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Rhodium-Mediated Dehydrogenation of Hydroboranes and Group 14 Compounds: Base-Stabilized Silylene and Germylene Complexes vs. Transmetalation

Shou-Jen Hsiang[a] and Paul G. Hayes*[a]

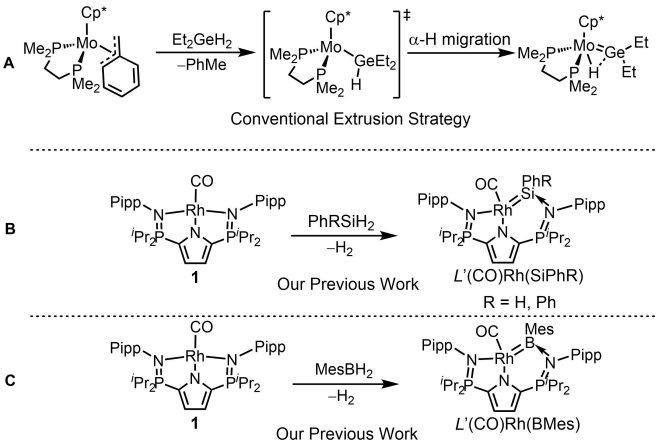
Monocarbonyl rhodium complex *L*Rh(CO), **1**, which is stabilized by a pyrrole-based bis(phosphinimine) pincer ligand ($L = \kappa^3$-*NNN*′ = 2,5-[^{i}Pr$_2$P=N(4-^{i}PrC$_6$H$_4$)]$_2$-N′(C$_4$H$_2$)$^-$), serves as a versatile platform for the dehydrogenation of group 14 substrates. Reaction with primary and secondary silanes and germanes (MesSiH$_3$, Et$_2$SiH$_2$, Ph$_2$GeH$_2$, ^{t}BuGeH$_3$; Mes = mesityl) liberates H$_2$ and yields base-stabilized tetrylene compounds of the form κ^2-*L*(CO)Rh(ER$_2$) (E = Si: R = Mes, H, **2**; R = Et, **5**; E = Ge: R = Ph, **6**; R = ^{t}Bu, H, **8**). The ":ER$_2$" fragment in these species bridges between the rhodium center and a phosphinimine donor. Preliminary reactions between pinacol (Pin) and κ^2-*L*(CO)Rh(ER$_2$), E = Si, Ge, indicate that such complexes can serve as silylene and germylene synthons, releasing :ER$_2$ and catalytically generating PinER$_2$. In contrast, combination of complex **1** and MesGeH$_3$ does not yield the anticipated dehydrogenation product, but rather, transmetalation similar to that observed upon reaction between **1** and 3,5-dimethylphenylborane prevails.

Introduction

Marked by a decreased tendency to engage in multiple-bonding, larger size, and higher-energy valence orbitals, silicon, germanium, and tin possess unique properties when compared to carbon, the lightest group 14 element.[1] Accordingly, mid-late transition metal complexes bearing silylene (L$_n$M = SiR$_2$) functionalities exhibit different reaction chemistry than their much better known carbon-based congeners, partly due to the umpolung M$^{\delta-}$—Si$^{\delta+}$ bond.[2] Notably, silylene complexes are important intermediates in the Direct Process which generates chlorosilanes that are essential for the production of silicones.[3] Transition metal germylene and stannylene complexes are less well studied, and given the diverse chemistry they exhibit, efforts to better understand these classes of compound, and the potential value they offer the chemical industry, is warranted.[4]

There are several established routes for generating heavier tetrylene complexes, including anionic substituent abstraction, coordination or transfer of stable R$_2$E: moieties (E = group 14 element), and sequential E–H bond oxidative addition/α–hydrogen migration.[2a,4e] While the latter method is appealing because one can use simple organic substrates (e.g., R$_2$EH$_2$), it affords species that retain reactive metal hydride functionalities that can participate in undesired reactions and obfuscate the extent of formal M=E multiple bond character. For example, the reaction between Cp*(dmpe)Mo(η^3-CH$_2$Ph) (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) and Et$_2$GeH$_2$ leads to Cp*(dmpe)Mo(H)GeEt$_2$ which contains a bridging hydride that is well within the van der Waals radii of both the Mo and Ge atoms (Scheme 1A).[4c]

Previously, our group disclosed the dehydrogenation of primary and secondary aryl silanes by reaction with the monocarbonyl rhodium (I) species *L*Rh(CO) (**1**; $L = \kappa^3$-NNN′ = 2,5-[^{i}Pr$_2$P=N(4-^{i}PrC$_6$H$_4$)]$_2$-N′(C$_4$H$_2$)$^-$) to afford base-stabilized rhodium silylene species of the form κ^2-*L*(CO)Rh(SiRPh) (R = Ph, H; κ^2-*L* = κ^2-NN′-Rh,κ^1-N-E; E = Si) (Scheme 1B).[5] Additionally, reaction between complex **1** and the primary borane MesBH$_2$ (Mes = 1,3,5-Me$_3$C$_6$H$_2$) generates the base-stabilized rhodium borylene κ^2-*L*(CO)Rh(BMes) (Scheme 1C).[6] This general methodology is



Scheme 1. A) Double Si–H activation extrusion strategy B) Reaction of complex **1** with silanes C) Reaction of **1** with MesBH$_2$.

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unique for silanes in that the consecutive Si–H bond activation leads to loss of molecular H_2, creating a neutral, hydride-free product.

Base stabilization of a formal metal silylene species is not uncommon, owing to the substantial Lewis acidity of the silicon atom. Accordingly, coordination of Lewis bases to metal silylenes is an archetypal reaction of this class of compound.[2] As with similar base-stabilized species, NBO analysis indicates that our compounds have limited Rh–Si and Rh–B π-bonding interactions, partly due to the strong σ- and π- donating properties of the phosphinimine groups.[5–6] Nonetheless, these complexes can be considered as silylene and borylene synthons, respectively. The silicon- and germanium-containing complexes reported herein are described as "base-stabilized silylenes/germylenes"[2c] and depicted with a M=E double bond (E = Si, Ge), in accordance with common practice in the relevant scientific literature.[2a,b]

Extension of known silylene extrusion methods to germanium and tin poses additional challenges that typically require increasingly stringent reaction conditions and substrate choice. For example, the Tilley group reported that while $[PhB(CH_2PPh_2)_3]Ir(H)(\eta^3\text{-}C_8H_{13})$ reacted with Mes_2GeH_2 to yield the terminal germylene $[PhB(CH_2PPh_2)_3](H)_2Ir{=}GeMes_2$, reaction with Mes_2SnH_2 rapidly led to a mixture of iridium-containing products.[7] Below, we detail a systematic study wherein we probe the generality of our protocol for the dehydrogenation of main group compounds. Specifically, reaction between our electron-rich, monomeric, rhodium complex *L*Rh(CO) (**1**) and silane, germane, and stannane substrates revealed that while the system is tolerant of all employed aryl/alkyl silanes, substantial steric bulk precludes H_2 loss from certain germanes, as well as diphenylstannane. Such findings draw parallels to an unexpected transmetalation pathway found upon reaction of complex **1** with *meta*-substituted aryl boranes.

Results and Discussion

Synthesis of Base-stabilized Silylenes and Comparison to Analogous Borylene

Complex **1** has been previously demonstrated to react with primary and secondary phenyl silanes to yield base-stabilized silylenes (see above).[5] In the case of the addition of $PhSiH_3$ to **1**, a rare example of a neutral Si–H substituted silylene was isolated.[5] In an effort to garner a deeper understanding of this unusual type of compound, complex **1** was reacted with $MesSiH_3$ in toluene at 50 °C. The product of this reaction exhibits two equal intensity peaks at δ 50.2 and δ 41.1 in its ^{31}P NMR spectrum. Resonances attributed to H_2 (δ 4.47) and Si–*H* were observed (δ 6.51, $^1J_{SiH} = 182$ Hz) in the ^1H NMR spectrum, suggesting formation of the anticipated silylene κ^2-*L*(CO)Rh(Si(H)Mes), (**2**). Free rotation about the Si–Mes bond is restricted on the ^1H NMR timescale, leading to three distinct mesityl CH_3 resonances. Similarly, four separate aromatic peaks were found for the *para*-isopropylphenyl (Pipp) substituent on the phosphinimine nitrogen coordinated to silicon. The ^{29}Si NMR signal was located at δ 38.0, which is substantially upfield-shifted compared to the resonances for κ^2-*L*(CO)Rh(Si(H)Ph) and κ^2-*L*(CO)Rh($SiPh_2$), which appear at δ 54.6 and δ 51.4, respectively. Crystals suitable for X-ray diffraction analysis were grown from a −35 °C Et_2O solution saturated with complex **2**; the solid-state structure confirmed the identity of **2** as the mesityl-substituted, base-stabilized, silylene κ^2-*L*(CO)Rh(Si(H)Mes) (Figure 1A). The Rh–Si distance of 2.272(1) Å in **2** is marginally longer than the Rh–Si length (2.262(1) Å) in isostructural κ^2-*L*(CO)Rh(Si(H)Ph), presumably due to the increase in steric bulk at silicon (Table 1).[5]

The observed generality of dehydrogenating silane substrates is in direct contrast with attempts to prepare borylene species from $^{meta}XylFBH_2$ and $MesBH_2$ ($^{meta}XylF = 3,5\text{-}(CF_3)_2C_6H_3$).[6] While reaction of **1** with $MesBH_2$ indeed affords the anticipated dehydrogenation product κ^2-*L*(CO)Rh(BMes), an unexpected compound was obtained when the *meta*-substituted borane $^{meta}XylFBH_2$ was employed.[6] Specifically, further study revealed that regardless of the electronic nature of the xylyl substituents (CF_3 vs. CH_3), reduction of steric bulk about boron leads to a Lewis acid-base adduct between the borane and a phosphinimine nitrogen. Similar to that previously reported for κ^2-*L'*(CO)Rh($^{meta}XylFBH_2$), the rhodium centre in κ^2-*L*(CO)Rh($^{meta}XylBH_2$) (**3**, $^{meta}Xyl = 3,5\text{-}Me_2C_6H_3$) appears to be stabilized by a B–H agostic interaction as suggested by an upfield B–*H* signal in the ^1H NMR spectrum (δ −3.10).[6] Allowing this species to sit

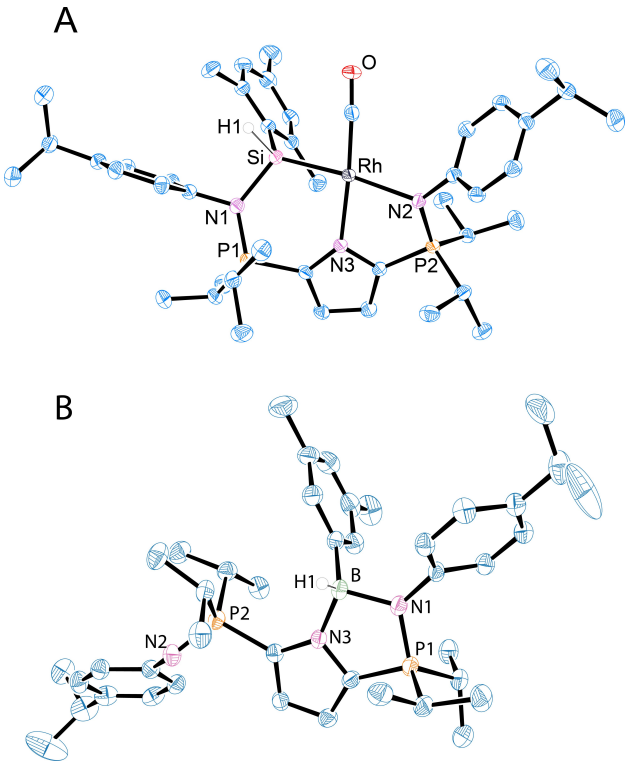
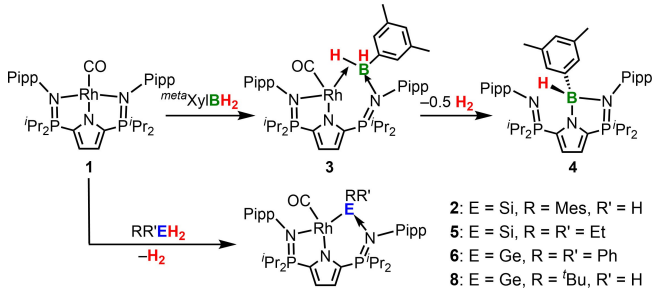


Figure 1. ORTEP diagram of A) complex **2** and B) compound **4**, with thermal ellipsoids depicted at the 50% probability level. All carbon-bound hydrogens, as well as co-crystallized solvent molecules and disorder models, have been omitted for clarity. Selected bond distances (Å) and angles [°] for **2**: Rh–Si 2.272(1), Si–N1 1.835(3), N1–Si–Rh 115.1(1). Selected bond distances (Å) for **4**: B–N1 1.5997(1), B–N3 1.5859(1).

Table 1. Select bond distances (Å), angles (°), and solution-state ^{31}P and ^{29}Si NMR chemical shifts (δ) of silylene and germylene compounds.

Compound	Rh–E[a]	P=N$_{(E)}$	P=N$_{(Rh)}$	N–E (Å)[a]	N$_{(Pipp)}$–Rh	C≡O	Rh–E–N ∠	^{31}P (ppm)	^{29}Si (ppm)
2 (SiMes)	2.272(1)	1.637(3)	1.606(2)	1.835(3)	2.225(3)	1.162(4)	115.1(1)	50.2, 41.1	38.0
5 (SiEt$_2$)	2.278(1)	1.640(4)	1.616(3)	1.857(3)	2.235(3)	1.160(5)	112.8(1)	49.4, 39.9	67.5
6 (GePh$_2$)	2.3438(4)	1.630(2)	1.611(2)	1.980(2)	2.189(1)	1.163(3)	111.96(5)	47.6, 43.8	N/A
κ^2-*L*(CO)Rh(SiPh$_2$)[5]	2.2702(7)	1.636(2)	1.607(2)	1.842(2)	2.224(2)	1.149(4)	113.61(9)	53.1, 43.1	51.4
κ^2-*L*(CO)Rh(Si(H)Ph)[5]	2.262(1)	1.637(2)	1.596(2)	1.834(3)	2.196(3)	1.161(4)	113.54(8)	53.0, 43.5	54.6

[a] E = Group 14 element, Si or Ge.



Scheme 2. Generation of complexes **2**–**6** and **8**.

in quiescent benzene-d_6 solution for 12 h at ambient temperature led to complete conversion into (κ^2-NN′-2,5-[^{i}Pr$_2$P=N-(4-^{i}PrC$_6$H$_4$)]$_2$-N′(C$_4$H$_2$)$^-$)B(H)(^{meta}Xyl), (**4**), as indicated by multinuclear NMR spectroscopy (Scheme 2). An isotopic labelling experiment using κ^2-*L*(^{13}CO)Rh(^{meta}XylBH$_2$), **3-^{13}CO**, confirmed that the formation of compound **4** was coupled with loss of the ^{13}CO resonance in the ^{13}C NMR spectrum, as well as the precipitation of an intractable black solid. In addition, an upfield signal in the ^{31}P NMR spectrum (δ 13.4) was consistent with a dissociated phosphinimine donor. Single crystals of compound **4** grown from a saturated pentane/toluene (5:1) solution unambiguously established that a transmetalation process afforded the borane ligated species (κ^2-NN′-2,5-[^{i}Pr$_2$P=N-(4-^{i}PrC$_6$H$_4$)]$_2$-N′(C$_4$H$_2$)$^-$)B(H)(^{meta}Xyl) (Figure 1B). The fate of rhodium is not known.

Extrusion processes appear to be highly sensitive to the steric profile of the main group substrates. For example, Braunschweig et al. have found that *ortho*-substituted aryl boranes are necessary for dehydrogenative borylene formation from their ruthenium complex Ru(PCy$_3$)$_2$HCl(H$_2$).[8] Meanwhile, the Tilley and Hashimoto groups utilize sterically demanding reagents, such as Mes$_2$SiH$_2$ and TsiGeH$_3$ to generate terminal silylene ([(dippe)Pt(H)=SiMes$_2$][BAr$^F_4$], dippe = 1,2-bis(diisopropylphosphino)ethane; Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$) and germylene ([Cp*(OC)$_2$Fe(H)=Ge(H)Tsi], Tsi = C(SiMe$_3$)$_3$) complexes, respectively.[4e,9] In our system, primary and secondary silanes appear to sit in a "goldilocks" zone that permit access to a wide array of silylene complexes.

Synthesis of Alkyl-substituted Silylenes

While routes to silylene complexes have been reported from a variety of primary and secondary aryl silanes, to the best of our knowledge the synthesis of stable alkyl-substituted silylenes from their respective alkyl silanes is exceedingly rare. While Tilley et al. were able to prepare [PhBP$_3$](H)$_2$Ir=SiR$_2$ (R = Mes, Ph, Et, Me) in situ; the compounds where R ≠ Mes were deemed thermally unstable and decomposed upon removal of solvent.[7] With this in mind, an excess of Et$_2$SiH$_2$ was added to complex **1** in toluene and the reaction mixture was heated to 45 °C for one hour. Monitoring by ^{31}P NMR spectroscopy indicated complete consumption of monocarbonyl **1**, along with concomitant generation of a single product that resonates at δ 49.5 and δ 39.9. Although signal overlap rendered it difficult to ascertain ^{29}Si–^{1}H coupling constants, 2D COSY, HSQC, and HMBC experiments corroborated the presence of Si–*CH$_2$CH$_3$* groups. The ^{29}Si{^{1}H} NMR spectrum exhibited a doublet of doublet of doublets (ddd) at δ 67.5, due to coupling to both phosphorus nuclei, as well as rhodium (^{103}Rh = 100 %, I = $^1/_2$). Notably, this signal is downfield shifted by 16 ppm compared to κ^2-*L*(CO)Rh(SiPh$_2$) and is consistent with the targeted base-stabilized, alkyl-substituted, silylene complex κ^2-*L*(CO)Rh(SiEt$_2$), (**5**). Complex **5** is stable in aromatic solvents at ambient temperature and can be isolated as a yellow powder in high yield (81 %). X-ray quality crystals grown from a saturated Et$_2$O solution at −35 °C confirmed the structure of **5**, which has a slightly longer Rh–Si distance (2.282(1) Å) than that found in our other silylenes (Figure 2, Table 1).

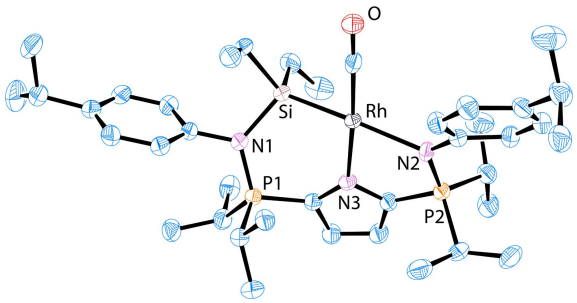


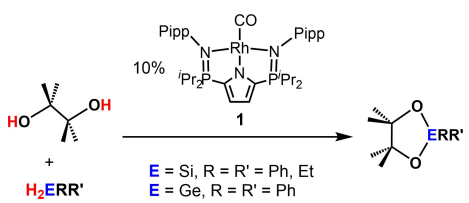
Figure 2. ORTEP diagram of **5** with thermal ellipsoids drawn at the 50 % probability level. Hydrogen atoms and disorder model omitted for clarity. Selected bond distances (Å) and angles [°]: Rh–Si 2.282(1), Si–N1 1.857(3), N1–Si–Rh 112.8(1).

The ability of this platform to incorporate alkyl-substituted silanes expands the subsequent breadth of available chemistry. Previously reported dialkylsilylene complexes were often accessed via salt metathesis strategies. For example, Müller reacted Me_2SiCl_2 and $[Na_2Fe(CO)_4]$ to yield the base-stabilized iron silylene $(CO)_4Fe{=}Si(Me)_2{\leftarrow}HMPT$ (HMPT = hexamethylphosphoramide). As previously mentioned, Tilley et al. have exploited in situ extrusion processes.[7,10] Unlike our system, both of these methods are limited by conditions required to regenerate the starting metal complex which complicates the conversion of stoichiometric chemical reactions into catalytic processes.

Silylene Transfer

Previously we reported that reaction of our base-stabilized borylene complex κ^2-*L*(CO)Rh(BMes) causes :BMes group transfer to yield the boronic ester PinBMes, along with regeneration of complex **1**.[6] We therefore anticipated that a similar pathway might be viable for our silylene complexes. Such a transformation was particularly attractive because unlike hydroboranes, hydrosilanes do not spontaneously react with pinacol. Furthermore, catalytic generation of $PinSiR_2$ can be readily envisioned. To this end, a PTFE-sealed NMR tube was charged with pinacol and diphenylsilane as a 1:1 mixture in benzene-d_6. As expected, after 16 h at 80 °C no reaction was observed by NMR spectroscopy. Upon cooling to ambient temperature, 0.1 equivalents of complex **1** was added to the reaction mixture, resulting in immediate effervescence of a gas (presumably H_2). Within 5 min ^{1}H and ^{13}C NMR spectra indicated formation of 4,4,5,5-tetramethyl-2,2-diphenyl-1,3-dioxa-2-silacyclopentane ($PinSiPh_2$). Full conversion of the hydrosilane was achieved after 30 min at 40 °C (Scheme 3). In order to demonstrate generality, the alkylsilane Et_2SiH_2 was reacted with pinacol and 10 mol% complex **1** (Scheme 3) in benzene-d_6. Spontaneous liberation of H_2 was observed, though the catalysis was substantially slower than with Ph_2SiH_2, requiring 1.2 h at 40 °C to reach completion, as indicated by multinuclear NMR spectroscopy.

Dehydrocoupling reactions catalyzed by rhodium species are well documented and typically involve oxidative addition as the first step in the catalytic cycle. For instance, Wilkinson's catalyst, $(PPh_3)_3RhCl$, can couple sterically hindered organosilanes and alcohols at ambient temperature.[11] The authors reported rapid H/D scrambling when Et_3SiH and Ph_3SiD were added to the active catalyst. Recent advances in the dehydrocoupling of hydrosilanes with alcohols demonstrate that the process can be accomplished by Lewis acid (e.g. $B(C_6F_5)_3$) Si–H activation, addition of a strong base (i.e. NaOH) to form a pentacoordinate Si intermediate, and Lewis-base activation of the silicon atom.[12] As previously mentioned, the strongly basic phosphinimine donor is a ready participant in the activation of small molecules, and may partake in Lewis base-catalyzed hydrosilane functionalization.[5,6] Accordingly, we postulated that pinacol might initially react with a phosphinimine-activated silane ($R_3PArN{\cdots}SiH_2R_2$),[12b,c] rather than with a fully dehydrogenated $:SiR_2$ moiety.



Scheme 3. Catalytic dehydrocoupling of pinacol and group 14 compounds.

In an effort to probe the reaction mechanism of catalytic $PinSiPh_2$ generation, 0.1 equivalents of κ^2-*L*(CO)Rh($SiPh_2$) was reacted with pinacol and diphenylsilane. Although $PinSiPh_2$ was produced, the reaction was much slower than when 10 mol% of complex **1** was utilized – 4 h at 80 °C was required to reach completion. Careful monitoring via NMR spectroscopy over the course of the reaction revealed a slow initial rate that increased over time, presumably due to an accumulation of **1** in situ. When stoichiometric quantities (1:1) of κ^2-*L*(CO)Rh($SiPh_2$) and pinacol were combined in benzene-d_6, heated at 80 °C, and monitored by NMR spectroscopy, Ph_2SiPin and complex **1** indeed formed, but the process required 32 h to consume ~90% of the reactants. These experiments suggest that the operative pathway between monocarbonyl complex **1**, Ph_2SiH_2, and pinacol does not involve κ^2-*L*(CO)Rh($SiPh_2$). Finally, it is important to note that the control reaction between pinacol, Ph_2SiH_2 and metal-free proteo-ligand, H*L*, did not afford product, even after heating at 80 °C for 24 h.

Reaction of Complex 1 with Aryl and Alkylgermanes

Encouraged by the ability of complex **1** to dehydrogenate a variety of silanes, we sought to expand the substrate scope to include the heavier group 14 element germanium. Reaction of **1** with the secondary germane Ph_2GeH_2 in toluene at 50 °C for three hours led to formation of κ^2-*L*(CO)Rh($GePh_2$), (**6**), as the sole rhodium-containing product. The ^{31}P NMR spectrum exhibits two equal intensity singlets at δ 47.6 and δ 43.8, consistent with the targeted C_s-symmetric base-stabilized germylene. Complex **6** readily crystallized from a saturated Et_2O solution at −35 °C; X-ray diffraction experiments confirmed the identity of κ^2-*L*(CO)Rh($GePh_2$) (Figure 3).

Selected bond distances given in Table 1 demonstrate that germylene **6** is isostructural with the diphenylsilylene congener κ^2-*L*(CO)Rh($SiPh_2$). The angles about germanium range from 98.75(8)° to 125.55(7)°, indicating distorted tetrahedral geometry (τ_4 = 0.86) due to strong phosphinimine N→Ge σ-donation that presumably minimizes Rh→Ge π-interactions.[13] The Rh–Ge distance of 2.3438(4) Å is similar to the terminal Ir=Ge bond (2.339(1) Å) in aforementioned $[PhB(CH_2PPh_2)_3](H)_2Ir{=}GeMes_2$, and longer than the Ru=Ge length of 2.2821(6) Å in Cp*-(^{i}Pr$_2$MeP)(H)Ru=GeH(2,4,6-^{i}Pr$_3$-C$_6$H$_2$).[7,14] A search of the Cambridge Crystal Structure Database, revealed that the rhodium germanium bond in complex **6** is amongst the shortest reported.[15]

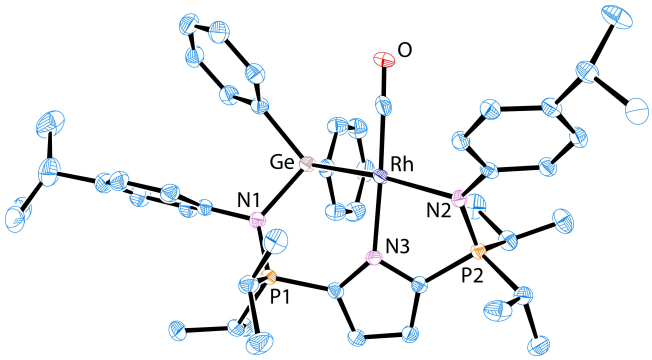
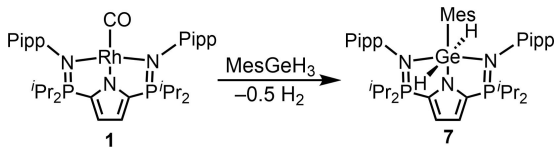


Figure 3. ORTEP diagram of complex **6** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and disorder model omitted for clarity. Selected bond distances (Å) and angles [°]: Rh–Ge 2.3438(4), Ge–N1 1.980(2), N1–Ge–Rh 111.96(5).

In order to establish if hydrogen-substituted germylenes are accessible, $MesGeH_3$ was added to monocarbonyl rhodium complex **1** at ambient temperature in benzene-d_6 solvent. Initial monitoring via ^{31}P NMR spectroscopy revealed formation of a new species with peaks at δ 57.1 and δ 46.9 in a 1:1 ratio. However, over several hours an insoluble black solid precipitated and the only ^{31}P NMR resonance remaining was a singlet at δ 34.4. Numerous attempts to seek reaction parameters conducive to generation of the targeted compound proved unsuccessful. An experiment utilizing ^{13}CO labelled **1** (*L*Rh(^{13}CO), **1-CO**) and $MesGeH_3$ indicated a lack of CO in the final product, suggesting that a transmetalation process similar to that which generated compound **4** (see above) had occurred (Scheme 4). The ^1H NMR spectrum of a crude mixture contained signals that can be attributed to ligand *L* and the germanium mesityl group, as would be expected for the anticipated product *L*GeH_2Mes, (**7**). In addition, a sharp singlet at δ 4.21, which integrates to 2H, lacks crosspeaks in ^1H–^{13}C HSQC experiments, and hence, has been assigned to GeH_2. Finally, it should be noted that over the course of the reaction liberated H_2 was observed in the ^1H NMR spectrum. Unfortunately, all efforts to isolate analytically pure samples of compound **7** resulted in decomposition to unidentified products.

Since efforts to prepare κ^2-*L*(CO)Rh(Ge(H)Mes) were unsuccessful, we targeted an alkyl-substituted germylene, in an attempt to inductively stabilize the Lewis acidic germylene. Specifically, addition of the primary germane ^{t}BuGeH_3 to **1** afforded κ^2-*L*(CO)Rh(Ge(H)^{t}Bu), (**8**), after 5 h in toluene at 50 °C. Despite the different steric and electronic properties of the germanium substituents in complexes **6** and **8**, the chemical shifts of the ^{31}P NMR signals are similar (**6**: δ 47.6 and δ 43.8; **8**: δ 47.4 and δ 43.5). A pseudotriplet ($^3J_{HP} = {}^2J_{HRh} = 10.6$ Hz) in the ^1H NMR spectrum was assigned to the germanium bound hydrogen. Low quality crystals, grown from a saturated pentane solution, established the anticipated connectivity in germylene **8**. Complex **8** represents a rare example of a neutral, H-substituted tetrylene accessed from a primary main group substrate. Normally, the kinetic stability of such species mandates extremely bulky substituents on the main group element; for example, Cp*$(OC)_2$(H)M=Ge(H)Tsi (M = Cr, Mo), reported by Hashimoto and colleagues.[9,16]



Scheme 4. Generation of compound **7** by transmetalation.

Germylene Transfer

Following the synthesis of these germylene species, the catalytic dehydrocoupling of diphenyl germane with pinacol using 10 mol% complex **1** as a catalyst, was attempted. No reaction was observed after 30 min at ambient temperature, though partial conversion from complex **1** to **6** became apparent spectroscopically after one hour at 40 °C. Heating the mixture to 80 °C for 16 h led to complete consumption of complex **1**, along with approximately 5% production of $PinGePh_2$. Another 24 h under the same conditions afforded an additional 5% of $PinGePh_2$ (Scheme 3). Although catalytic dehydrocoupling appears to work with Ph_2GeH_2, the reaction is obviously quite sluggish and the reasons behind the drastic change in reaction rate are not yet understood. Detailed studies into substituent and group 14 element effects on this process are ongoing.

Reaction of Complex 1 with Ph_2SnH_2

The mixed results encountered when attempting to dehydrogenate germanes prompted study of the reaction between complex **1** and Ph_2SnH_2. Upon addition of the secondary stannane to a benzene-d_6 solution of **1** at ambient temperature, an immediate change in color from bright orange to dark red was observed. Analysis of the mixture by ^{31}P NMR spectroscopy after removal of solvent and extraction with diethyl ether revealed the presence of multiple phosphorus-containing products. The major product within this mixture exhibited a single peak located at δ 33.5 in the ^{31}P NMR spectrum, suggesting C_s or C_{2v} symmetry. Attempts to acquire ^{119}Sn NMR spectra over numerous chemical shift windows yielded no discernable resonances. Similar to compounds **4** and **7**, no evidence could be obtained for the retention of CO. Although it is possible that this species is the result of transmetalation, and is analogous to germane **7**, the complicated ^1H NMR spectrum and a lack of definitive $^{117}Sn/^{119}Sn$ coupling in both the ^1H and ^{31}P NMR spectra render us unable to unambiguously identify the compound.

Conclusions

A series of neutral, base-stabilized rhodium silylene and germylene complexes has been prepared via dehydrogenation

of primary and secondary silanes and germanes. The system appears to tolerate a wide array of both alkyl and aryl silanes, but is incompatible with mesityl germane and diphenylstannane. The products of the latter reactions are presumed to be the result of a transmetalation pathway wherein the monoanionic pincer ligand is captured by the main group element. The mechanism for this process is unknown and it is possible that different pathways are responsible for the formation of boron-containing **4** vs. that which leads to compound **7**. Regardless, the fact that only 0.5 equivalents of H_2 is liberated from the main group fragment, implies that the operative mechanism is unlikely to include κ^2-*L*(CO)Rh(ER$_x$).

Proof of concept experiments indicate that stoichiometric and catalytic silylene group transfer is possible. Ongoing studies aim to exploit this reactivity to create value-added silyl- and germyl-containing compounds. Additional efforts aim to garner a deeper understanding of the rich chemistry available to the little-known hydrogen-substituted tetrylenes described above.

Experimental Section

General Considerations

All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk and cannula techniques, or in an MBraun inert atmosphere (argon) glove box unless otherwise noted. All glassware was stored in a pre-heated (110 °C) oven or flame-dried prior to use. Solvents used for air-sensitive procedures were purified using an MBraun solvent purification system (SPS), stored in PTFE-sealed glass vessels over sodium benzophenone ketyl (THF, diethylether, pentane, benzene, and toluene), and distilled at the time of use. Benzene-d_6 was dried over sodium benzophenone ketyl, distilled *in vacuo* and stored over 4 Å molecular sieves in PTFE-sealed glass vessels under argon. MesSiH$_3$ and MesGeH$_3$ were prepared according to literature procedures.[17] Diphenylstannane was prepared via reduction of diphenyltindichloride with lithium aluminum hydride in diethyl ether solution following literature procedures.[18] Diethylsilane, tetrachlorogermane, and *tert*-butylgermane were purchased from Gelest, degassed and stored over 4 Å molecular sieves in PTFE-sealed glass vessels. Pinacol, tetrachlorosilane, diphenyltindichloride and 2-bromomesitylene were purchased from Sigma-Aldrich and used without further purification. Complexes **1**, κ^2-*L*(CO)Rh(Si(H)Ph), and κ^2-*L*(CO)Rh(SiPh$_2$) were synthesized according to previous literature procedures.[5] Unless otherwise noted, all NMR spectra were recorded at ambient temperature with a Bruker Avance II NMR spectrometer (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 96.29 MHz for ^{11}B and 121.48 MHz for ^{31}P) or Avance III NMR spectrometer (700.44 MHz for ^{1}H, 139.10 MHz for ^{29}Si, 224.63 MHz for ^{11}B, 176.13 MHz for ^{13}C, and 283.54 MHz for ^{31}P). All ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to SiMe$_4$ using the ^{1}H (benzene-d_6: 7.16 ppm) and ^{13}C (benzene-d_6: 128.06 ppm) chemical shifts of the solvent as reference. ^{11}B NMR chemical shifts were referenced externally to BF$_3$·Et$_2$O (δ 0.0). ^{31}P NMR chemical shifts were referenced to external 85% H_3PO_4 in H_2O (δ 0.0). ^{1}H and ^{13}C NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sp = septet, m = multiplet, br = broad, ov = overlapping), coupling constant(s) (Hz), integration, assignment. Assignment of resonances were supplemented by ^{1}H–^{1}H COSY, ^{13}C{^{1}H} APT, and ^{1}H–^{13}C{^{1}H} HSQC/HMBC experiments. Elemental analyses (%CHN) were conducted at the University of Lethbridge on an Elementar Americas Vario MicroCube Analyzer (C, H, N, O, S capabilities) using bulk recrystallized compounds. "Universal Combustion Additive", purchased from Elemental Microanalysis, was added to all standards, blanks, and samples. Infrared spectroscopy was conducted with a Bruker Tensor 37 FT spectrometer (0.6 cm^{-1} resolution) using bulk recrystallized compounds (vs = very sharp, s = sharp, w = wide).

Synthesis and Characterization of New Compounds

κ^2-*L*(CO)Rh(Si(H)Mes) (2). Recrystallized **1** (25 mg, 0.036 mmol) was dissolved in 5 mL of toluene and cooled to −30 °C. In a separate flask, excess H_3SiMes (27 mg, 0.18 mmol) was dissolved in 3 mL of toluene and then added dropwise to the solution of **1** over approximately one minute. The mixture was transferred into a sealed vessel and heated at 45 °C for 5 h. After removal of the solvent under reduced pressure, the product was washed with 3×0.5 mL of pentane. The crude solid was recrystallized over 3 days from 5 mL of Et_2O at −30 °C to yield 16.5 mg (50% yield) of **2** as light yellow crystals. The compound co-crystallized with one equivalent of Et_2O. Anal Calcd for $C_{44}H_{64}N_3O_2P_2RhSi\cdot C_4H_{10}O$: C, 62.80; H, 8.12; N, 4.58. Found: C, 62.42; H, 8.14; N, 4.41. ^{1}H NMR (benzene-d_6, 23 °C): δ 7.56 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Pipp Ar *H*); 7.20 (br d, $^3J_{HH}$ = 8.0 Hz, 1H, Pipp Ar *H*); 7.10 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Pipp Ar *H*); 7.00 (br d, $^3J_{HH}$ = 8.0 Hz, 1H, Pipp Ar *H*); 6.95 (s, 1H, Mes Ar *H*); 6.62 (s, 1H, Mes Ar *H*); 6.58 (br d, $^3J_{HH}$ = 8.0 Hz, Pipp Ar *H*); 6.59 (ov m, 1H, 3,4-pyrrole C*H*; 1H, Pipp Ar *H*, 1H Si–*H*); 6.43 (ov dd, $^3J_{PH}$ = $^3J_{PH}$ = 3.6 Hz, 3,4-pyrrole C*H*); 3.25 (ov s, 3H, Mes CH_3); 2.75 (sp, $^3J_{HH}$ = 6.9 Hz, 1H, Pipp ArC*H*(CH$_3$)$_2$); 2.57 (sp, $^3J_{HH}$ = 6.9 Hz, 1H, Pipp ArC*H*(CH$_3$)$_2$); 2.38 (m, 1H, PC*H*(CH$_3$)$_2$); 2.24–2.16 (ov m, 2H, PC*H*(CH$_3$)$_2$; 3H, Mes CH_3); 2.15 (s, 3H, Mes CH_3); 2.02 (dsp, $^2J_{HP}$ = 14.4 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, PC*H*(CH$_3$)$_2$); 1.87 (dd, $^3J_{HP}$ = 16.2 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, PCH(CH_3)$_2$); 1.22 (dd, $^3J_{HP}$ = 15.5 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, PCH(CH_3)$_2$); 1.13 (dd, $^3J_{HP}$ = 18.1 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, PCH(CH_3)$_2$); 1.10 (dd, $^3J_{HP}$ = 16.6 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, PCH(CH_3)$_2$); 1.05 (ov d, $^3J_{HH}$ = 6.9 Hz, 3H, Pipp ArCH(CH_3)$_2$); 1.03 (ov d, $^3J_{HH}$ = 6.9 Hz, 3H, Pipp ArCH(CH_3)$_2$); 1.00 (dd, $^3J_{HP}$ = 15.3 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, PCH(CH_3)$_2$); 0.94 (dd, $^3J_{HP}$ = 15.1 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, PCH(CH_3)$_2$); 0.50 (dd, $^3J_{HP}$ = 17.8 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, PCH(CH_3)$_2$); 0.13 (dd, $^3J_{HP}$ = 14.7 Hz, $^3J_{HH}$ = 7.24 Hz, 3H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 193.44 (d, $^1J_{CRh}$ = 76.8 Hz, Rh–*C*O); 151.25 (s, Ar *C*); 146.94 (s, Ar *C*); 144.57 (s, Mes Ar *C*); 143.02 (s, Mes Ar *C*); 141.70 (s, Ar *C*); 140.82 (d, $^2J_{CP}$ = 2.2 Hz, Ar *C*); 139.12 (br m, Mes Ar *C*); 138.24 (ov d, $^1J_{CP}$ = 144.4 Hz, 2,5-pyrrole *C*); 138.14 (ov d, $^1J_{CP}$ = 144.4 Hz, 2,5-pyrrole *C*); 136.85 (s, Mes Ar *C*); 131.72 (d, J_{CP} = 5.6 Hz, Ar *C*H); 128.93 (s, Mes Ar *C*H); 128.50 (s, Mes Ar *C*H); 126.94 (s, Ar *C*H); 126.80 (d, J_{CP} = 8.2 Hz, Ar *C*H); 126.46 (s, Ar *C*H); 126.33 (s, Ar *C*H); 120.25 (dd, $^2J_{CP}$ = 25.3 Hz, $^3J_{CP}$ = 10.6 Hz, 3,4-pyrrole *C*H); 114.49 (dd, $^2J_{CP}$ = 24.6 Hz, $^3J_{CP}$ = 11.4 Hz, 3,4-pyrrole *C*H); 33.80 (s, ArCH(CH$_3$)$_2$); 33.72 (s, ArCH(CH$_3$)$_2$); 28.18 (d, $^1J_{CP}$ = 56.4 Hz, PCH(CH$_3$)$_2$); 27.44 (d, $^1J_{CP}$ = 52.0 Hz, PCH(CH$_3$)$_2$); 27.02 (d, $^1J_{CP}$ = 52.0 Hz, PCH(CH$_3$)$_2$); 25.82 (s, Mes *C*H$_3$); 24.64 (s, Mes *C*H$_3$); 24.51 (s, ArCH(*C*H$_3$)$_2$); 24.21 (d, $^1J_{CP}$ = 61.9 Hz, *C*H(CH$_3$)$_2$); 24.15 (s, ArCH(CH$_3$)$_2$); 21.40 (s, Mes *C*H$_3$); 18.04 (d, $^2J_{CP}$ = 3.3 Hz, PCH(CH$_3$)$_2$); 16.88 (s, PCH(CH$_3$)$_2$); 16.60 (d, $^2J_{CP}$ = 1.9 Hz, PCH(CH$_3$)$_2$); 16.55 (d, $^2J_{CP}$ = 2.4 Hz, PCH(CH$_3$)$_2$); 16.26 (d, $^2J_{CP}$ = 2.4 Hz, PCH(CH$_3$)$_2$); 16.16 (d, $^2J_{CP}$ = 2.4 Hz, PCH(CH$_3$)$_2$); 15.93 (d, $^2J_{CP}$ = 3.7 Hz, PCH(CH$_3$)$_2$); 14.75 (d, $^2J_{CP}$ = 3.4 Hz, PCH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (benzene-d_6, 23 °C): δ 50.2 (s, 1P, *P*–N–Rh); 41.1 (s, 1P, *P*–N–Si). ^{29}Si{^{1}H} NMR (benzene-d_6, 23 °C): δ 38.0 (ddd, $^3J_{SiP}$ = 2.0 Hz, $^2J_{SiP}$ = 9.3 Hz, $^1J_{SiRh}$ = 52.6 Hz). IR (cm^{-1}): 1920 (s, CO stretch).

κ^2-*L*(CO)Rh(^{meta}XylBH$_2$) (3). κ^2-*L*(CO)Rh(^{meta}XylBH$_2$) was prepared according to the following modified literature procedure.[4] Recrystallized **1** (15 mg, 0.022 mmol) was dissolved in a minimum quantity of toluene (~0.25 mL). In a separate flask, ^{meta}XylBH$_2$

(2.6 mg, 0.022 mmol) was dissolved in a minimum amount of toluene (~0.1 mL) and then added to the stirring solution of **1**. Immediately after addition of borane, the solvent was removed *in vacuo* to yield 17 mg of **3** as an off-white residue (97% yield). Compound **3** rapidly begins to convert to compound **4** in solution, and all isolated samples of **3** contain trace amounts of compounds **1** and **4** as indicated by ^{31}P and ^{1}H NMR spectroscopy (see Figures S5 and S6). Thus, elemental analysis and ^{13}C NMR spectroscopic data are not included. ^{1}H NMR (benzene-d_6, 23 °C): δ 7.47 (ov d, $^{3}J_{HH}$ = 8.2 Hz, 2H, Pipp Ar *H*); 7.46 (ov d, $^{3}J_{HH}$ = 8.2 Hz, 2H, Pipp Ar *H*); 7.26 (s, 2H, *ortho*-Xyl Ar *H*); 7.02 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, Pipp Ar *H*); 6.87 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, Pipp Ar *H*); 6.74 (s, 1H, *para*-Xyl Ar *H*); 6.49 (m, 2H, 3,4-pyrrole C*H*); 2.71 (sp, $^{3}J_{HH}$ = 6.9 Hz, 1H, ArC*H*(CH$_3$)$_2$); 2.61 (sp, $^{3}J_{HH}$ = 6.9 Hz, 1H, ArC*H*(CH$_3$)$_2$); 2.37 (m, 4H, PC*H*(CH$_3$)$_2$); 2.25 (s, 6H, Xyl C*H*$_3$); 1.14 (ov d, $^{3}J_{HH}$ = 6.9 Hz, 6H, ArCH(C*H*$_3$)$_2$); 1.13 (ov dd, $^{3}J_{HH}$ = 7.2 Hz, 6H, PCH(C*H*$_3$)$_2$); 1.06 (ov d, $^{3}J_{HH}$ = 6.9 Hz, 6H, ArCH(C*H*$_3$)$_2$); 1.02 (dd, $^{3}J_{HP}$ = 16.0 Hz, $^{3}J_{HH}$ = 6.9 Hz, 6H, PCH(C*H*$_3$)$_2$); 0.97 (dd, $^{3}J_{HP}$ = 15.7 Hz, $^{3}J_{HH}$ = 7.2 Hz, 6H, PCH(C*H*$_3$)$_2$); 0.86 (ov dd, $^{3}J_{HH}$ = 7.1 Hz, 3H, PCH(C*H*$_3$)$_2$); −3.10 (br s, 2H, B*H*$_2$).). ^{31}P{^{1}H} NMR (benzene-d_6, 23 °C): δ 49.0 (s, 1P, *P*–N–Rh); 46.8 (s, 1P, *P*–N–B). ^{11}B{^{1}H} NMR (benzene-d_6, 23 °C): δ −9.3 (br s, B).

(κ^2-NN′-2,5-[^{i}Pr$_2$P=N(4-^{i}PrC$_6$H$_4$)]$_2$-N′(C$_4$H$_2$)$^-$)B(H)^{meta}Xyl (4). κ^2-*L*-(CO)Rh(^{meta}XylBH$_2$) (10 mg, 0.012 mmol) was allowed to sit as a quiescent toluene solution at ambient temperature for 12 h. The solution was filtered through a pad of Celite, followed by removal of the solvent *in vacuo*. The crude residue was washed with 0.5 mL of pentane and dried under vacuum to yield 6.9 mg of compound **4** as an off-white solid (95% yield). Compound **4** can also be synthesized independently by adding a 1 mL toluene solution of HL (20 mg, 0.035 mmol) to a 1 mL toluene solution of ^{meta}XylBH$_2$ (4.2 mg, 0.035 mmol), resulting in immediate effervescence. Removal of solvent *in vacuo*, followed by washing the residue with 3×5 mL of pentane yielded 15 mg of the product as an off-white solid (98% yield). In both cases, the product is contaminated with small amounts of a Lewis acid-base byproduct wherein a second moiety of ^{meta}XylBH$_2$ is bound to the free phosphinimine donor of the ligand, rendering it impossible to obtain an analytically pure sample. ^{1}H NMR (benzene-d_6, 23 °C): δ 7.62 (m, 1H, 3,4-pyrrole C*H*); 7.35 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Pipp Ar *H*); 7.05–7.15 (ov m, 2H, *ortho*-Xyl C*H*; ov d, $^{3}J_{HH}$ = 7.5 Hz, 2H, Pipp Ar *H*; ov d, 2H, Pipp Ar *H*); 6.96 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Pipp Ar *H*); 6.74 (s, 1H, *para*-Xyl C*H*); 6.35 (dd, $^{3}J_{HH}$ = 3.6 Hz, $^{3}J_{HP}$ = 0.4 Hz, 1H, 3,4-pyrrole C*H*); 4.72 (br s, 1H, B*H*); 3.01 (m, 1H, PC*H*(CH$_3$)$_2$); 2.85 (sp, $^{3}J_{HH}$ = 6.9 Hz, 1H, ArC*H*(CH$_3$)$_2$); 2.62 (sp, $^{3}J_{HH}$ = 6.9 Hz, 1H, ArC*H*(CH$_3$)$_2$); 2.19 (s, 6H, 3,5-Xyl C*H*$_3$); 1.91 (m, 2H, PC*H*(CH$_3$)$_2$); 1.51 (dd, $^{3}J_{HP}$ = 16.5 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H, PCH(C*H*$_3$)$_2$); 1.35 (dd, $^{3}J_{HP}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.0 Hz, 3H, PCH(C*H*$_3$)$_2$); 1.28 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, ArCH(C*H*$_3$)$_2$); 1.15 (m, 1H, PC*H*(CH$_3$)$_2$); 1.06 (dd, $^{3}J_{HH}$ = 6.9 Hz, *J* = 1.3 Hz, 6H, ArCH(C*H*$_3$)$_2$); 0.97 (dd, $^{3}J_{HP}$ = 16.6 Hz, $^{3}J_{HH}$ = 6.8 Hz, 3H, PCH(C*H*$_3$)$_2$); 0.92 (ov dd, $^{3}J_{HP}$ = 17.2 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H, PCH(C*H*$_3$)$_2$); 0.86–0.90 (ov m, 6H, PCH(C*H*$_3$)$_2$); 0.70 (dd, $^{3}J_{HP}$ = 17.6 Hz, $^{3}J_{HH}$ = 7.1 Hz, 3H, PCH(C*H*$_3$)$_2$); 0.59 (dd, $^{3}J_{HP}$ = 16.9 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H, PCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 151.62 (d, $^{2}J_{CP}$ = 2.9 Hz, Pipp Ar *C*); 143.36 (s, Pipp Ar *C*); 141.26 (s, Pipp Ar *C*); 136.07 (s, Xyl Ar *C*); 135.99 (s, Pipp Ar *C*); 133.91 (d, *J* = 77.8 Hz, 2,5-pyrrole *C*); 132.71 (s, Xyl Ar *C*H); 128.66 (dd, *J* = 14.6, 11.1 Hz, 3,4-pyrrole C*H*); 128.35 (ov s, Xyl Ar *C*H); 128.08 (ov s, Xyl *C*); 127.19 (s, Pipp Ar *C*H); 126.60 (s, Pipp Ar *C*H); 124.77 (d, $^{3}J_{CP}$ = 15.5 Hz, Pipp Ar *C*H); 124.53 (d, $^{3}J_{CP}$ = 5.4 Hz, Pipp Ar *C*H); 117.33 (dd, *J* = 128.7, 7.4 Hz, 2,5-pyrrole *C*); 113.92 (dd, *J* = 19.1, 9.2 Hz, 3,4-pyrrole *C*H); 33.88 (s, Pipp ArCH(CH$_3$)$_2$); 33.62 (s, Pipp ArCH(CH$_3$)$_2$); 29.13 (d, $^{1}J_{CP}$ = 64.8 Hz, PCH(CH$_3$)$_2$); 28.06 (d, $^{1}J_{CP}$ = 82.0 Hz, PCH(CH$_3$)$_2$); 27.38 (d, $^{1}J_{CP}$ = 52.5 Hz, PCH(CH$_3$)$_2$); 26.46 (d, $^{1}J_{CP}$ = 55.0 Hz, PCH(CH$_3$)$_2$); 24.88 (s, Pipp ArCH(*C*H$_3$)$_2$); 24.19 (s, Pipp ArCH(*C*H$_3$)$_2$); 24.03 (s, Pipp ArCH(*C*H$_3$)$_2$); 21.61 (s, Xyl Ar(*C*H$_3$)); 19.91 (d, $^{2}J_{CP}$ = 2.6 Hz, PCH(*C*H$_3$)$_2$); 19.12 (d, $^{2}J_{CP}$ = 4.3 Hz, PCH(*C*H$_3$)$_2$); 16.92–16.98 (ov d, 2 x PCH(*C*H$_3$)$_2$); 16.74 (s, PCH(*C*H$_3$)$_2$); 16.33 (d, $^{2}J_{CP}$ = 3.1 Hz, PCH(*C*H$_3$)$_2$); 15.51–15.54 (ov m, 2 x PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (benzene-d_6, 23 °C): δ 51.0 (s, 1P, *P*–N–B); 13.4 (s, 1P, *P*=N). ^{11}B{^{1}H} NMR (benzene-d_6, 23 °C): δ 2.5 (br s, B).

κ^2-*L*(CO)Rh(SiEt$_2$) (5). Recrystallized **1** (15 mg, 0.022 mmol) was dissolved in 5 mL of toluene. In a separate vial, excess H$_2$SiEt$_2$ (10 mg, 0.11 mmol) was dissolved in 3 mL of toluene then added dropwise to the solution of **1** over approximately one minute. The solution was stirred at 45 °C for one hour. Upon cooling to ambient temperature, the solution was clear and dark yellow in colour. After removal of the solvent under reduced pressure, the residue was washed with 3×0.5 mL of pentane, and the crude solid recrystallized from Et$_2$O at −30 °C over 2 days to yield 13.5 mg (81% yield) of **5** as a light yellow crystals. Anal Calcd for C$_{39}$H$_{62}$N$_3$OP$_2$RhSi: C, 59.91; H, 7.99; N, 5.37. Found: C, 59.80; H, 7.98; N, 5.19. ^{1}H NMR (benzene-d_6, 23 °C): δ 7.64 (d, $^{3}J_{HH}$ = 7.1 Hz, 2H, Pipp Ar *H*); 7.14–7.17 (ov m, 4H, Pipp Ar *H*); 6.96 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, Pipp Ar *H*); 6.51 (ov dd, $^{3}J_{HH}$ = $^{3}J_{PH}$ = 3.5 Hz, 1H, 3,4-pyrrole C*H*); 6.42 (ov dd, $^{3}J_{HH}$ = $^{3}J_{PH}$ = 3.5 Hz, 1H, 3,4-pyrrole C*H*); 2.80 (sp, $^{3}J_{HH}$ = 6.9 Hz, 1H, ArC*H*(CH$_3$)$_2$); 2.68 (sp, $^{3}J_{HH}$ = 6.9 Hz, 1H, ArC*H*(CH$_3$)$_2$); 2.33 (m, 2H, PC*H*(CH$_3$)$_2$); 2.23 (m, 2H, PC*H*(CH$_3$)$_2$); 1.45 (t, $^{3}J_{HH}$ = 7.7 Hz, 6H, SiCH$_2$C*H*$_3$); 1.22 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, ArCH(C*H*$_3$)$_2$); 1.15 (dd, $^{3}J_{HP}$ = 15.3 Hz, $^{3}J_{HH}$ = 7.2 Hz, 6H, PCH(C*H*$_3$)$_2$); 1.11 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, ArCH(C*H*$_3$)$_2$); 1.05 (dd, $^{3}J_{HP}$ = 15.7 Hz, $^{3}J_{HH}$ = 7.2 Hz, 6H, PCH(C*H*$_3$)$_2$); 1.01–0.91 (ov m, 4H, SiC*H*$_2$CH$_3$); 0.94 (ov dd, $^{3}J_{HP}$ = 15.3 Hz, $^{3}J_{HH}$ = 7.2 Hz, 6H, PCH(C*H*$_3$)$_2$); 0.83 (dd, $^{3}J_{HP}$ = 16.7 Hz, $^{3}J_{HH}$ = 7.2 Hz, 6H, PCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 195.75 (d, $^{1}J_{CRh}$ = 78.3 Hz, Rh–*C*O); 151.25 (s, Ar *C*); 146.97 (s, Ar *C*); 140.27 (s, Ar *C*); 139.19 (s, Ar *C*); 138.09 (d, $^{1}J_{CP}$ = 16.3 Hz, 2,5-pyrrole *C*); 137.27 (d, $^{1}J_{CP}$ = 16.2 Hz, 2,5-pyrrole *C*); 130.42 (d, $^{3}J_{CP}$ = 3.97 Hz, Ar *C*H); 126.95 (s, Ar *C*H); 126.49 (s, Ar *C*H); 126.36 (d, $^{3}J_{CP}$ = 9.2 Hz, Ar *C*H); 119.64 (dd, $^{2}J_{CP}$ = 25.0 Hz, $^{3}J_{CP}$ = 10.24 Hz, 3,4-pyrrole *C*H); 114.53 (dd, $^{2}J_{CP}$ = 24.4 Hz, $^{3}J_{CP}$ = 11.1 Hz, 3,4-pyrrole *C*H); 33.81 (s, ArC*H*(CH$_3$)$_2$); 33.78 (s, ArC*H*(CH$_3$)$_2$); 26.82 (d, $^{1}J_{CP}$ = 51.7 Hz, PCH(CH$_3$)$_2$); 26.00 (d, $^{1}J_{CP}$ = 59.9 Hz, PCH(CH$_3$)$_2$); 24.53 (s, ArCH(CH$_3$)$_2$); 24.13 (s, ArCH(CH$_3$)$_2$); 16.77–16.68 (ov d, 2x PCH(*C*H$_3$)$_2$); 16.57–16.50 (ov d, 2x PCH(*C*H$_3$)$_2$); 15.07 (s, Si*C*H$_2$CH$_3$); 10.31 (s, SiCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (benzene-d_6, 23 °C): δ 49.5 (s, 1P, *P*–N–Rh); 39.9 (s, 1P, *P*–N–Si). ^{29}Si{^{1}H} NMR (benzene-d_6, 23 °C): δ 67.5 (ddd, $^{3}J_{SiP}$ = 1.6 Hz, $^{2}J_{SiP}$ = 6.5 Hz, $^{1}J_{SiRh}$ = 57.1 Hz). IR (cm^{-1}): 1900 (s, CO stretch).

κ^2-*L*(CO)Rh(GePh$_2$) (6). Crystalline **1** (25 mg, 0.036 mmol) was dissolved in 5 mL of toluene. In a separate flask, excess H$_2$GePh$_2$ (41 mg, 0.18 mmol) was dissolved in 3 mL of toluene and then added dropwise to the solution of **1** over approximately one minute. The solution was heated to 50 °C, stirred for three hours, then allowed to cool to ambient temperature, resulting in a bright yellow solution. Solvent was removed under vacuum and the crude solid recrystallized from 3 mL of pentane over 24 h to afford 20.1 mg (61% yield) of **6** as light orange blocks. Anal Calcd for C$_{47}$H$_{62}$N$_3$OP$_2$RhGe: C, 61.19; H, 6.77; N, 4.58. Found: C, 60.91; H, 6.81; N, 4.41. ^{1}H NMR (benzene-d_6, 23 °C): δ 7.83 (m, 4H, GePh *H*); 7.59 (m, 2H, Pipp Ar *H*); 7.18–7.11 (ov m, 6H, GePh *H*; 2H, 4-iPr-C$_6$*H*$_4$); 6.65–6.60 (ov m, 1H, 3,4-pyrrole; 2H, 4-iPr-C$_6$*H*$_4$); 6.56 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, 4-iPr-C$_6$*H*$_4$); 6.44 (ov dd, $^{3}J_{HP}$ = $^{3}J_{HH}$ = 3.5 Hz, 1H, 3,4-pyrrole); 2.78 (sp, $^{3}J_{HH}$ = 6.9 Hz, 1H, ArC*H*(CH$_3$)$_2$); 2.53 (sp, $^{3}J_{HH}$ = 6.9 Hz, 1H, ArC*H*(CH$_3$)$_2$); 2.32 (m, 2H, PC*H*(CH$_3$)$_2$); 2.15 (m, 2H, PC*H*(CH$_3$)$_2$); 1.19 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, ArCH(C*H*$_3$)$_2$); 1.08–1.02 (ov m, 12H PC*H*(CH$_3$)$_2$); 0.99 (dd, $^{3}J_{HP}$ = 15.8 Hz, $^{3}J_{HH}$ = 6.9 Hz, 6H, PCH(C*H*$_3$)$_2$); 0.92 (dd, $^{3}J_{HP}$ = 16.4 Hz, $^{3}J_{HH}$ = 6.9 Hz 6H, PCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 193.42 (d, $^{1}J_{CRh}$ = 71.7 Hz, Rh–*C*O); 151.54 (s, Ar *C*); 148.47 (s, GePh *C*); 146.15 (s, Ar *C*); 141.78 (s, Ar *C*); 141.48 (s, Ar *C*); 137.68 (br m, 2,5-pyrrole *C*); 136.33 (s, GePh *C*H); 130.55 (d, $^{3}J_{CP}$ = 5.0 Hz, Ar *C*H); 127.72 (s, GePh *C*H); 127.70 (s, GePh *C*H); 127.11 (s, Ar *C*H); 127.06 (s, Ar *C*H); 126.88 (br s, Ar *C*H); 123.70 (br m, 2,5-pyrrole *C*); 120.22 (br m, 3,4-pyrrole *C*H); 114.81 (br m, 3,4-pyrrole *C*H); 34.17 (s, ArC*H*(CH$_3$)$_2$); 34.11 (s, ArC*H*(CH$_3$)$_2$); 26.99 (d, $^{1}J_{CP}$ = 52.0 Hz, PCH(CH$_3$)$_2$); 26.66 (d, $^{1}J_{CP}$ = 59.4 Hz, PCH(CH$_3$)$_2$); 24.80 (s, Ar CH(CH$_3$)$_2$);

24.60 (s, Ar CH(CH_3)$_2$); 17.43 (d, $^2J_{CP}$ = 3.0 Hz, PCH(CH_3)$_2$); 17.10 (d, $^2J_{CP}$ = 1.9 Hz, PCH(CH_3)$_2$); 16.98 (d, $^2J_{CP}$ = 2.5 Hz, PCH(CH_3)$_2$); 16.82 (d, $^2J_{CP}$ = 2.1 Hz, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (benzene-d_6, 23 °C): δ 47.6 (s, 1P, *P*–N–Rh); 43.8 (s, 1P, *P*–N–Ge). IR (cm^{-1}): 1914 (s, CO stretch).

***L*GeH$_2$Mes (7)**. Recrystallized **1** (25 mg, 0.036 mmol) was dissolved in 5 mL of toluene. In a separate vial, excess H_3GeMes (29.2 mg, 0.150 mmol) was dissolved in 3 mL of toluene and the resultant solution was added dropwise to the stirring solution of **1** over approximately one minute. The initially homogenous orange-yellow solution separated into an orange residue and clear colorless supernatant over the course of 2 h of stirring at ambient temperature. The residue was only sparingly soluble in conventional non-halogenated solvents (e.g., Et_2O, toluene, pentane). Multinuclear NMR spectroscopy revealed **7** as the major product, though it was contaminated with intractable impurities. ^{1}H NMR (benzene-d_6, 23 °C): δ 7.52 (d, $^3J_{HH}$ = 8.2 Hz, 4H, Pipp Ar *H*); 7.10 (d, $^3J_{HH}$ = 8.2 Hz, 4H, Pipp Ar *H*); 6.73 (s, 2H, Mes C*H*); 6.62 (s, 2H, 3,4-pyrrole C*H*); 4.21 (s, 2H, GeH_2); 2.57 (sp, $^3J_{HH}$ = 6.8 Hz, 2H, ArC*H*(CH_3)$_2$); 2.26 (s, 6H, Mes CH_3); 2.10 (s, 3H, Mes CH_3); 2.08 (m, 4H, PC*H*(CH_3)$_2$); 1.20 (sp, $^3J_{HH}$ = 6.8 Hz, 2H, ArC*H*(CH_3)$_2$); 0.95 (ov dd, $^3J_{HP}$ = 16.7 Hz, $^3J_{HH}$ = 7.0 Hz, 12H, PCH(CH_3)$_2$); 0.92 (ov dd, $^3J_{HP}$ = 16.7 Hz, $^3J_{HH}$ = 7.0 Hz, 12H, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (benzene-d_6, 23 °C): δ 34.4 (s).

κ^2-*L*(CO)Rh(Ge(H)^{t}Bu) (8). Recrystallized **1** (25 mg, 0.036 mmol) was dissolved in 5 mL of toluene. In a separate vial, excess H_3Ge^tBu (24 mg, 0.18 mmol) was dissolved in 3 mL of toluene then added dropwise to the stirring solution of **1** over approximately one minute. The stirring solution was heated to 50 °C for 5 h resulting in a yellow-orange solution. The solvent was removed *in vacuo* and 2 mL of pentane was added, dissolving the residue. Upon cooling to −35 °C, crystals rapidly formed leading to 14 mg (47% yield) of **8** as light orange-yellow crystals. Anal Calcd for $C_{39}H_{62}N_3OP_2RhGe$: C, 56.68; H, 7.56; N, 5.08. Found: C, 55.98; H, 7.57; N, 4.99. ^{1}H NMR (benzene-d_6, 23 °C): δ 7.66 (d, $^3J_{HH}$ = 7.81 Hz, 2H, Pipp Ar *H*); 7.43 (d, $^3J_{HH}$ = 7.13 Hz, 2H, Pipp Ar *H*); 7.17 (ov d, 2H, Pipp Ar *H*); 7.01 (d, $^3J_{HH}$ = 7.81 Hz, 2H, Pipp Ar *H*); 6.56 (ov dd, $^3J_{HH}$ = $^3J_{HP}$ = 3.14 Hz, 1H, 3,4-pyrrole); 6.38 (ov dd, $^3J_{HH}$ = $^3J_{HP}$ = 3.14 Hz, 1H, 3,4-pyrrole); 5.90 (t, $^3J_{HP}$ = $^2J_{HRh}$ = 10.62, 1H, Ge–*H*); 2.80 (sp, $^3J_{HH}$ = 6.80 Hz, 1H, ArC*H*(CH_3)$_2$); 2.70 (sp, $^3J_{HH}$ = 6.97 Hz, 1H, ArC*H*(CH_3)$_2$); 2.28 (m, 2H, PC*H*(CH_3)$_2$); 2.17 (m, 2H, PC*H*(CH_3)$_2$); 1.70 (dd, $^3J_{HP}$ = 15.61 Hz, $^3J_{HH}$ = 6.80 Hz, 3H, PCH(CH_3)$_2$); 1.39 (s, 9H, GeCCH_3); 1.40–1.20 (ov m, 12H, ArCH(CH_3)$_2$; PCH(CH_3)$_2$); 1.14–1.09 (ov m, 9H, ArCH(CH_3)$_2$; PCH(CH_3)$_2$); 0.93 (dd, $^3J_{HP}$ = 15.33 Hz, $^3J_{HH}$ = 7.04 Hz, 3H, PCH(CH_3)$_2$); 0.87 (dd, $^3J_{HP}$ = 14.93 Hz, $^3J_{HH}$ = 7.33 Hz, 3H, PCH(CH_3)$_2$); 0.56 (dd, $^3J_{HP}$ = 14.99 Hz, $^3J_{HH}$ = 7.27 Hz, 3H, PCH(CH_3)$_2$); 0.47 (dd, $^3J_{HP}$ = 17.07 Hz, $^3J_{HH}$ = 6.80 Hz, 3H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 194.13 (d, $^1J_{CRh}$ = 74.62 Hz, Rh–*C*O); 151.23 (s, Ar *C*); 145.91 (s, Ar *C*); 145.60 (s, Ar *C*); 140.59 (s, Ar *C*); 136.65 (d, $^1J_{CP}$ = 15.5 Hz, 2,5-pyrrole *C*); 135.83 (d, $^1J_{CP}$ = 16.0 Hz, 2,5-pyrrole *C*); 130.70 (d, J_{CP} = 4.2 Hz, Ar *C*H); 126.98 (s, Ar *C*H); 126.50 (s, Ar *C*H); 126.16 (d, J_{CP} = 9.4 Hz, Ar *C*H); 120.39 (dd, $^2J_{CP}$ = 23.9, $^3J_{CP}$ = 10.4 Hz, 3,4-pyrrole *C*H); 114.85 (dd, $^2J_{CP}$ = 24.6, $^3J_{CP}$ = 10.9 Hz, 3,4-pyrrole *C*H); 33.83 (s, Ar *C*HCH$_3$); 33.78 (s, Ar *C*HCH$_3$); 31.19 (d, J = 2.3 Hz, Ge *C*(CH_3)$_3$); 29.83 (s, Ge C(CH_3)$_3$); 27.44 (d, $^1J_{CP}$ = 52.2 Hz, P*C*H(CH_3)$_2$); 26.26 (d, $^1J_{CP}$ = 51.5 Hz, P*C*H(CH_3)$_2$); 26.01 (d, $^1J_{CP}$ = 57.3 Hz, P*C*H(CH_3)$_2$); 24.19 (d, $^1J_{CP}$ = 46.8 Hz, P*C*H(CH_3)$_2$); 24.61 (s, Ar CH(*C*H$_3$)$_2$); 24.43 (s, Ar CH(*C*H$_3$)$_2$); 24.18 (d, $^2J_{CP}$ = 4.1 Hz, PCH(*C*H$_3$)$_2$); 19.30 (d, $^2J_{CP}$ = 3.3 Hz, PCH(*C*H$_3$)$_2$); 17.14 (d, $^2J_{CP}$ = 2.5 Hz, PCH(*C*H$_3$)$_2$); 17.08 (d, $^2J_{CP}$ = 3.3 Hz, PCH(*C*H$_3$)$_2$); 17.03 (d, $^2J_{CP}$ = 1.9 Hz, PCH(*C*H$_3$)$_2$); 17.0 (s, Ar CH(*C*H$_3$)$_2$); 16.51 (d, $^2J_{CP}$ = 2.5 Hz, PCH(*C*H$_3$)$_2$); 16.22 (d, $^2J_{CP}$ = 2.3 Hz, PCH(*C*H$_3$)$_2$); 15.37 (d, $^2J_{CP}$ = 3.1 Hz, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (benzene-d_6, 23 °C): δ 47.4 (s, 1P, *P*–N–Rh); 43.5 (s, 1P, *P*–N–Ge). IR (cm^{-1}): 1898 (s, CO stretch).

Reaction Between 1 and Ph_2SnH_2. Recrystallized **1** (15 mg, 0.022 mmol) was dissolved in 5 mL of toluene and the mixture cooled to −30 °C. Under the occlusion of light, Ph_2SnH_2 (5.9 mg, 0.022 mmol) was dissolved in 3 mL of toluene and added dropwise to the stirring solution of complex **1** over approximately one minute. Upon addition of Ph_2SnH_2 the solution immediately changed from bright orange to dark red in color. The solution was stirred for 2 h. Removal of solvent *in vacuo* resulted in a yellow-red oily residue containing multiple unidentified products. Extraction of the oil with Et_2O resulted in a mixture wherein the major product is hypothesized to be a transmetalated species similar to **7** (See Supporting Information).

General Procedures for Dehydrogenative Coupling

Reaction between complex **1**, R_2EH_2, and pinacol: A PTFE-sealed NMR tube was charged with approximately 0.5 mL of a benzene-d_6 solution of 1 : 1 R_2EH_2 and pinacol. Complex **1** (10% catalyst loading) was dissolved in approximately 0.5 mL of benzene-d_6 and added to the NMR tube. Immediate effervescence was observed. Formation of PinER$_2$ was monitored by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The spectra for PinSiPh$_2$ matched literature values.[19]

Control reactions between κ^2-*L*(CO)Rh(SiPh$_2$), complex **1** or HL and the 1 : 1 Ph_2SiH_2/pinacol mixture followed similar procedures described above and also used a 10% loading of metal complex or ligand. For κ^2-*L*Rh(CO)(SiPh$_2$), conversion to complex **1** was estimated by integration of diagnostic resonances in the ^{31}P NMR spectra. The reaction was followed by NMR spectroscopy by acquiring spectra every 30 min for a period of 5 h. For HL, no reaction was observed via NMR spectroscopy, even after heating the mixture at 80 °C for 24 h.

Stoichiometric reaction between κ^2-*L*(CO)Rh(SiPh$_2$) and pinacol: A PTFE-sealed NMR tube was charged with κ^2-*L*(CO)Rh(SiPh$_2$) (10 mg, 0.011 mmol) and pinacol (1.3 mg, 0.011 mmol), and dissolved in 1 mL of benzene-d_6. No effervescence was observed. The NMR tube was heated at 80 °C and monitored by NMR spectroscopy. After 32 h, 90%+ was converted to complex **1** and Ph_2SiPin as established by relative integrations of signals in the ^{1}H and ^{31}P NMR spectra.

Supporting Information

Supporting Information: Crystallographic details and NMR spectra.

Deposition Number(s) 2284446 (for **5**), 2284459 (for **2**), 2284460 (for **6**) and 2284461 (for **4**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: dehydrogenation · germylene · rhodium · silylene · transmetalation

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