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Pincer Ligands

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Pushing the σ-Donor Strength in Iridium Pincer Complexes: Bis(silylene) and Bis(germylene) Ligands Are Stronger Donors than Bis(phosphorus(III)) Ligands**

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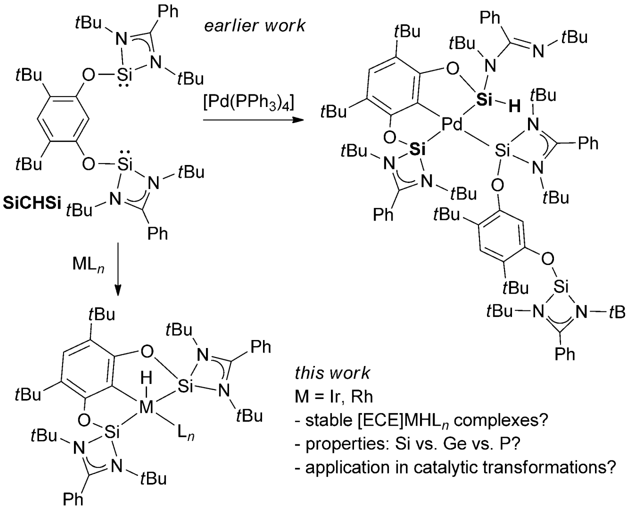
Dedicated to Professor Cameron Jones on the occasion of his 50th birthday

The development of new ligands to control the reactivity of transition-metal (TM) centers in complexes is a fundamental goal in organometallic chemistry. The "pincer" (EDE) motif describes tridentate, meridonal coordinating ligands that offer a plethora of opportunities to fine-tune the properties of TM complexes.[1] The arms (E) usually consist of neutral, two-electron Lewis basic donor moieties (for example, E = PR_2, NR_2, or SR), which are connected over a linker group (often CH_2, N, or O) to the neutral or mono-anionic anchoring site (D; for example, a pyridyl or phenyl group). With respect to iridium as the metal center, pincer ligands have been used for the generation of low-coordinated, highly electron-rich complexes used in the activation of strong bonds such as the N–H of ammonia or aniline,[2] the selective H–D exchange of olefinic protons with deuterobenzene,[3] and alkane dehydrogenation.[4]

Pincer ligands containing N-heterocyclic-stabilized divalent silicon (silylenyl) moieties RSi: (R = amidinate or β-diketiminate) instead of the common PR_2, NR_2, or SR donor arms E appear promising to achieve stronger σ-donating properties, which could facilitate the activation of even less reactive bonds.[5] In fact, the determination of the CO stretching vibrations in $[LNi(CO)_3]$ complexes with six-membered diketiminate Si^{II} ligands L revealed a A_1 band as low as 2046 cm^{-1} versus 2056 cm^{-1} for L = $PtBu_3$, and 2052 cm^{-1} for L = 1,3-bis(2,6-di-isopropylphenyl)imidazolidin-2-ylidene (SIPr).[6] Therefore, we wanted to combine the unique properties of the pincer motif with divalent silicon and germanium donor moieties as a means to develop the activation of X–H bonds by TM complexes.

We recently reported the synthesis of the first bis(silylene) SiCHSi pincer ligand and its unexpected coordination chemistry with Pd^0.[7] The sole product from the reaction of SiCHSi with $[Pd(PPh_3)_4]$ was the mixed silylene(Si^{II})–silyl(Si^{IV})-pincer complex depicted in Scheme 1. Computational studies indicated that this complex forms by a mechanism in which the ligand underwent a C–H oxidative addition to give an {(SiCSi)Pd(H)} intermediate, followed by a hydride shift from Pd onto Si and single coordination of a second SiCHSi ligand. We now report the different coordination behavior of the SiCHSi ligand toward the Group 9 metals iridium and rhodium. Furthermore, we describe the synthesis of the first GeCHGe pincer ligand and the use of the respective {(SiCSi)Ir} and {(GeCGe)Ir} complexes for catalytic C–H borylation of arenes. The SiCSi and GeCGe ligands show a strikingly stronger σ-donor ability than analogous P^{III} pincer ligands.

Addition of SiCHSi to a solution of $[\{IrCl(coe)_2\}_2]$ in C_6D_6 led to the immediate and quantitative formation of a new



Scheme 1. Earlier and present studies with the SiCHSi pincer ligand.

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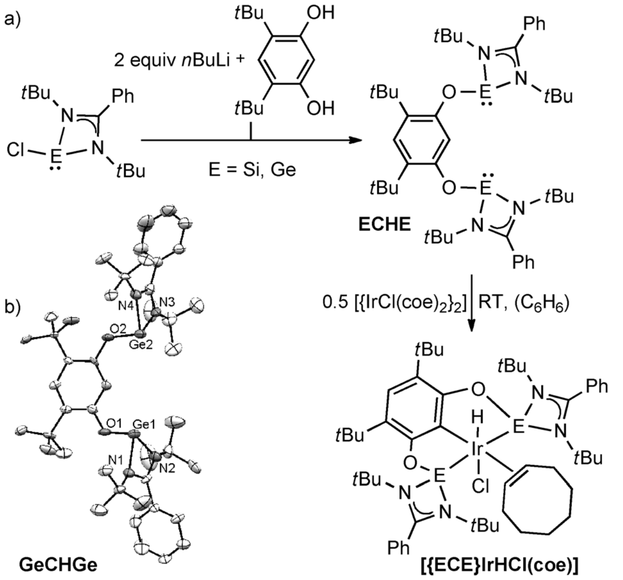
compound corresponding to a hydride signal in the ^{1}H NMR spectrum at ca. $\delta = -25.6$ ppm. After purification, the ^{1}H and ^{13}C NMR spectroscopic characterization revealed (in addition to the hydride signal) three sets of singlets for the *tert*-butyl groups, one set of signals for the phenyl groups, and one set of signals corresponding to coordinated cyclooctene (coe). These data, in combination with one singlet at $\delta = 54.9$ ppm in the ^{29}Si NMR spectrum, indicated that the product was the complex [(SiCSi)IrHCl(coe)] depicted in Scheme 2.

Single-crystal X-ray diffraction revealed the structural features of this complex (Figure 1 a).[8] The Ir–Si bond lengths of 2.305(1) and 2.301(1) Å are nearly identical to those in the silylene(Si^{II})–silyl(Si^{IV}) pincer palladium complex (see above; Pd–Si^{II} 2.3038(11) and 2.3271(12) Å, Pd–Si^{IV} 2.3561(12) Å). As expected, these values fall in between the average Ir^{III}–Si^{IV} distances of about 2.39 Å for octahedral Ir–silyl complexes and the distances of about 2.24 Å for non-σ-donor-stabilized Ir^{III}–silylene complexes.[9,10] The C–C$_{coe}$ bond of the olefinic group, 1.409(9) Å, is one of the longest reported[11] and resembles the high electron density observed at the Ir center through Si^{II}→M donation (see below).



Scheme 2. a) Synthesis of ECE pincer ligands and the reactivity with [{IrCl(coe)$_2$}$_2$]. b) Molecular structure of GeCHGe.

With [(SiCSi)IrHCl(coe)] in hand, we sought to determine whether the homologous bis(germylene) ligand GeCHGe could afford the corresponding iridium and rhodium complexes [ECE]MHCl(coe), and how the properties of these ECE ligands compare to those of the isoelectronic P^{III}-based compounds.

The first bis(germylene) ligand GeCHGe was synthesized by deprotonation of 4,6-di-*tert*-butylresorcinol and a subsequent salt metathesis reaction with the respective chlorogermylene precursor.[12] The GeCHGe compound was isolated after recrystallization in hexane in 83 % yield and structurally characterized by single-crystal X-ray analysis (Scheme 2). Addition of GeCHGe to a solution of [{IrCl(coe)$_2$}$_2$] in C$_6$D$_6$ led to the immediate formation of a new compound corresponding to a hydride signal at $\delta = -26.8$ ppm in the ^{1}H NMR spectrum. Further spectroscopic characterization of the isolated complex showed the same general features as those of the Si analogue [(SiCSi)IrHCl(coe)].

To learn more about the coordination and reactivity characteristics of the new ligands, we tested Vaska's complex, [IrCl(CO)(PPh$_3$)$_2$], and [IrH(CO)(PPh$_3$)$_3$] as metal precursors. Reaction of both ECHE ligands (E = Si, Ge) with [IrCl(CO)(PPh$_3$)$_2$] led to a mixture of unknown products. However, heating solutions of SiCHSi with [IrH(CO)(PPh$_3$)$_3$] in C$_6$D$_6$ for 1 h at 100 °C led to the clean conversion of the starting material to a new hydride species, which corresponded to a singlet at $\delta = -10.2$ ppm in the ^{1}H NMR spectrum. Solely signals for free PPh$_3$ were observed in the ^{31}P NMR spectrum. Along with the hydride signal with a relative integral of two, one set of aromatic signals and two sets of signals for the six *tert*-butyl groups were observed at $\delta = 1.34$ and 1.82 ppm with an integral of 36 to 18, respectively. The IR spectrum showed one CO stretching vibration at $\nu = 1968$ cm^{-1} and one weak band for the hydrides at $\nu = 2251$ cm^{-1}. These data indicate that the product is [(SiCSi)Ir(H)$_2$(CO)] in Scheme 3.

In contrast, GeCHGe slowly decomposed when heated in solution with [IrH(CO)(PPh$_3$)$_3$] at 100 °C for a prolonged

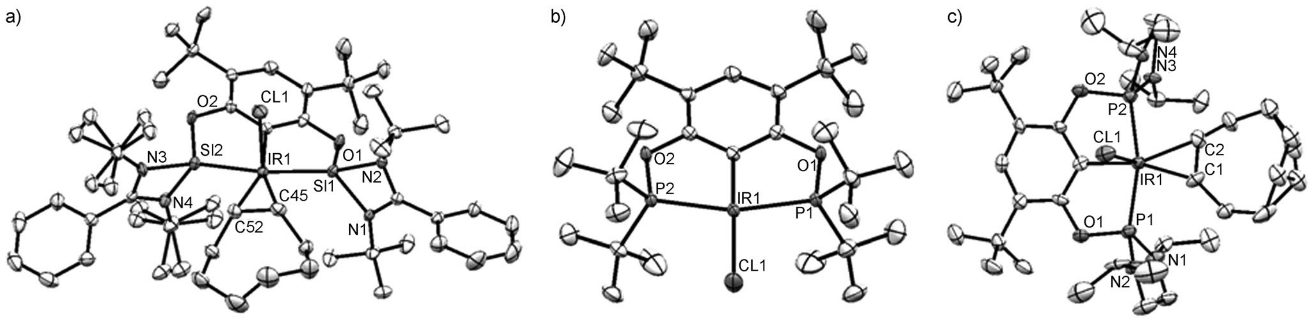
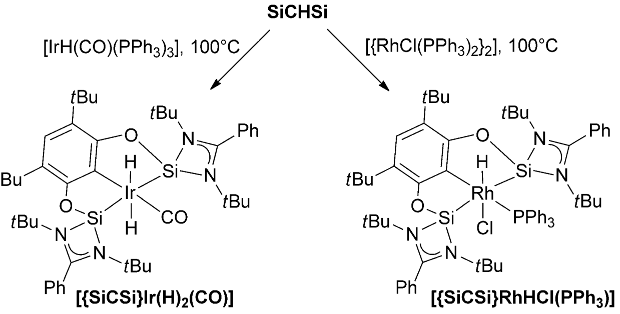
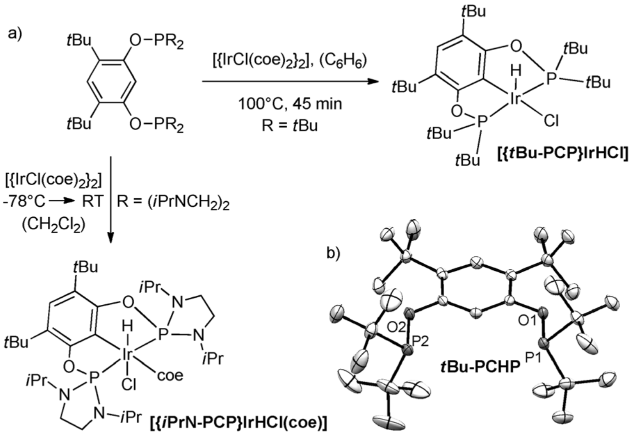


Figure 1. Molecular structures with selected bond lengths [Å] and angles [°] of a) [(SiCSi)IrHCl(coe)]: Ir1–Si1 2.301(1), Ir1–Cl1 2.514(1), Ir1–Si2 2.305(1), Ir1–C31 2.127(4), Ir1–C45 2.222(4), Ir1–C52 2.232(4); N1-Si1-N2 70.4(1), N2-Si1-Ir1 134.3(1), N3-Si2-Ir1 137.4(1), Ir1-Si2-N4 126.1(1), N4-Si2-N3 71.3(2), N1-Si1-Ir1 129.7(1); b) [(*t*Bu-PCP)IrHCl]: Ir1–C1 2.014(5), Ir1–Cl1 2.412(2), Ir1–P2 2.293(1), Ir1–P1 2.294(1); Cl1-Ir1-P2 99.44(4), Cl1-Ir1-P1 99.43(4), P1-Ir1-C1 80.4(1), P2-Ir1-C1 80.7(1); and c) [(*i*PrN-PCP)IrHCl(coe)]: P1–Ir1 2.290(2), Ir1–Cl1 2.506(2), Ir1–P2 2.282(2), C9–Ir1 2.053(6), Ir1–C9 2.053(6), Ir1–C1 2.285(7), Ir1–C2 2.307(7); Ir1-P1-N2 126.9(2), Ir1-P1-N1 121.1(2); Ir1-P2-N4 128.9(2), Ir1-P2-N3 119.3(2), N1-P1-N2 93.2(3), N4-P2-N3 92.9(3). Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.



Scheme 3. Synthesis of {(SiCSi)Ir^{III}} and {(SiCSi)Rh^{III}} complexes by substitution of PPh$_3$ and concomitant C–H oxidative addition.



Scheme 4. a) Synthesis of five-coordinate Ir^{III} phosphinite and a six-coordinate Ir^{III} phosphorodiamidate complexes. b) Molecular structure of *t*Bu-PCHP.

period of time. There was no sign of the formation of a new hydride species. This outcome might be explained by the lower electron-donating properties of GeCHGe compared to SiCHSi (see below). That is, initial substitution of one PPh$_3$ ligand would lead to an intermediate [(κ^1-*E*-ECHE)IrH(CO)(PPh$_3$)$_2$] complex, which in the case of GeCHGe might not be electron-rich enough to undergo a (probably) irreversible C–H oxidative addition reaction to form [(GeCGe)Ir(H)$_2$(CO)].

Obtaining defined complexes from rhodium and ECHE proved to be more challenging than from iridium. Reactions conducted with [{RhCl(coe)$_2$}$_2$] or [{RhCl(CO)$_2$}$_2$] as the metal precursor produced undefined reaction mixtures, but Wilkinson's dimer [{RhCl(PPh$_3$)$_2$}$_2$] (generated in situ) reacted with the SiCHSi ligand to cleanly form a new hydride species. The ^{1}H NMR spectrum contained a doublet of doublets ($^2J_{HP} = 11.0$ Hz, $^2J_{HRh} = 22.1$ Hz, 1H) at $\delta = -17.2$ ppm, three sets of signals for the *tert*-butyl groups at $\delta = 0.90$ (18H), 1.34 (18H) and 1.88 (18H) ppm, a doublet at 36.6 ppm ($^1J_{PRh} = 97.6$ Hz) in the ^{31}P NMR spectrum, and a doublet of doublets at $\delta = 66.4$ ppm ($^2J_{SiP} = 20.6.0$ Hz, $^1J_{SiRh} = 59.4$ Hz) in the ^{29}Si NMR spectrum. The chemical shift of the hydride and the coupling constants ($^2J_{HP}$ and $^1J_{PRh}$) are sensitive to the TM coordination environment and can be used for structural assignment. These data indicated the structure of [(SiCSi)RhHCl(PPh$_3$)] to be the one depicted in Scheme 3.[13]

To determine differences and similarities of our novel ECE complexes with well-established P^{III} ligand systems, we synthesized the related ligands *t*Bu-PCHP and *i*PrN-PCHP[14] (Scheme 4). Reaction of the phosphinite ligand *t*Bu-PCHP with [{IrCl(coe)$_2$}$_2$] led to the five-coordinate complex [(*t*Bu-PCP)IrHCl] (see Figure 1b for the crystal structure and the Supporting Information for further information). This outcome is not surprising, as many similar resorcinol-based {[PCP]IrHCl} complexes without the two additional *tert*-butyl groups in the phenyl backbone have been reported.[4,15] This preference for a five- over a six-coordination might be explained by a less electron-rich metal center, which in case of ECE requires an additional π-accepting ligand (coe) for stabilization of the metal center.

Reaction of the sterically and electronically more related *i*PrN-PCHP ligand with [{IrCl(coe)$_2$}$_2$] at room temperature led to a mixture of products, but addition at −78 °C and slow warming to room temperature showed the clean conversion to one new hydride species at $\delta = -24.6$ ppm (triplet, $^2J_{HP} = 15.1$ Hz), along with signals for coordinated coe. Identification of the olefinic resonances by ^{1}H–^{13}C correlation spectroscopy revealed the chemical shifts of $\delta = 4.31$ and 81.6 ppm in the ^{1}H and ^{13}C NMR spectra, respectively. X-ray diffraction analysis of single crystals for this new compound confirmed the coordination of coe (Figure 1c) and formation of [(*i*PrN-PCP)IrHCl(coe)]. The molecular structure shows disordering in the periphery of the coordinated coe, but the olefinic group remains unaffected. The C–C$_{coe}$ bond of the olefinic group is 1.35(1) Å, which is slightly longer than circa 1.34 Å for an uncoordinated C–C double bond and considerably shorter than the C–C bond of 1.409(9) Å in [(SiCSi)IrHCl(coe)].

The NMR chemical shifts of the olefinic groups can serve as a probe for the electronic properties of the metal, according to the Chatt–Dewar–Duncanson bonding model: a more electron-rich metal center leads to stronger π-back-bonding to the olefin, resulting in a lengthening of the C–C double bond and a higher-field chemical shift of the olefinic protons and carbons in the NMR spectra.[16] Determination and comparison of the chemical shift of the olefinic groups for [(SiCSi)IrHCl(coe)] (^{1}H $\delta = 3.37$, ^{13}C $\delta = 55.8$ ppm, X-ray 1.409(9) Å), [(GeCGe)IrHCl(coe)] (^{1}H $\delta = 4.06$ ppm, ^{13}C $\delta = 65.1$ ppm) and [(*i*PrN-PCP)IrHCl(coe)] (^{1}H $\delta = 4.31$, ^{13}C $\delta = 81.6$ ppm, X-ray 1.35(1) Å) allows the conclusion to be drawn that the ligand donor strength decreases in the following order: SiCSi > GeCGe > *i*PrN-PCP > *t*Bu-PCP.

Catalytic C–H borylation[17] of arenes with pinacolborane (HBPin) was chosen to probe our novel complexes for activity in C–H functionalization reactions. The [(ECE)IrHCl(coe)] complexes are coordinatively saturated and Cl–H substitution to form a [(ECE)Ir(H)$_2$(coe)] species with subsequent hydrogenation of the coordinated coe was envisioned as a facile pathway for activation.

In an initial NMR experiment, we added about 20 molar equiv of HBPin to a solution of [(SiCSi)IrHCl(coe)] in C$_6$D$_6$. After heating to 100 °C for 2 h, we observed the formation of small amounts of borylated benzene (PhBPin) and hydrogenated cyclooctene by NMR and GC-MS. Continuing heating for several hours did not show the growth of the

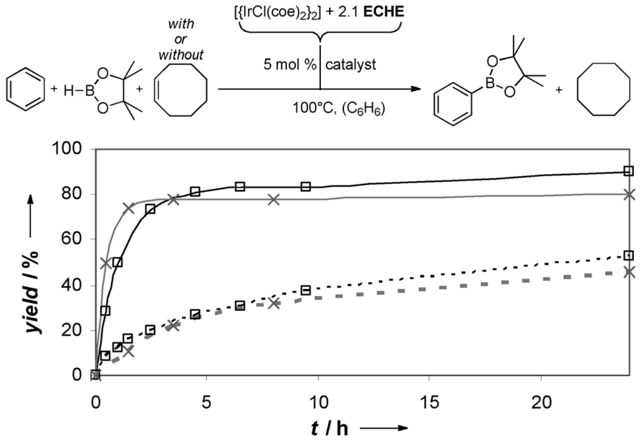
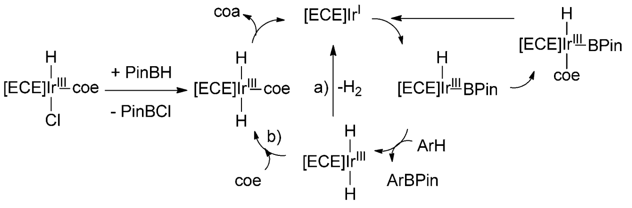


Figure 2. C–H borylation of benzene using HBPin with 5 mol% precatalyst generated in situ (SiCHSi: black/squares; GeCHGe: gray/crosses) in the presence (straight lines) and absence (dashed lines) of additional coe.

product peaks in NMR over time. However, addition of coe to the same sample led to fast formation of the product in high yield. Figure 2 shows the reaction profiles using 5 mol% in-situ generated [(SiCSi)IrHCl(coe)] and [(GeCGe)IrHCl(coe)] (from ECE and [{IrCl(coe)$_2$}$_2$]) with and without one equivalent of added coe. The reaction proceeds significantly faster with both ligand systems and is higher yielding in the presence of coe: 90 versus 53%, and 80 versus 46% yield after 24 h for SiCHSi and GeCHGe, respectively. These data strongly contrast those with the P^{III} based systems in this study. The concentration of coe had little effect using *t*Bu-PCHP as the ligand: 64 versus 60% yield of PhBPin were determined after 24 h in the presence or absence of coe, respectively.

Addition of coe had a dentrimental effect in the case of *i*PrN-PCHP. Not only did the yields of PhBPin decrease from 55 to 21% in the presence of additional coe, but the selectivity changed from C–H borylation towards hydroboration of coe (35%). Toluene as a substrate still showed the formation of 91% (*meta*/*para* = 1.6:1) and 39% (*meta*:*para* = 1.5:1) yield of the C–H borylation products for SiCHSi and GeCHGe, but sterically more demanding substrates like *ortho*- and *meta*-xylene showed only 3–15% of ArBPin, and the main products came from coe hydroboration and vinylic C–H borylation (see the Supporting Information for further details).

The catalytic performance of the {(ECE)Ir} pincer systems used in this study is significantly lower compared to our benchmark systems using bidentate nitrogen ligands,[16] which is most likely due to the enormous increase of the steric bulk around the metal center. However, our main goal was to identify differences and similarities of Si^{II}/Ge^{II} to P^{III} based systems. Scheme 5 shows a mechanistic hypothesis derived from our own results and previous studies in C–H borylation and alkane dehydrogenation.[4,16] The steps involved are oxidative addition of HBPin to Ir^{I}, C–H activation of the arene, formation of ArBPin and a {Ir^{III}(H)$_2$} species either via a oxidative addition/reductive elimination or a σ-bond metathesis pathway, and a) direct release of H$_2$, or b) hydrogenation of coe to close the cycle. In alternative to the arene, an olefin could coordinate and undergo vinylic C–H borylation or hydroboration. Five-coordinate, phosphinite-based [(PCP)Ir(H)$_2$] complexes are used as starting materials in alkane dehydrogenation reactions and are known to release H$_2$ at elevated temperature,[4] thereby following pathway (a). In contrast, SiCSi and GeCGe prefer a six-coordinated environment, and, taking the stronger donor properties into account, most likely have a higher barrier for the reductive elimination and release of H$_2$. Therefore, addition of coe as a H$_2$ acceptor has a beneficial effect on the turnover frequency and number.



Scheme 5. Proposed mechanism for the C–H borylation of arenes.

In summary, we synthesized and characterized the first iridium and rhodium bis(silylene) and bis(germylene) pincer complexes. A spectroscopic and structural comparison of the iridium complexes to related P^{III} compounds revealed the strikingly stronger σ-donating properties of the divalent silicon and germanium systems, and a significant change in reactivity and selectivity in catalytic C–H borylation reactions with arenes. These studies show that N-heterocyclic silylene and germylene ligands are not just simple substitutes for isoelectronic P^{III} compounds, but they are an emerging class of ligands with unique donor properties.

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