), 1552 (vs), 1587 (w), 1627 (w) (C=\(\text{N}\)), 2866 (m), 2926 (s), 2962 (vs), 3022 (w), 3062 (w).

5.4.22 Synthesis of [\(\text{L}^3\text{Si(=Se)OCu}\)]\(_2\) (27)

To a mixture of (MesCu\(_4\)) (0.144 g, 0.17 mmol) and 25 (0.451 g, 0.68 mmol) was added THF (30 mL) at \(-20^\circ\text{C}\). The mixture was allowed to warm to room temperature and stirred for another 12 hours. All volatiles were removed in vacuo, and the residue was washed with \(n\)-hexane (5 mL) and extracted into toluene (20 mL). The obtained yellow filtrate was concentrated to ca. 5 mL and left at \(-20^\circ\text{C}\) for 24 hours to afford a yellow crystalline product. Yield: 0.67 g, 82%. Mp: 295-296 \(^\circ\text{C}\) (dec.). There are \(cis\) and \(trans\) isomers that have equilibrium present in the solution, so two sets of signal for each moiety observed, and the ratio of isomers 27a and 27b is 1:0.49 according to the integral of \(\gamma\)-H of \(\beta\)-diketiminato ligand.

\(^1\)H NMR  
(CDCl\(_3\), 25 \(^\circ\text{C}\), 400 MHz, ppm): isomer 27b: \(\delta = 1.01\) (d, 12 \(H\), \(^3J = 6.8\) Hz, CH(CH\(_3\))\(_2\)), 1.09 (d, 24 \(H\), \(^3J = 6.8\) Hz, CH(CH\(_3\))\(_2\)), 1.33 (d, 12 \(H\), \(^3J = 6.8\) Hz, CH(CH\(_3\))\(_2\)), 1.86 (s, 12 \(H\), \(\alpha\)-CH\(_3\)), 3.03 (sept, 4 \(H\), \(^3J = 6.8\) Hz, CH(CH\(_3\))\(_2\)), 3.40 (sept, 4 \(H\), \(^3J = 6.8\) Hz, CH(CH\(_3\))\(_2\)), 5.56 (s, 2 \(H\), \(\gamma\)-H), 7.17-7.39 (m, 12 \(H\), Ar-H); isomer 27a: \(\delta = 1.02\) (d, 12 \(H\), \(^3J = 6.8\) Hz, CH(CH\(_3\))\(_2\)), 1.14 (d, 24 \(H\), \(^3J =
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6.8 Hz, CH(CH$_3$)$_2$, 1.33 (d, 12 H, $^3$J = 6.8 Hz, CH(CH$_3$)$_2$), 1.86 (s, 12 H, α-CH$_3$), 3.22 (sept, 4 H, $^3$J = 6.8 Hz, CH(CH$_3$)$_2$), 3.48 (sept, 4 H, $^3$J = 6.8 Hz, CH(CH$_3$)$_2$), 5.47 (s, 2 H, γ-H), 7.17-7.39 (m, 12 H, Ar-H).

$^{13}$C{$_1$H} NMR (CDCl$_3$, 25 °C, 100 MHz, ppm): 23.2, 23.7, 24.0, 24.1, 24.4, 24.5, 24.5, 24.6, 24.7, 25.7, 26.5, 27.6, 28.1, 28.2, 28.6, 28.7, 29.3 ($^{13}$C resonance signals for iPr and α-CH$_3$ groups in 27a and 27b), 100.3 (β-C in 27a), 100.7 (β-C in 27b), 123.0, 124.0, 124.4, 124.5, 124.7, 124.9, 128.1, 136.7, 137.8, 144.4, 145.2, 146.2, 146.3, 146.4, 168.3, 168.6 (Ar-$^{13}$C signals for 27a and 27b).

$^{29}$Si{$_1$H} NMR (CDCl$_3$, 25 °C, 79 MHz, ppm): δ = –42.2 (isomer 27b), –40.1 (isomer 27a).

ESI-MS: m/z 1209.2968 ([M + H]$^+$), calcd: 1209.2977. 1147.3765 ([M – Cu + 2 H]$^+$), calcd: 1147.3759.

Elemental analysis calcd for C$_{65}$H$_{90}$Cu$_2$N$_4$O$_2$Se$_2$Si$_2$: C, 60.02; H, 6.97; N, 4.31. Found: C, 59.82; H, 6.95; N, 4.46.

IR (KBr, cm$^{-1}$): ν = 501 (w), 527 (m), 568 (m), 660 (w), 724 (w), 759 (m), 799 (s), 898 (m), 932 (w), 947 (w), 1022 (s), 1066 (s), 1176 (w), 1231 (w), 1251 (m), 1323 (s), 1387 (vs), 1445 (s), 1462 (s), 1546 (vs), 1587 (w), 1621 (w), 2866 (m), 2926 (s), 2964 (vs), 3022 (w), 3062 (w).

5.4.23 Procedure for aziridination reactions with 26 and 27

Under N$_2$ atmosphere, the pre-catalyst 26 or 27 (11 mg for 26 and 12 mg for 27, 0.005 mmol) was placed in a Schlenk flask with molecular sieves, and dry CH$_2$Cl$_2$ (10 mL) was added to the flask followed with styrene (0.5 mL, 4 mmol). After the mixture was stirred for 15 min., PhI=NTs (0.15 g, 0.4 mmol) was added portion-wise in 1 hour. The mixture was stirred for another 3 hours, and then it was purified with silica-column chromatography using
CH$_2$Cl$_2$ as eluent. The product is characterized with NMR spectroscopy and they are identical to that reported in the literatures. The yields (26: 85%, 27: 87%) were determined by $^1$H NMR spectra using mesitylene as internal standard.

### 5.4.2.4 Synthesis of $^{L_Cy}(H)Ge$ (28)

![Chemical Structure](image)

$L^{Cy}$GeCl (0.628 g, 1 mmol) was placed in a schlenk flask (100 mL) in the glovebox. Toluene (30 mL) was transferred into the flask via cannula under stirring at room temperature and a clear yellow solution was formed. The solution was cooled to $-78 \, ^\circ\text{C}$, and K[BH(sBu)$_3$] (1 mL, 1 mmol, 1 M solution in THF) was added dropwise to the solution via syringe. The mixture was allowed to warm to room temperature and stirred for another 12 hours. The obtained red solution was concentrated to 10 mL and filtered. The filtrate was left at 0 $^\circ$C for 24 hours to afford a yellow crystalline product 28. The product was collected by decantation of the supernatant and the obtained solid was dried in vacuo for several hours. Yield: 0.50 g (0.84 mmol, 84%). Mp. 178 $^\circ$C (dec.).

$^1$H NMR (200.1 MHz, benzene-d$_6$, 298 K): $\delta = 0.53$ (d, 3 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.10 (d, 3 H, $^3J_{H-H} = 7.0$ Hz, CH(CH$_3$)$_2$), 1.25 (d, 3 H, $^3J_{H-H} = 6.6$ Hz, CH(CH$_3$)$_2$), 1.28 (d, 9 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.37-1.44 (m, 7 H, Cy-CH$_2$ (4 H) + CH(CH$_3$)$_2$ (3 H)), 1.47 (d, 3 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.75-2.01 (m, 4 H, Cy-CH$_2$), 3.13 (sept, 1 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 3.55 (sept, 1 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 4.75 (s, 1 H, $^\gamma$-H (PhCHNAr)), 7.04-7.41 (m, 11 H, Ar-H and Ph-H).

$^{13}$C{$^1$H} NMR (50.3 MHz, benzene-d$_6$, 298 K): $\delta = 22.5, 22.9$ (CH(CH$_3$)$_2$), 23.0 (Cy-CH$_2$), 23.5(CH(CH$_3$)$_2$), 23.7 (Cy-CH$_2$), 23.8 (CH(CH$_3$)$_2$), 25.2, 26.1, 26.2, 26.9 (CH(CH$_3$)$_2$), 27.9 (Cy-CH$_2$), 28.1, 28.2, 28.3, 28.4(CH(CH$_3$)$_2$), 29.9 (Cy-CH$_2$), 74.8 ($^\gamma$-C), 109.1 (CH$_2$CCNAr), 123.2, 123.8, 124.0, 124.2, 126.4, 127.0, 127.1, 128.2, 128.3 (Ar-CH), 134.4, 140.3, 143.7, 145.0, 146.9, 147.1, 147.2, 148.1 (Ar-C)
and CH$_2$CCNAr).

Elemental analysis for C$_{37}$H$_{48}$GeN$_2$: cacl'd: C, 74.89; N, 4.72; H, 8.15; found: C, 74.19; N, 4.48; H, 8.30.

5.4.25 Synthesis of L$_{Cy}$GeOCH(=O) (29)

L$_{Cy}$GeCl (1.26 g, 2 mmol) was placed in a schlenk flask (100 mL) in the glovebox. Toluene (30 mL) was transferred into the flask via cannula under stirring at room temperature and a clear yellow solution was formed. The solution was cooled to $-78$ °C, and K[BH(sBu)$_3$] (2 mL, 2 mmol, 1 M solution in THF) was added dropwise to the solution via syringe. The mixture was then placed in a cooled water-salt bath (ca. $-5$ °C), and allowed to stir at this temperature for 12 hours. Then the atmosphere was changed to CO$_2$ by a freeze-pump-thaw cycle, and the mixture was stirred at CO$_2$ atmosphere for 12 hours. All the volatiles were removed in vacuo and the residue was washed with hot (ca. 50 °C) n-hexane (20 mL), the solution was filtrated. The remaining residue is the pure product 29 on the basis of $^1$H NMR spectroscopy. The filtrate was left at room temperature for 12 hours to yield the crystals of 29, which are suitable for X-ray single crystal diffraction analysis. Total yield: 1.01 g (1.55 mmol, 77%). Mp. 165 °C (dec.).

$^1$H NMR (200.1 MHz, benzene-d$_6$, 298 K): $\delta$ = 0.91 (d, 3 H, $^3$J$_{H-H}$ = 6.6 Hz, CH(CH$_3$)$_2$), 1.02 (d, 3 H, $^3$J$_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 1.12-1.23 (m, 16 H, Cy-H (4 H) + CH(CH$_3$)$_2$ (12 H)), 1.27 (d, 3 H, $^3$J$_{H-H}$ = 6.6 Hz, CH(CH$_3$)$_2$), 1.33 (d, 3 H, $^3$J$_{H-H}$ = 6.6 Hz, CH(CH$_3$)$_2$), 1.86-2.21 (m, 4 H, Cy-H), 3.03-3.31 (m, 2 H, CH(CH$_3$)$_2$), 3.44-3.72 (m, 2 H, CH(CH$_3$)$_2$), 6.67-6.92 (m, 7 H, Ar-H and Ph-H), 7.03-7.22 (m, 4 H, Ar-H and Ph-H), 8.78 (s, 1 H, -OCH(=O)).

$^{13}$C({$^1$H}) NMR (50.3 MHz, benzene-d$_6$, 298 K): $\delta$ = 21.0 (Cy-CH$_2$), 22.3(Cy-CH$_2$), 22.9, 23.3, 24.2, 24.3, 24.4, 26.8 (CH(CH$_3$)$_2$), 27.2, 27.6 (CH(CH$_3$)$_2$), 27.9 (CH(CH$_3$)$_2$), 28.6, 28.7(CH(CH$_3$)$_2$), 28.8 (Cy-CH$_2$), 28.9(CH(CH$_3$)$_2$), 31.1(Cy-CH$_2$), 107.0 (y-C), 123.2, 124.2,
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125.3, 126.9, 127.0, 127.5, 127.7, 127.8, 127.9, 128.0, 128.6 (Ar-CH), 137.9, 139.9, 140.4, 143.0, 145.1, 146.0, 146.7 (Ar-C), 164.4 (-OCH(-O)), 165.8 (Cy-CN), 168.7 (Ph-CN).

Elemental analysis for C_{38}H_{48}GeN_{2}O_{2} (%): calcd: C, 71.60; N, 4.39; H, 7.59; found: C, 71.56; N, 4.37; H, 7.93.

APCI-HR-MS: calcd for [C_{37}H_{47}GeN_{2}(M – CO_{2}H)]^{+}: m/z 593.2946; found: m/z 593.2936.

IR (KBr): $\nu = 2870$ (OC=O−H), 1657 (OC=O−H) cm$^{-1}$.

5.4.26 Synthesis of L$^{3}$GeOCH$_{2}$OAl(H)L$^{3}$ (30)

L$^{3}$GeOCH(=O) (29') (0.268 g, 0.5 mmol) and L$^{3}$AlH$_{2}$ (0.224 g, 0.5 mmol) were placed in a schlenk flask (100 mL) in the glovebox. Toluene (30 mL) was transferred to the mixture via cannula under stirring at −50 °C. The solution was allowed to warm to room temperature and stirred for another 12 hours to give a clear yellow solution. The solution was concentrated to ca. 5 mL and filtrated. The obtained filtrate was left at 0 °C for 24 hours to give yellow crystals of compound 30. The product was collected by decantion of the supernatant and dried in vacuo for several hours. Yield: 0.36 g (0.37 mmol, 74%). Mp. 96 °C (dec.).

$^1$H NMR (400.2 MHz, CDCl$_3$, 298 K): $\delta = 0.62$ (d, 6 H, $^3J_{H-H} = 6.4$ Hz, CH(CH$_3$)$_2$), 0.79 (d, 6 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 0.94 (d, 6 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.01 (d, 6 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.02 (d, 6 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.07 (d, 6 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.15 (d, 6 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.21 (d, 6 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.62 (s, 6 H, $\alpha$-CH$_3$), 1.67 (s, 6 H, $\alpha$-CH$_3$), 2.98-3.12 (m, 6 H, CH(CH$_3$)$_2$), 3.17 (sept, 2 H, $^3J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 4.48 (s, 2 H, OCH$_2$O), 4.90 (s, 1 H, $\gamma$-H), 5.02 (s, 1 H, $\gamma$-H), 6.84-6.86 (m, 2 H, Ar-H), 6.98-7.03 (m, 2 H, Ar-H), 7.06-7.26 (m, 8 H, Ar-H). The resonance signal for Al-H is not observed in the spectrum.
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$^{13}$C{$^{1}$H} NMR (100.1 Hz, CDCl$_3$, 298 K): $\delta$ = 23.1 ($\alpha$-CH$_3$), 23.4($\alpha$-CH$_3$), 24.1, 24.2, 24.6, 24.7, 25.1, 25.8 (CH(CH$_3$)$_2$), 27.3, 27.7, 28.0, 28.7 (CH(CH$_3$)$_2$), 85.9 (OCH$_2$O), 96.2 ($\gamma$-C), 96.4 ($\gamma$-C), 123.3, 123.9, 124.1, 124.8, 126.3, 126.7, 126.8, 128.2, 129.0 (Ar-CH), 139.4, 140.7, 143.1, 143.8, 143.9, 146.0 (Ar-C), 163.2 (CNAr), 169.9 (CNAr).

Elemental analysis for C$_{59}$H$_{85}$AlGeN$_4$O$_2$ (%): caclcd: C, 72.17; N, 5.71; H, 8.72; found: C, 72.40; N, 5.86; H, 8.55.

APCI-HR-MS: caclcd for [C$_{59}$H$_{86}$AlGeN$_4$O$_2$ (M + H)]$: m/z$ 983.5772; found: $m/z$ 983.5751.

5.4.27 Synthesis of L$^3$Al(OCH$_2$O)$_2$AlL$^3$ (31)

![Diagram of compound 31]

Compound 30 (0.491 g, 0.5 mmol) is placed in a schlenk flask (50 mL) in the glovebox. THF (10 mL) was transferred to the flask via cannula at room temperature. The yellow solution was heated at 60 $^\circ$C for 12 hours under stirring, and an orange-red solution was formed. All volatiles were removed in vacuo. The residue was extracted firstly with n-hexane (10 mL) (to remove the L$^3$GeH), and then it was extracted with toluene (10 mL) to give a yellow filtrate. The toluene solution was concentrated to ca. 5 mL and filtrated. The filtrate was left at 0 $^\circ$C for 24 hours to give colorless crystals of compound 31. The product was collected by removing the mother liquor and dried in vacuo for several hours. The mother liquor was further concentrated to ca. 3 mL, and afforded another portion of product after crystallization at $\sim$30 $^\circ$C. Total yield: 0.15 g (0.15 mmol, 60%). Mp. 191 $^\circ$C.

$^1$H NMR (200.1 MHz, CDCl$_3$, 298 K): $\delta$ = 0.78 (d, 24 H, $^3$J$_{H-H}$ = 6.6 Hz, CH(CH$_3$)$_2$), 0.95 (d, 24 H, $^3$J$_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 1.55 (s, 12 H, $\alpha$-CH$_3$), 3.06 (sept, 8 H, $^3$J$_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 4.74 (s, 4 H, OCH$_2$O), 5.00 (s, 2 H, $\alpha$-H), 6.96 (s, 3 H, Ar-H), 7.00 (s, 4 H, Ar-H), 7.14-7.21 (m, 5 H, Ar-H).
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\(^{13}\)C\({}^1\)H NMR \((50.3 \text{ Hz, CDCl}_3, 298 \text{ K}): \delta = 23.5 (\alpha-\text{CH}_3), 24.4(\text{CH(\text{CH}_3)}_2), 24.7(\text{CH(\text{CH}_3)}_2), 27.9 (\text{CH(\text{CH}_3)}_2), 85.7 (\text{OCH}_2\text{O}), 97.1 (\gamma-\text{C}), 124.1, 126.8 (\text{Ar-CH}), 140.4, 144.2 (\text{Ar-C}), 170.3 (\text{CNAr}).

Elemental analysis for C\(_60\)H\(_{86}\)Al\(_2\)N\(_4\)O\(_4\) (%): caclcd: C, 73.44; N, 5.71; H, 8.83; found: C, 73.72; N, 5.89; H, 8.65.

APCI-HR-MS: cacled for [C\(_60\)H\(_{87}\)Al\(_2\)N\(_4\)O\(_4\) (M + H)]\(^+\): \(m/z\) 981.6353; found: \(m/z\) 981.6340.

5.4.28 Conversion of 29 and 29’ to CH\(_3\)OD with Me\(_3\)N\(\cdot\)AlH\(_3\)

The germylene-formate 29 or 29’ (0.25 mmol) and Me\(_3\)N\(\cdot\)AlH\(_3\) (0.75 mmol) was placed in a schlenk flask in the glovebox. Toluene (10 mL) was added to the flask via syringe at room temperature under stirring. The mixture was allowed to stir for another two hours, and cooled to 0 °C, D\(_2\)O was added to the solution and stirred for 10 minutes. The formed solid was separated by centrifuge, and a clear two phase was formed. The aqueous phase was collected and 1,4-dioxane was added to it as an internal standard to determine the yields of CH\(_3\)OD by \(^1\)H NMR spectroscopy. Yields of CH\(_3\)OD: 42% (29) and 46% (29’).

5.4.29 Synthesis of [bisNHC-AlBr\(_2\)]\(^+\)Br\(^-\) (32)

The bisNHC ligand (2.49 g, 5.3 mmol) and anhydrous AlBr\(_3\) (1.33 g, 5 mmol) were placed in a Schlenk flask (250 mL) in the glovebox. Toluene (80 mL) was transferred to the flask via cannula under vigorous stirring at −78 °C. The formed brown suspension was allowed to warm up to room temperature and stirred for another 12 hours. The off-white product of 32 was collected by filtration, washed with n-hexane (10 mL) twice and dried in vacuo for 12 hours. Yield: 3.38 g, 4.6 mmol (92%). M.p. 209 °C. The crystal suitable for X-ray diffraction analysis was obtained by recrystallization in CH\(_2\)Cl\(_2\)/n-hexane at −30 °C.

\(^1\)H NMR \((200.1 \text{ MHz, CD}_2\text{Cl}_2, 298 \text{ K, ppm}): \delta = 1.05 (d, 12 \text{ H, CH(CH}_3)_2, 3J_{\text{H},\text{H}} = 6.8 \text{ Hz}), 1.18 (d, 12 \text{ H, CH(CH}_3)_2, 3J_{\text{H},\text{H}} = 6.8 \text{ Hz}), 2.36
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(sept, 4 H, CH(CH₃)₂, 3J_H,H = 6.8 Hz), 7.22 (d, 2 H, CH=CH, 3J_H,H = 1.6 Hz), 7.27 (d, 4 H, Ar-H, 3J_H,H = 7.6 Hz), 7.51 (t, 2 H, Ar-H, 3J_H,H = 7.6 Hz), 7.83 (s, 2 H, NCH₂N), 8.85 (d, 2 H, CH=CH, 3J_H,H = 1.6 Hz).

¹³C {¹H} NMR (50.2 MHz, CD₂Cl₂, 298 K, ppm): δ = 23.0, 26.0 (CH(CH₃)₂), 28.8 (CH(CH₂)₂), 59.9 (NCH₂N), 124.6 (CH=CH), 125.2, 125.5 (Ar-CH), 128.5, 129.3 (Ar-C), 131.7 (Ar-CH), 132.6, 145.7 (Ar-C). The ¹³C resonance signal for NCN was not observed.

Elemental analysis for C₃₁H₄₀AlBr₃N₄•½n-hexane: cacld: C, 52.46; N, 7.20; H, 6.09. Found: C, 52.33; N, 7.25; H, 5.83.

5.4.30 Synthesis of bisNHC-Al(Br)[Fe(CO)₄] (33)

Compound 32 (0.37 g, 0.5 mmol) and K₂Fe(CO)₄ (0.11 g, 0.5 mmol) were placed in a Schlenk flask (100 mL) in the glovebox. THF (60 mL) was transferred to the flask via cannula under stirring at −78 °C, and a slight yellow suspension was formed. The mixture was allowed to warm to room temperature and stirred for another 5 hours. It was filtered to remove the inorganic precipitate; the obtained light yellow filtrate was concentrated to ca. 5 mL and left at 0 °C for 12 hours to afford compound 33 as a colorless crystalline solid. Yield: 0.27 g, 0.36 mmol (72%). M.p. 283 °C (dec.).

¹H NMR (200.1 MHz, THF-d₈, 298 K, ppm): δ = 0.95 (d, 6 H, CH(CH₃)₂, 3J_H,H = 6.8 Hz), 1.22 (d, 6 H, CH(CH₃)₂, 3J_H,H = 6.6 Hz), 1.32 (d, 6 H, CH(CH₃)₂, 3J_H,H = 6.6 Hz), 2.50 (sept, 2 H, CH(CH₃)₂, 3J_H,H = 6.8 Hz), 3.00 (sept, 2 H, CH(CH₃)₂, 3J_H,H = 6.6 Hz), 6.65 (s, 2 H, NCH₂N), 7.15-7.34 (m, 6 H, Ar-H), 7.39 (d, 2 H, CH=CH, 3J_H,H = 1.6 Hz), 7.75 (d, 2 H, CH=CH, 3J_H,H = 1.6 Hz).
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$^{13}$C{\textsuperscript{1}H} NMR (100.2 MHz, THF-d$_8$, 298 K, ppm): $\delta$ = 22.3, 22.5, 25.4, 25.6 (CH(CH$_3$)$_2$), 27.8, 28.2 (CH(CH$_3$)$_2$), 60.9 (NCH$_2$N), 121.3 (CH=CH), 123.7, 124.0 (Ar-CH), 125.9 (CH=CH), 130.2 (Ar-CH), 134.6 (Ar-C), 145.6, 145.9 (Ar-CN), 170.1 (NCN), 219.2 (CO).

IR (KBr, cm$^{-1}$): $\nu$ = 1982, 1897, 1859, 1819 (CO).

Electroal analysis for C$_{35}$H$_{40}$AlBrFeN$_4$O$_4$•THF: caclcd: C, 57.44; N, 6.87; H, 5.93. Found: C, 57.42; N, 7.19; H, 5.60.

5.4.31 Synthesis of bisNHC-Al(2-cyclo-OC$_4$H$_7$)[Fe(CO)$_4$] (34)

Compound 33 (74 mg, 0.1 mmol) and KH (12 mg, 0.3 mmol) were placed in a Schlenk flask (50 mL). THF (20 mL) was transferred to the flask via cannula at room temperature. The mixture was stirred for 48 hours, then it was filtered, the filtrate was concentrated to ca. 3 mL and left at $-30^\circ$C for 24 hours affording compound 34 as a colorless crystalline solid. The product was collected by decantation of the supernatant and dried in vacuo for several hours. Yield: 50 mg, 0.068 mmol (68%). M.p. 258 $^\circ$C (dec.).

$^1$H NMR (400.2 MHz, THF-d$_8$, 298 K, ppm): $\delta$ = 0.47 (m, 1 H, CH$_2$ in cyclo-C$_4$H$_7$O), 0.76 (m, 1 H, CH$_2$ in cyclo-C$_4$H$_7$O), 0.95 (d, 3 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 0.97 (d, 3 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 0.98 (d, 3 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 1.04 (d, 3 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 1.09 (d, 3 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.4 Hz), 1.13 (d, 3 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 1.30 (d, 3 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 1.31 (d, 3 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.4 Hz), 1.52 (m, 1 H, CH$_2$ in cyclo-C$_4$H$_7$O), 2.05-2.21 (m, 4 H, CH$_2$ in cyclo-C$_4$H$_7$O (1 H) + AlCHO (1 H) + CH(CH$_3$)$_2$ (2 H)), 3.09 (m, 1 H, (m, 1 H, CH$_2$ in cyclo-C$_4$H$_7$O)), 3.41 (sept, 1 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 3.50 (sept, 1 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 6.64 (d, 1 H, NCH$_2$N, $^2$J$_{H,H}$ = 13.2 Hz), 6.74 (d, 1 H, NCH$_2$N, $^2$J$_{H,H}$ = 13.2 Hz), 7.13-7.35 (m, 6
H, Ar-CH), 7.36 (d, 1 H, CH=CH, \(^3J_{HH} = 1.6\) Hz), 7.38 (d, 1 H, CH=CH, \(^3J_{HH} = 1.6\) Hz), 7.72 (d, 1 H, CH=CH, \(^3J_{HH} = 1.6\) Hz), 7.73 (d, 1 H, CH=CH, \(^3J_{HH} = 1.6\) Hz).

\(^{13}\)C\(^{1}H\) NMR (100.2 MHz, THF-\(d_8\), 298 K, ppm): \(\delta = 22.8, 23.3, 23.6, 23.7, 25.9, 26.1, 26.2, 26.4, 26.5, 26.7 (\text{CH(CH}_3)_2\text{ and CH}_2\text{-OC}_4\text{H}_7), 28.4, 28.6, 29.3 (\text{CH(CH}_3)_2), 62.0 (\text{NCH}_2\text{N}), 69.1 (\text{OCH}_2), 74.7 (\text{br, Al-CHO}), 122.2, 122.7 (\text{CH=CH}), 124.1, 124.2, 124.5, 125.0 (\text{Ar-CH}), 126.3, 126.4 (\text{CH=CH}), 130.6, 130.7 (\text{Ar-CH}), 136.1, 136.4 (\text{Ar-C}), 146.8, 146.9, 147.0, 147.2 (\text{Ar-CN}), 177.0, 177.4 (\text{NCN}), 222.0 (\text{CO}).

IR (KBr, cm\(^{-1}\)):
\(v = 2739 (\text{AlC−H}), 1966, 1860, 1850 (\text{CO}).\)

Elemental analysis for C\(_{39}\)H\(_{47}\)AlFeN\(_4\)O\(_5\): cacld: C, 63.76; N, 7.63; H, 6.45. Found: C, 63.09; N, 6.96; H, 6.82.

### 5.4.32 Synthesis of bisNHC-Al(2-cyclo-OC\(_5\)H\(_9\))[Fe(CO)]\(_4\) (35)

Compound 33 (74 mg, 0.1 mmol) and KH (12 mg, 0.3 mmol) were placed in a Schlenk flask (50 mL). THP (20 mL) was transferred to the flask via cannula at room temperature. The mixture was stirred for 48 hours at 55 °C, and then all the volatile was removed under reduced pressure. The residue was extracted with THF (20 mL), and filtered to obtain a brown solution. The solution was concentrated to ca. 10 mL and left at −30 °C for 24 hours affording compound 35 as colorless precipitate. The product was collected by decantation of the supernatant and dried in vacuo for several hours. Unfortunately, the attempts to obtain the single crystal of 35 suitable for X-ray diffraction analysis were unsuccessful. Yield: 52 mg, 0.070 mmol (70%). M.p. 252 °C (dec.).

\(^1\)H NMR (400.2 MHz, THF-\(d_8\), 298 K, ppm): \(\delta = 0.23 (\text{m, 1 H, CH}_2\text{-OC}_4\text{H}_9), 0.76\text{-}0.93 (\text{m, 2 H, CH}_2\text{-OC}_4\text{H}_9), 0.94 (\text{d, 3 H, }^{3}J_{HH} = 6.8 \text{ Hz, CH(CH}_3)_2), 0.99 (\text{d, 6 H, }^{3}J_{HH} = 6.8 \text{ Hz, CH(CH}_3)_2), 1.07 (\text{dd, 6 H, }^{3}J_{HH} = 6.8 \text{ Hz, CH(CH}_3)_2), 1.17 (\text{d, 3 H, }^{3}J_{HH} = 6.8 \text{ Hz, CH(CH}_3)_2),
1.29 (d, 3 H, $^3J_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.37 (d, 3 H, $^3J_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 1.05-1.25 (m, 4 H, CH$_2$-OC$_5$H$_9$), 1.97 (m, 1 H, AlOCH$_2$), 2.10 (sept, 1H, $^3J_{HH} = 6.8$ Hz, CH(CH$_3$)$_2$), 2.26 (m, 1H, CH(CH$_3$)$_2$), 2.62 (m, 1 H, Al-OCH$_2$), 3.02 (m, 1 H, Al-OC$_5$H$_9$), 3.61 (m, 1H, C$_3$H$(CH_3)_2$), 6.64 (d, 1 H, $^2J_{HH} = 12.8$ Hz, N$_2$CH), 6.67 (d, 1 H, $^2J_{HH} = 12.8$ Hz, NCH$_2$N), 7.15-7.43 (m, 8 H, Ar-C$_7$H$_4$(6 H) + C$_3$H$(CH_3)_2$), 7.71 (d, 1 H, $^2J_{HH} = 1.6$ Hz, C$_3$H$(CH_3)_2$).

$^{13}$C{${}^1$H} NMR (100.2 MHz, THF-$d_8$, 298 K, ppm): $\delta = 22.6, 23.6, 23.7, 24.0, 25.6, 26.1, 26.4, 26.5, (CH(CH$_3$)$_2$), 27.3, 28.1, 28.7, (CH$_2$-OC$_5$H$_9$), 28.3, 28.8, 29.2, 29.3 (CH(CH$_3$)$_2$), 61.8 (NCH$_2$N), 71.0 (OCH$_2$-OC$_5$H$_9$), ca. 75.0 (OCH-OC$_5$H$_9$) (not observed in the $^{13}$C NMR spectrum, but it can be assigned from the $^1$H, $^{13}$C-HMQC NMR spectrum, see Figure 11s), 122.3, 1227, (CH=CH) 124.4, 124.6, 125.3, 126.4, 126.5, 130.6, 130.9, (Ar-CH + CH=CH) 136.6, 136.7, 146.3, 146.7, 146.8, 147.8, (Ar-C) 177.1, 177.3, (NCN) 222.0 (CO).

IR (KBr, cm$^{-1}$): $\nu = 1964, 1872, 1869, 1848$.

Elemental analysis for C$_{40}$H$_{49}$AlFeN$_4$O$_5$: calcd: C, 64.17; N, 7.48; H, 6.60. Found: C, 63.89; N, 7.13; H, 6.83.


5.4.33 Synthesis of bisNHC-Al(OnBu)[Fe(CO)$_4$] (36)

![Structure of compound 36](image)

Compound 33 (0.37 g, 0.5 mmol) was placed in a Schlenk flask (100 mL). THF (50 mL) was transferred to the flask via cannula, then K[BHR$_3$] (R = Et or sBu) (0.5 mL, 0.5 mmol, 1 M in THF) was added to the mixture via syringe under vigorous stirring at –20 °C. The mixture was allowed to warm up to room temperature and stirred for 12 hours. The mixture was filtered, and the obtained filtrate was concentrated to ca. 5 mL and left at –30 °C for 24 hours to yield...
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an off-white solid of the product 36. The product was collected by filtration with filter funnel, washed with n-hexane (5 mL), and dried in vacuo for several hours. Yield: 0.23 g, 0.31 mmol (62%). M.p. 225 °C (dec.).

$^1$H NMR (400.2 MHz, THF-d$_8$, 298 K, ppm): $\delta = 0.49$-0.55 (m, 7 H, CH$_2$CH$_2$CH$_2$O), 0.99 (d, 6 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 1.00 (d, 6 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.6 Hz), 1.12 (d, 6 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.6 Hz), 1.33 (d, 6 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 2.29 (sept, 2 H, CH(CH$_3$)$_2$, $^3$J$_{H,H}$ = 6.8 Hz), 2.74 (t, 2 H, CH$_2$CH$_2$CH$_2$O), 3.34 (sept, 2 H, OCH$_2$CH$_2$CH$_2$O), 6.56 (d, 1 H, NC=C=N, $^2$J$_{H,H}$ = 13.2 Hz), 6.58 (d, 1 H, NCH$_2$N, $^2$J$_{H,H}$ = 13.2 Hz), 7.17-7.41 (m, 8 H, Ar-CH (6 H) + CH=CH (2 H)), 7.69 (d, 2 H, CH=CH, $^3$J$_{H,H}$ = 1.2 Hz).

$^{13}$C{$_^1$H} NMR (100.2 MHz, THF-d$_8$, 298 K, ppm): $\delta = 14.7$ (OCH$_2$CH$_2$CH$_2$CH$_3$), 19.4 (OCH$_2$CH$_2$CH$_2$CH$_3$), 23.5, 24.4, 25.4, 26.2 (CH(CH$_3$)$_2$), 28.5, 29.2 (CH(CH$_3$)$_2$), 37.3 (OCH$_2$CH$_2$CH$_2$CH$_3$), 61.6 (OCH$_2$CH$_2$CH$_2$CH$_3$), 62.3 (NCH$_2$N), 121.9 (CH=CH), 124.1, 125.1 (Ar-CH), 126.0 (CH=CH), 130.8 (Ar-CH), 136.1 (Ar-C), 146.2, 147.5 (Ar-CN), 222.1 (CO). The $^{13}$C signal for NCN was not observed in the $^{13}$C{$_^1$H} NMR spectrum.

IR (KBr, cm$^{-1}$): $\nu = 1967, 1917, 1860$.

Elemental analysis for C$_{39}$H$_{49}$AlFeN$_4$O$_5$: cacld: C, 63.59; N, 7.61; H, 6.70. Found: C, 63.79; N, 7.33; H, 6.85.

5.4.34 Synthesis of [bisNHC-GaCl$_2$]$^+$Cl$^-$ (37)

The bisNHC ligand (2.49 g, 5.3 mmol) was dissolved in toluene (50 mL), and then it was cooled to −78 °C. A solution of GaCl$_3$ (0.88 g, 5.0 mmol) in toluene (50 mL) was added to the cooled solution of bisNHC via cannula within 10 minutes under vigorous stirring. A
suspension was formed immediately after the addition of GaCl₃, and the obtained mixture was allowed to warm up to room temperature, and stirred for another 12 hours. The off-white product of 37 was obtained by filtration with filter funnel, washed with n-hexane (10 mL) for two times and dried in vacuo for 12 hours. Yield: 2.90 g, 4.5 mmol (90%). M.p. 198 °C. The crystal suitable for X-ray diffraction analysis was grown from a saturated CH₂Cl₂ solution at 0 °C.

$^{1}$H NMR (200.1 MHz, CD₂Cl₂, 298 K, ppm): $\delta$ = 1.06 (d, 12 H, CH(CH₃)₂, $^{3}J_{HH}$ = 6.8 Hz), 1.17 (d, 12 H, CH(CH₃)₂, $^{3}J_{HH}$ = 6.8 Hz), 2.35 (sept, 4 H, CH(CH₃)₂, $^{3}J_{HH}$ = 6.8 Hz), 7.28 (d, 2 H, CH=CH, $^{3}J_{HH}$ = 1.2 Hz), 7.12-7.41 (m, 4 H, Ar-H, except the peaks at 7.32 ppm), 7.49-7.57 (m, 2 H, Ar-H), 7.65 (s, 2 H, NCH₂N), 8.70 (d, 2 H, CH=CH, $^{3}J_{HH}$ = 1.8 Hz).

$^{13}$C{¹H} NMR (50.2 MHz, CD₂Cl₂, 298 K, ppm): $\delta$ = 23.0, 25.9 (CH(CH₃)₂), 28.9 (CH(CH₃)₂), 60.9 (NCH₂N), 124.7 (CH=CH), 125.5, 125.9 (Ar-CH), 128.5, 129.3 (Ar-C), 131.9 (Ar-CH), 132.2 (Ar-C), 145.7 (Ar-C). The $^{13}$C signal for NCN was not observed, probably due to the coupling with Ga atom.

Elemental analysis for C₃₁H₄₀Cl₃GaN₄•1/2 CH₂Cl₂: cacld: C, 55.05; N, 8.15; H, 6.01. Found: C, 55.22; N, 7.76; H, 6.31.

5.4.35 Synthesis of bisNHC-Ga(Cl)[Fe(CO)₄] (38)

Compound 37 (0.33 g, 0.5 mmol) and K₂Fe(CO)₄ (0.11 g, 0.5 mmol) were placed in a Schlenk flask (100 mL) in the glovebox. THF (60 mL) was transferred to the flask via cannula under stirring at −78 °C, and a slight yellow suspension was formed. The mixture was allowed to warm to room temperature and stirred for another 5 hours. It was filtered to remove the inorganic precipitate; the obtained light yellow filtrate was concentrated to ca. 5 mL and left at 0 °C for 12 hours to afford compound 38 as a colorless crystalline solid. Yield:
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0.25 g, 0.34 mmol (68%). M.p. 246 °C (dec.). Due to the low solubility in commonly used organic solvents (THF, CH₂Cl₂, etc.), all the attempts to get the NMR spectra of this compound failed.

IR (KBr, cm⁻¹): ν = 1992, 1905, 1880, 1847 (CO).

Elemental analysis for C₃₅H₄₀ClFeGaN₄O₄: calcld: C, 56.67; N, 7.55; H, 5.44. Found: C, 56.25; N, 7.91; H, 5.66.

5.4.36 Synthesis of bisNHC-Ga(H)[Fe(CO)₄] (39)

Compound 38 (0.37 g, 0.5 mmol) was placed in a Schlenk flask (100 mL) in the glovebox. THF (60 mL) was transferred to the flask via cannula to form a light yellow suspension, then K[BH(sBu)₃] (0.5 mL, 0.5 mmol, 1 M in THF) was added to the mixture via syringe under vigorous stirring at room temperature. After stirring for 12 hours, the mixture was filtered, the obtained filtrate was concentrated to ca. 5 mL, and left at 0 °C for 24 hours to afford compound 39 as a colorless needle-crystalline product. The product was collected by decantation of the supernatant, and dried in vacuo for several hours. Yield: 0.27 g, 0.38 mmol (76%). M.p. 265 °C (dec.).

¹H NMR (400.2 MHz, THF-d₈, 298 K, ppm): δ = 0.98 (d, 6 H, CH(CH₃)₂, 3J_H,H = 7.2 Hz), 1.03 (d, 6 H, CH(CH₃)₂, 3J_H,H = 6.8 Hz), 1.21 (d, 6 H, CH(CH₃)₂, 3J_H,H = 6.4 Hz), 2.54 (sept, 2 H, CH(CH₃)₂, 3J_H,H = 6.8 Hz), 2.71 (sept, 2 H, CH(CH₃)₂, 3J_H,H = 6.8 Hz), 4.58 (br, 1 H, Ga-H), 6.49 (d, 1 H, NCH₂N, 2J_H,H = 13.2 Hz), 6.70 (d, 1 H, NCH₂N, 2J_H,H = 13.2 Hz), 7.20-7.37 (m, 6 H, Ar-H), 7.40 (br, 2 H, CH=CH), 7.70 (d, 2 H, CH=CH, 3J_H,H = 1.2 Hz).

¹³C{¹H} NMR (100.2 MHz, THF-d₈, 298 K, ppm): δ = 23.3, 23.6, 25.8, 26.4 (CH(CH₃)₂), 28.9, 29.3 (CH(CH₃)₂), 62.6 (NCH₂N), 122.3 (CH=CH), 124.2, 125.3 (Ar-CH), 126.0 (CH=CH), 131.0 (Ar-CH),
Experimental Section

135.3 (Ar-C), 145.4, 147.3 (Ar-CN), 181.5 (NCN), 221.6 (CO).

IR (KBr, cm\(^{-1}\)): \(\nu = 1974, 1887, 1859, 1834\) (CO), 1875 (Ga-H).

Elemental analysis for C\(_{35}\)H\(_{41}\)FeGaN\(_4\)O\(_4\): cacl: C, 59.43; N, 7.92; H, 5.84. Found: C, 59.79; N, 7.67; H, 5.58.
6. REFERENCES


References


References


References


[86] This compound was synthesized by the deprotonation of C₆F₅OH with (IPr)CuOH as developed by S. Nolan et al. see Ref. 85.


[91] The reaction is considered to complete when more than 95% of the starting material is consumed.

References


References

In the latter case, the germylene hydride complex is unstable, so compound 28 is formed as the final product.


References


[146] I also tried the reduction with KC₈ and sodium naphthalenide, however, the reacton only afforded unidentified products.


2728-2729.
### 7. APPENDIX

#### 7.1 Crystal data and structure refinement

Table 7.1.1 Crystal data and structure refinement for NHSi→Cu complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>6</th>
</tr>
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<td>formula</td>
<td>C_{22}H_{39}ClCuF_{3}N_{4}O_{3}Si</td>
<td>C_{26}H_{48}CuF_{3}N_{4}O_{3}Si</td>
<td>C_{24}H_{45}CuF_{3}N_{5}O_{3}Si</td>
<td>C_{62}H_{92}Cu_{2}F_{6}N_{8}O_{8}S_{2}Si_{4}</td>
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<tr>
<td>Mr.</td>
<td>623.71</td>
<td>661.37</td>
<td>632.34</td>
<td>1495.00</td>
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<td>P2_1/c</td>
<td>P-1</td>
<td>P2_1/c</td>
<td>Pbcn</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>a [Å]</td>
<td>16.8856(10)</td>
<td>11.3849(5)</td>
<td>10.0327(8)</td>
<td>18.2652(6)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>9.7807(8)</td>
<td>11.8599(4)</td>
<td>30.6715(15)</td>
<td>18.2872(6)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>18.7204(13)</td>
<td>12.8308(4)</td>
<td>10.8305(7)</td>
<td>22.2926(8)</td>
</tr>
<tr>
<td>a [°]</td>
<td>90.570(3)</td>
<td>96.796(3)</td>
<td>106.542(7)</td>
<td>106.542(7)</td>
</tr>
<tr>
<td>β [°]</td>
<td>104.089(6)</td>
<td>95.478(3)</td>
<td>95.478(3)</td>
<td></td>
</tr>
<tr>
<td>γ [°]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V [Å³]</td>
<td>2998.7(4)</td>
<td>1712.04(11)</td>
<td>3194.8(4)</td>
<td>7446.2(4)</td>
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<tr>
<td>Z</td>
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<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calcd} [mg m^{-3}]</td>
<td>1.382</td>
<td>1.283</td>
<td>1.315</td>
<td>1.334</td>
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<td>wavelength [Å]</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>μ (MoKα) [mm^{-1}]</td>
<td>0.975</td>
<td>0.784</td>
<td>0.836</td>
<td>0.761</td>
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<td>size [mm³]</td>
<td>0.36×0.08×0.03</td>
<td>0.30×0.19×0.09</td>
<td>0.12×0.08×0.04</td>
<td>0.18×0.14×0.13</td>
</tr>
<tr>
<td>Θ limits [°]</td>
<td>3.50 to 25.00</td>
<td>3.48 to 25.00</td>
<td>3.30 to 25.00</td>
<td>3.53 to 25.00</td>
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<td>completeness to Θ = 25.00° [%]</td>
<td>99.7</td>
<td>99.7</td>
<td>98.4</td>
<td>99.7</td>
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<td>reflns measured</td>
<td>13155</td>
<td>13532</td>
<td>15782</td>
<td>30395</td>
</tr>
<tr>
<td>independent reflns</td>
<td>5275 [R(int) = 0.0620]</td>
<td>6023 [R(int) = 0.0304]</td>
<td>5525 [R(int) = 0.0732]</td>
<td>6550 [R(int) = 0.0744]</td>
</tr>
<tr>
<td>parameters</td>
<td>353</td>
<td>374</td>
<td>366</td>
<td>483</td>
</tr>
<tr>
<td>R1 (R1, all data)</td>
<td>0.0591 (0.0842)</td>
<td>0.0323 (0.0406)</td>
<td>0.0707 (0.1079)</td>
<td>0.0708 (0.0917)</td>
</tr>
<tr>
<td>wR2 (wR2 all data)</td>
<td>0.1034 (0.1132)</td>
<td>0.0787 (0.0819)</td>
<td>0.1148 (0.1263)</td>
<td>0.1410 (0.1508)</td>
</tr>
<tr>
<td>GOF</td>
<td>1.095</td>
<td>1.030</td>
<td>1.126</td>
<td>1.097</td>
</tr>
<tr>
<td>max., min. peaks [eÅ^{-3}]</td>
<td>0.410 (-0.454)</td>
<td>0.448 (-0.307)</td>
<td>0.581 (-0.376)</td>
<td>1.513 (-0.580)</td>
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Table 7.1.2 Crystal data and structure refinement for complexes 8-10 and 12

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<tr>
<th>Complex</th>
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<th>9•toluene</th>
<th>10•toluene</th>
<th>12</th>
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<td>Formula</td>
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<td>C_{60}H_{85}CuN_4Si</td>
<td>C_{60}H_{85}CuN_4Si</td>
<td>C_{60}H_{85}CuN_4O_2Si</td>
</tr>
<tr>
<td>M_r</td>
<td>969.95</td>
<td>1005.98</td>
<td>989.98</td>
<td>985.95</td>
</tr>
<tr>
<td>space group</td>
<td>P2_1/n</td>
<td>P2_1/c</td>
<td>P2_1/c</td>
<td>P2_1/n</td>
</tr>
<tr>
<td>crystal system</td>
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<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>b [Å]</td>
<td>23.0955(14)</td>
<td>14.1530(6)</td>
<td>14.0896(3)</td>
<td>13.4161(16)</td>
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<td>α [°]</td>
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<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β [°]</td>
<td>93.819(6)</td>
<td>105.579(5)</td>
<td>105.351(3)</td>
<td>118.41(3)</td>
</tr>
<tr>
<td>γ [°]</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V [Å^3]</td>
<td>5562.7(6)</td>
<td>5696.5(4)</td>
<td>5692.8(2)</td>
<td>5717.6(17)</td>
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<tr>
<td>Z</td>
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<td>4</td>
<td>4</td>
<td>4</td>
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<tr>
<td>ρ_{calc} [mg m^{-3}]</td>
<td>1.158</td>
<td>1.173</td>
<td>1.155</td>
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</tr>
<tr>
<td>wavelength [Å]</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>μ (MoKα) [mm^{-1}]</td>
<td>0.456</td>
<td>0.448</td>
<td>0.446</td>
<td>0.446</td>
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<td>crystal size [mm^3]</td>
<td>0.32×0.19×0.07</td>
<td>0.15×0.13×0.10</td>
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<tr>
<td>Θ limits [°]</td>
<td>3.27 to 25.00</td>
<td>3.41 to 25.00</td>
<td>3.32 to 25.00</td>
<td>3.46 to 25.00</td>
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<tr>
<td>completeness to Θ = 25.00° [%]</td>
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<td>99.3</td>
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<td>reflns measured</td>
<td>41182</td>
<td>20824</td>
<td>43337</td>
<td>21442</td>
</tr>
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<td>independent reflns</td>
<td>9777 [R_{int}=0.1436]</td>
<td>9997 [R_{int}=0.0555]</td>
<td>10004 [R_{int}=0.0672]</td>
<td>9984 [R_{int}=0.1911]</td>
</tr>
<tr>
<td>parameters</td>
<td>624</td>
<td>680</td>
<td>684</td>
<td>663</td>
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<tr>
<td>R_1 (R_1 all data)</td>
<td>0.0860 (0.1376)</td>
<td>0.0644 (0.1050)</td>
<td>0.0568 (0.0822)</td>
<td>0.0739 (0.1755)</td>
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<tr>
<td>wR_2 (wR_2 all data)</td>
<td>0.1228 (0.1426)</td>
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<td>0.1068 (0.1158)</td>
<td>0.0981 (0.1414)</td>
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<td>GOF</td>
<td>1.080</td>
<td>1.046</td>
<td>1.090</td>
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<td>max., min. peaks [eÅ^{-3}]</td>
<td>0.719 (-0.827)</td>
<td>0.769 (-0.546)</td>
<td>0.494 (-0.333)</td>
<td>0.657 (-1.011)</td>
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Table 7.1.3 Crystal data and structure refinement for complexes 13, 14, 17 and 18

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<th>Complex</th>
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<th>14</th>
<th>17</th>
<th>18</th>
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<tr>
<td>Formula</td>
<td>C_{63}H_{85}CuN_{4}O_{2}Si</td>
<td>C_{56}H_{77}CuN_{4}OSi</td>
<td>C_{43}H_{60}Br_{2}N_{4}NiSi</td>
<td>C_{39}H_{60}BrN_{4}NiPSi</td>
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<td>$M_r$</td>
<td>1021.98</td>
<td>913.85</td>
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<td>space group</td>
<td>$P2_1/c$</td>
<td>$P2_1/n$</td>
<td>$P2_1/2_12_1$</td>
<td>$P2_1/c$</td>
</tr>
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<td>crystal system</td>
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<td>monoclinic</td>
<td>Orthorhombic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>$a$ [Å]</td>
<td>19.6265(10)</td>
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<td>14.40130(10)</td>
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<td>$b$ [Å]</td>
<td>14.2646(9)</td>
<td>20.684(10)</td>
<td>16.2439(2)</td>
<td>14.77030(10)</td>
</tr>
<tr>
<td>$c$ [Å]</td>
<td>21.8780(11)</td>
<td>21.481(7)</td>
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<td>$\alpha$ [°]</td>
<td>90</td>
<td>90</td>
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<td></td>
</tr>
<tr>
<td>$\beta$ [°]</td>
<td>105.499(5)</td>
<td>91.19(3)</td>
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<td></td>
</tr>
<tr>
<td>$\gamma$ [°]</td>
<td>90</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V$ [Å$^3$]</td>
<td>5902.3(6)</td>
<td>5329(3)</td>
<td>4258.19(9)</td>
<td>4011.38(4)</td>
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<td>$Z$</td>
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<td>4</td>
<td>4</td>
<td>4</td>
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<tr>
<td>$\rho_{calc}$ [mg m$^{-3}$]</td>
<td>1.150</td>
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<td>$\mu$ [mm$^{-1}$]</td>
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<td>crystal size [mm$^3$]</td>
<td>0.24 x 0.13 x 0.09</td>
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<td>0.23 x 0.10 x 0.09</td>
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<td>$\Theta$ limits [°]</td>
<td>3.43 to 25.00</td>
<td>3.28 to 25.00</td>
<td>3.75 to 67.49</td>
<td>3.07 to 67.50</td>
</tr>
<tr>
<td>completeness to $\Theta = 25.00°$ [%]</td>
<td>99.7%</td>
<td>99.8%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>reflns measured$^{[*]}$</td>
<td>24157</td>
<td>37861</td>
<td>17181</td>
<td>26608</td>
</tr>
<tr>
<td>independent reflns</td>
<td>10337 [$R_{int} = 0.0841$]</td>
<td>9378 [$R_{int} = 0.0363$]</td>
<td>7638 [$R_{int} = 0.0323$]</td>
<td>7242 [$R_{int} = 0.0179$]</td>
</tr>
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<td>parameters</td>
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<td>474</td>
<td>439</td>
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<td>GOF</td>
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<td>$R_1$ ($wR_2$)</td>
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<td>$wR_2 = 0.0581$</td>
<td>$wR_2 = 0.0651$</td>
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<tr>
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<td>$R_1 = 0.0291$</td>
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<td>0.656 (-0.625)</td>
<td>0.500 (-0.448)</td>
<td>0.255 (-0.331)</td>
<td>0.538 (-0.622)</td>
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### Table 7.1.4 Crystal data and structure refinement for complexes 19-21 and 25

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<th>21</th>
<th>25-0.5 n-hexane</th>
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<tr>
<td>formula</td>
<td>C₄₂H₇₀Ni₃P₃Si</td>
<td>C₄₂H₇₀Ni₃P₃Si</td>
<td>C₄₂H₆₈Ni₄O₄Si</td>
<td>C₃₉H₅₉Ni₄Os₃Si</td>
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<td>formula weight</td>
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<td>Cc</td>
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<td>monoclinic</td>
<td>monoclinic</td>
<td>Triclinic</td>
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<td>11.7870(4)</td>
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<td>10.6226(7)</td>
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<tr>
<td>c/Å</td>
<td>18.6018(4)</td>
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<td>13.4488(2)</td>
<td>14.9165(8)</td>
</tr>
<tr>
<td>α/deg</td>
<td>91.911(2)</td>
<td>96.894(3)</td>
<td>92.091(2)</td>
<td>75.594(5)</td>
</tr>
<tr>
<td>β/deg</td>
<td>99.506(2)</td>
<td>96.894(3)</td>
<td>92.091(2)</td>
<td>75.594(5)</td>
</tr>
<tr>
<td>γ/deg</td>
<td>119.849(4)</td>
<td>96.894(3)</td>
<td>92.091(2)</td>
<td>75.594(5)</td>
</tr>
<tr>
<td>V/Å³</td>
<td>2196.54(13)</td>
<td>8704.4(5)</td>
<td>4059.12(12)</td>
<td>1909.89(19)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>8</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>ρ/calcd g/cm³</td>
<td>1.179</td>
<td>1.187</td>
<td>1.223</td>
<td>1.229</td>
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<tr>
<td>F(000)</td>
<td>1.821</td>
<td>1.838</td>
<td>1.295</td>
<td>1.049</td>
</tr>
<tr>
<td>crystal size/mm³</td>
<td>0.24 x 0.16 x 0.14</td>
<td>0.24 x 0.09 x 0.08</td>
<td>0.10 x 0.08 x 0.06</td>
<td>0.28 x 0.13 x 0.11</td>
</tr>
<tr>
<td>θ range/deg</td>
<td>2.43 to 67.49</td>
<td>2.43 to 67.50</td>
<td>3.05 to 67.50</td>
<td>3.28 to 26.00</td>
</tr>
<tr>
<td>collected data</td>
<td>14795</td>
<td>15961</td>
<td>27000</td>
<td>14582</td>
</tr>
<tr>
<td>unique data</td>
<td>7906 [R(int) = 0.0273]</td>
<td>10846 [R(int) = 0.0542]</td>
<td>7312 [R(int) = 0.0288]</td>
<td>7489 [R(int) = 0.0344]</td>
</tr>
<tr>
<td>completeness to θ</td>
<td>99.8%</td>
<td>99.9%</td>
<td>99.9%</td>
<td>99.8%</td>
</tr>
<tr>
<td>data/restraints/parameters</td>
<td>472</td>
<td>935</td>
<td>480</td>
<td>419</td>
</tr>
<tr>
<td>final R indices [I&gt;2σ(I)]</td>
<td>R₁ = 0.0364</td>
<td>R₁ = 0.0546</td>
<td>R₁ = 0.0846</td>
<td>R₁ = 0.0463</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>wR₂ = 0.0979</td>
<td>wR₂ = 0.1176</td>
<td>wR₂ = 0.2285</td>
<td>wR₂ = 0.1032</td>
</tr>
<tr>
<td>GOF on F²</td>
<td>1.033</td>
<td>0.992</td>
<td>1.081</td>
<td>1.049</td>
</tr>
<tr>
<td>Largest diff peak/hole (e-Å⁻³)</td>
<td>0.517 (-0.443)</td>
<td>0.698 (-0.445)</td>
<td>2.148 (-0.731)</td>
<td>0.642/–0.547</td>
</tr>
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Table 7.1.5 Crystal data and structure refinement for complexes 26-29

<table>
<thead>
<tr>
<th>Complex</th>
<th>26-2 Toluene</th>
<th>0.5 27-2 Toluene</th>
<th>28</th>
<th>29</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>72$H$</em>{98}$Cu$_2$N$_4$O$_2$Si$_2$</td>
<td>C$<em>{43}$H$</em>{57}$Cu$_2$N$_2$OSeSi</td>
<td>C$<em>{37}$H$</em>{48}$GeN$_2$O$_2$</td>
<td>C$<em>{37}$H$</em>{48}$GeN$_2$O$_2$</td>
</tr>
<tr>
<td>$M_r$</td>
<td>1298.92</td>
<td>788.50</td>
<td>593.36</td>
<td>637.37</td>
</tr>
<tr>
<td>space group</td>
<td>C2/c</td>
<td>P-1</td>
<td>P1</td>
<td>P2(1)/c</td>
</tr>
<tr>
<td>crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>$\alpha$ [°]</td>
<td>79.437(3)</td>
<td>71.459(4)</td>
<td>71.459(4)</td>
<td>73.996(4)</td>
</tr>
<tr>
<td>$\beta$ [°]</td>
<td>116.278(6)</td>
<td>85.487(3)</td>
<td>80.307(4)</td>
<td>105.434(9)</td>
</tr>
<tr>
<td>$\gamma$ [°]</td>
<td>73.996(4)</td>
<td>65.603(5)</td>
<td>65.603(5)</td>
<td>65.603(5)</td>
</tr>
<tr>
<td>$V$ [Å$^3$]</td>
<td>6952.4(5)</td>
<td>2021.05(15)</td>
<td>815.64(7)</td>
<td>3377.5(5)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ [mg m$^{-3}$]</td>
<td>1.241</td>
<td>1.296</td>
<td>1.208</td>
<td>1.253</td>
</tr>
<tr>
<td>$\mu$ [mm$^{-1}$]</td>
<td>0.752</td>
<td>1.504</td>
<td>0.965</td>
<td>0.942</td>
</tr>
<tr>
<td>crystal size [mm$^3$]</td>
<td>0.15 x 0.11 x 0.07</td>
<td>0.16 x 0.14 x 0.08</td>
<td>0.20 x 0.19 x 0.06</td>
<td>0.35 x 0.22 x 0.10</td>
</tr>
<tr>
<td>$\Theta$ limits [°]</td>
<td>3.24–26.00</td>
<td>3.32–25.00</td>
<td>3.56–24.99</td>
<td>3.44–25.00</td>
</tr>
<tr>
<td>completeness to $\Theta$ = 25.00° [%]</td>
<td>99.8</td>
<td>99.8%</td>
<td>99.7 %</td>
<td>99.8%</td>
</tr>
<tr>
<td>reflns measured</td>
<td>26083</td>
<td>14701</td>
<td>6052</td>
<td>14941</td>
</tr>
<tr>
<td>independent reflns</td>
<td>6820 ($R_{int} = 0.0523$)</td>
<td>7105 ($R_{int} = 0.0404$)</td>
<td>3868 ($R_{int} = 0.0137$)</td>
<td>5913 ($R_{int} = 0.0383$)</td>
</tr>
<tr>
<td>parameters</td>
<td>379</td>
<td>433</td>
<td>369</td>
<td>414</td>
</tr>
<tr>
<td>GOF</td>
<td>1.077</td>
<td>1.037</td>
<td>1.049</td>
<td>1.030</td>
</tr>
<tr>
<td>$R_1$ ($wR_2$)</td>
<td>$R_1 = 0.0494$</td>
<td>$R_1 = 0.0463$</td>
<td>$R_1 = 0.0224$</td>
<td>$R_1 = 0.0418$</td>
</tr>
<tr>
<td>$wR_2$</td>
<td>$wR_2 = 0.1026$</td>
<td>$wR_2 = 0.1005$</td>
<td>$wR_2 = 0.0582$</td>
<td>$wR_2 = 0.0909$</td>
</tr>
<tr>
<td>$R_1$ ($wR_2$ all data)</td>
<td>$R_1 = 0.0641$</td>
<td>$R_1 = 0.0631$</td>
<td>$R_1 = 0.0224$</td>
<td>$R_1 = 0.0570$</td>
</tr>
<tr>
<td>$wR_2$</td>
<td>$wR_2 = 0.1079$</td>
<td>$wR_2 = 0.1075$</td>
<td>$wR_2 = 0.0583$</td>
<td>$wR_2 = 0.0969$</td>
</tr>
<tr>
<td>max., min. peaks [eÅ$^{-3}$]</td>
<td>0.479/-0.517</td>
<td>0.948/-0.779</td>
<td>0.306/-0.179</td>
<td>0.633/-0.307</td>
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Table 7.1.6 Crystal data and structure refinement for complexes 30-33

<table>
<thead>
<tr>
<th></th>
<th>30</th>
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<th>32 and 32a</th>
<th>33</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C_{39}H_{44}AlGeN_{4}O_{2}</td>
<td>C_{39}H_{44}Al_{3}N_{4}O_{4}</td>
<td>C_{65}H_{72}AlBr_{2}Cl_{2}N_{8}</td>
<td>C_{69}H_{72}AlBrFeN_{4}O_{8}</td>
</tr>
<tr>
<td>formula weight</td>
<td>980.87</td>
<td>981.29</td>
<td>1822.40</td>
<td>1031.87</td>
</tr>
<tr>
<td>crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>C2/c</td>
<td>C2/c</td>
<td>P2_{1}/c</td>
<td>P2_{1}/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>24.8625(3)</td>
<td>24.8530(10)</td>
<td>13.5202(2)</td>
<td>14.5976(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>15.1844(2)</td>
<td>15.1491(6)</td>
<td>35.6701(4)</td>
<td>15.2398(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>14.7693(2)</td>
<td>14.8791(6)</td>
<td>17.4181(2)</td>
<td>23.9900(3)</td>
</tr>
<tr>
<td>α/deg</td>
<td>94.2710(10)</td>
<td>93.999(4)</td>
<td>110.7410(10)</td>
<td>100.1990(10)</td>
</tr>
<tr>
<td>β/deg</td>
<td>110.7410(10)</td>
<td>100.1990(10)</td>
<td>110.7410(10)</td>
<td>100.1990(10)</td>
</tr>
<tr>
<td>γ/deg</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V/Å³</td>
<td>5560.25(12)</td>
<td>5588.4(4)</td>
<td>7855.76(17)</td>
<td>5252.59(12)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calc}/g cm⁻³</td>
<td>1.172</td>
<td>1.166</td>
<td>1.541</td>
<td>1.305</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>1.228</td>
<td>0.844</td>
<td>6.744</td>
<td>3.791</td>
</tr>
<tr>
<td>F(000)</td>
<td>2108</td>
<td>2128</td>
<td>3616</td>
<td>2176</td>
</tr>
<tr>
<td>crystal size/mm³</td>
<td>0.12 x 0.08 x 0.08</td>
<td>0.17 x 0.14 x 0.08</td>
<td>0.34 x 0.12 x 0.05</td>
<td>0.36 x 0.31 x 0.23</td>
</tr>
<tr>
<td>θ range/deg</td>
<td>3.41-73.62</td>
<td>3.42-67.50</td>
<td>2.98-67.50</td>
<td>3.45-67.49</td>
</tr>
<tr>
<td>collected data</td>
<td>10763</td>
<td>17256</td>
<td>31929</td>
<td>22244</td>
</tr>
<tr>
<td>unique data</td>
<td>5448 (R_{int} = 0.0138)</td>
<td>5037 (R_{int} = 0.0509)</td>
<td>14155 (R_{int} = 0.0350)</td>
<td>9459 (R_{int} = 0.0328)</td>
</tr>
<tr>
<td>completeness to θ</td>
<td>97.1 %</td>
<td>100.0 %</td>
<td>99.9%</td>
<td>99.9%</td>
</tr>
<tr>
<td>data/restraints/parameters</td>
<td>5448 / 1 / 340</td>
<td>5037 / 0 / 327</td>
<td>14155 / 84 / 815</td>
<td>9459 / 656 / 724</td>
</tr>
<tr>
<td>GOF on F²</td>
<td>1.022</td>
<td>1.052</td>
<td>1.173</td>
<td>1.113</td>
</tr>
<tr>
<td>final R indices</td>
<td>R₁ = 0.0437</td>
<td>R₁ = 0.0529</td>
<td>R₁ = 0.0513</td>
<td>R₁ = 0.0582</td>
</tr>
<tr>
<td>[I&gt;2σ(I)]</td>
<td>wR₂ = 0.1225</td>
<td>wR₂ = 0.1409</td>
<td>wR₂ = 0.1150</td>
<td>wR₂ = 0.1660</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0474</td>
<td>R₁ = 0.0582</td>
<td>R₁ = 0.0595</td>
<td>R₁ = 0.0737</td>
</tr>
<tr>
<td></td>
<td>wR₂ = 0.1291</td>
<td>wR₂ = 0.1485</td>
<td>wR₂ = 0.1213</td>
<td>wR₂ = 0.1779</td>
</tr>
<tr>
<td>Largest diff peak/hole (eÅ⁻³)</td>
<td>0.469/-0.405</td>
<td>0.619/-0.316</td>
<td>0.858/-0.842</td>
<td>1.243/-0.968</td>
</tr>
</tbody>
</table>
Table 7.1.7 Crystal data and structure refinement for complexes 34 and 37-39

<table>
<thead>
<tr>
<th></th>
<th>34</th>
<th>37</th>
<th>38</th>
<th>39</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C$<em>{51}$H$</em>{55}$AlFeN$_4$O$_6$</td>
<td>C$<em>{33}$H$</em>{44}$Cl$_7$GaN$_4$</td>
<td>C$<em>{45}$H$</em>{50}$ClF$_2$FeGaN$_4$O$_4$</td>
<td>C$<em>{45}$H$</em>{57}$FeGaN$_4$O$_6$</td>
</tr>
<tr>
<td>formula weight</td>
<td>934.82</td>
<td>814.59</td>
<td>933.93</td>
<td>851.50</td>
</tr>
<tr>
<td>crystal system</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>Pna2$_1$</td>
<td>P2$_1$/c</td>
<td>P2$_1$/c</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>22.8641(2)</td>
<td>15.7084(5)</td>
<td>17.14540(10)</td>
<td>18.2078(4)</td>
</tr>
<tr>
<td>b/Å</td>
<td>8.57090(10)</td>
<td>12.9298(4)</td>
<td>16.94990(10)</td>
<td>15.6120(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>26.0274(2)</td>
<td>20.6112(8)</td>
<td>16.25140(10)</td>
<td>15.6949(4)</td>
</tr>
<tr>
<td>α/deg</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β/deg</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ/deg</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V/Å$^3$</td>
<td>5100.48(8)</td>
<td>4010.1(2)</td>
<td>4512.77(5)</td>
<td>4279.28(17)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρ$\text{calcld}$/g·cm$^{-3}$</td>
<td>1.217</td>
<td>1.349</td>
<td>1.375</td>
<td>1.322</td>
</tr>
<tr>
<td>μ/mm$^{-1}$</td>
<td>2.977</td>
<td>1.180</td>
<td>4.307</td>
<td>3.889</td>
</tr>
<tr>
<td>F(000)</td>
<td>1968</td>
<td>1680</td>
<td>1936</td>
<td>1792</td>
</tr>
<tr>
<td>crystal size/mm$^3$</td>
<td>0.32 x 0.27 x 0.12</td>
<td>0.28 x 0.21 x 0.20</td>
<td>0.13 x 0.12 x 0.10</td>
<td>0.46 x 0.08 x 0.04</td>
</tr>
<tr>
<td>θ range/deg</td>
<td>3.87–67.50</td>
<td>3.32–25.00</td>
<td>3.75–67.50</td>
<td>3.80–67.50</td>
</tr>
<tr>
<td>collected data</td>
<td>18735</td>
<td>17453</td>
<td>31438</td>
<td>16787</td>
</tr>
<tr>
<td>unique data</td>
<td>8128 (R$_{int}$ = 0.0239)</td>
<td>7049 (R$_{int}$ = 0.0540)</td>
<td>8127 (R$_{int}$ = 0.0208)</td>
<td>7704 (R$_{int}$ = 0.0872)</td>
</tr>
<tr>
<td>completeness to θ</td>
<td>99.8 %</td>
<td>99.7%</td>
<td>100.0 %</td>
<td>99.7%</td>
</tr>
<tr>
<td>data/restraints/parameters</td>
<td>8128 / 445 / 703</td>
<td>7049 / 0 / 424</td>
<td>8127 / 122 / 577</td>
<td>7704 / 235 / 572</td>
</tr>
<tr>
<td>GOF on F$^2$</td>
<td>0.849</td>
<td>1.050</td>
<td>1.033</td>
<td>1.060</td>
</tr>
<tr>
<td>final R indices</td>
<td>$R_1 = 0.0539$</td>
<td>$R_1 = 0.0547$</td>
<td>$R_1 = 0.0310$</td>
<td>$R_1 = 0.0762$</td>
</tr>
<tr>
<td>[$I &gt; 2\sigma(I)$]</td>
<td>$R_1 = 0.1378$</td>
<td>$wR_2 = 0.0953$</td>
<td>$wR_2 = 0.0864$</td>
<td>$wR_2 = 0.1944$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.0573$</td>
<td>$R_1 = 0.0815$</td>
<td>$R_1 = 0.0331$</td>
<td>$R_1 = 0.1146$</td>
</tr>
<tr>
<td></td>
<td>$wR_2 = 0.1415$</td>
<td>$wR_2 = 0.1040$</td>
<td>$wR_2 = 0.0897$</td>
<td>$wR_2 = 0.2299$</td>
</tr>
<tr>
<td>Largest diff peak/hole (e Å$^{-3}$)</td>
<td>1.106/-0.565</td>
<td>0.651/-0.597</td>
<td>0.847/-0.591</td>
<td>1.211/-1.302</td>
</tr>
</tbody>
</table>
7.2 Curriculum Vitae

**Personal Information:**

**Name and Gender:** Gengwen Tan, Male

**Date and Place of Birth:** 27ᵗʰ November 1987 in Yugen, Shangrao, Jiangxi Province, P. R. China

**Nationality:** Chinese

**Education Background:**


09/1998-07/2001: Junior high School in Yugen, Shangrao, Jiangxi Province (P. R. China)

09/2001-07/2004: High School in Yugen, Shangrao, Jiangxi Province (P. R. China)

09/2004-07/2008: Xiamen University (P. R. China), Department of Chemistry, Bachelor in Chemical Biology

07/2008: Bachelor of Science Degree

09/2008-07/2011: Xiamen University (P. R. China), Department of Chemistry, Master in Physical Chemistry, Prof. Dr. Hongping Zhu

07/2011: Master of Science Degree

10/2011-03/2015: Institut für Chemie der Technischen Universität Berlin, Doctoral study in Chemistry, Prof. Dr. Matthias Driess