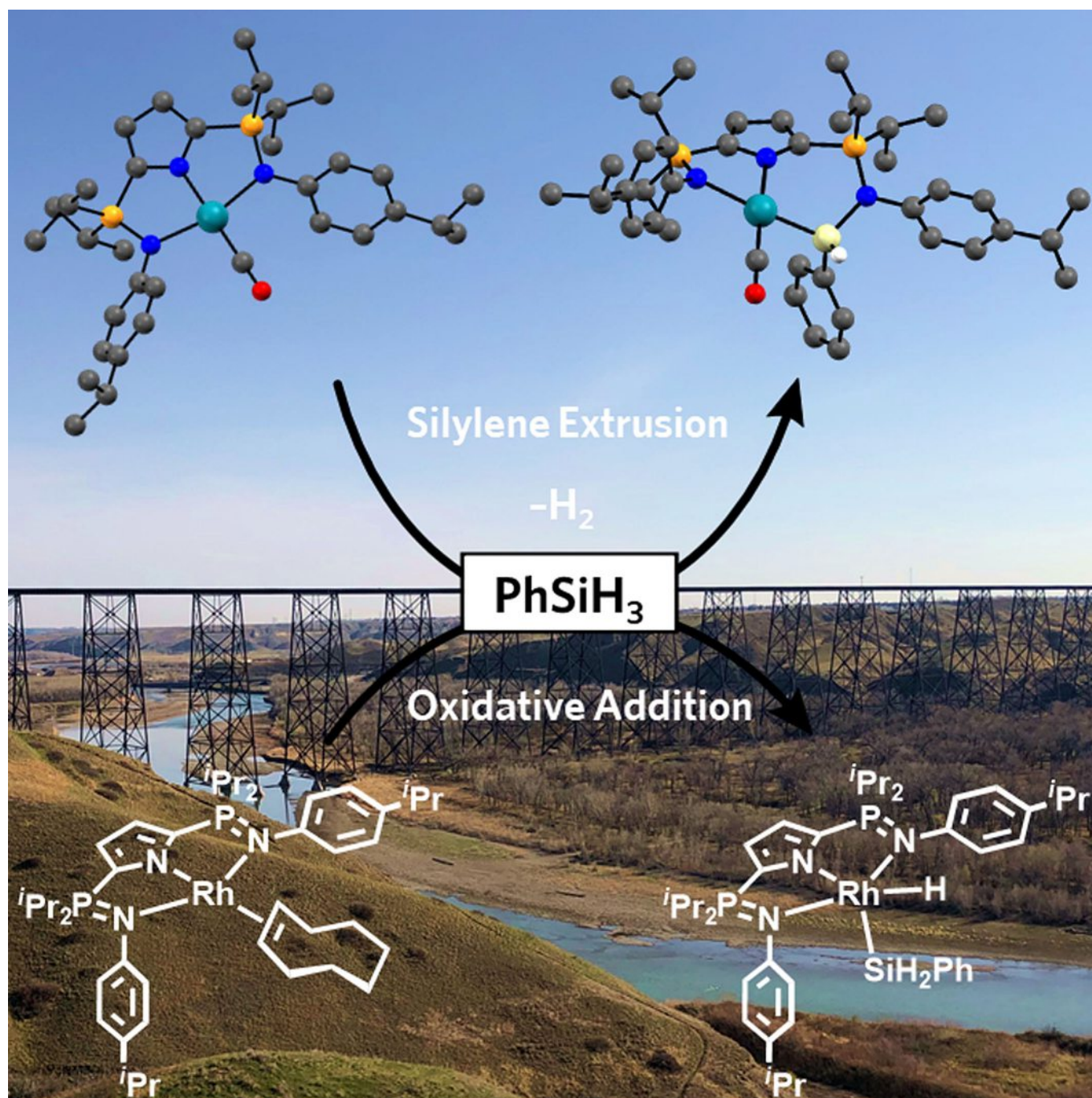ChemPubSoc
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█ **Synthetic Methods** |*Hot Paper*|

# An H-Substituted Rhodium Silylene

Connor S. MacNeil and Paul G. Hayes*[a]

Abstract: Divergent reactivity of organometallic rhodium(I) complexes, which led to the isolation of neutral rhodium silylenes, is described. Addition of PhRSiH$_2$ (R=H, Ph) to the rhodium cyclooctene complex (^{iPr}NNN)Rh(COE) (1-COE; ^{iPr}NNN = 2,5-[iPr$_2$P = N(4-iPrC$_6$H$_4$)]$_2$N(C$_6$H$_2$)$^-$, COE = cyclooctene) resulted in the oxidative addition of an Si—H bond, providing rhodium(III) silyl hydride complexes (^{iPr}NNN)Rh(H)SiHRPh (R=H, **2**-SiH$_2$Ph; Ph, **2**-SiHPh$_2$). When the carbonyl complex (^{iPr}NNN)Rh(CO) (**1**-CO) was treated with hydrosilanes, base-stabilized rhodium(I) silylenes κ^2-N,N-(^{iPr}NNN)(CO)Rh = SiRPh (R=H, **3**-SiHPh; Ph, **3**-SiPh$_2$) were isolated and characterized using multinuclear NMR spectroscopy and X-ray crystallography. Both silylene species feature short Rh—Si bonds [2.262(1) Å, **3**-SiHPh; 2.2702(7) Å, **3**-SiPh$_2$] that agree well with the DFT-computed structures. The overall reaction led to a change in the ^{iPr}NNN ligand bonding mode ($\kappa^3 \rightarrow \kappa^2$) and loss of H$_2$ from PhSiRH$_2$, as corroborated by deuterium labelling experiments.

Essential to the production of organosilicon compounds, hydrosilation (HS) of carbon-element multiple bonds is a principal application of platinum group metals.[1] Homogeneous catalysts based on platinum and rhodium typically follow Chalk-Harrod mechanisms providing high stereo-, regio-, and enantioselectivities.[2] Oxidative addition of an Si—H bond to either Pt or Rh is a common feature in such processes; for example, Ojima demonstrated it to be the first step in the HS of carbonyls using Wilkinson's catalyst, (PPh$_3$)$_3$RhCl.[3] Additional mechanisms have been proposed for carbonyl HS when primary and secondary silanes are utilized. Specifically, when Rh catalysts were combined with Ph$_2$SiH$_2$, Gade and co-workers observed an inverse KIE (k_H/k_D = 0.8),[4] incompatible with the well-known modified Chalk-Harrod and Ojima mechanisms.[5] Accordingly, they proposed a pathway that invokes a transient, but key, rhodium silylene (Rh = SiR$_2$) intermediate. In addition, density functional theory (DFT) studies by Gade and Hofmann favored a silylene-based mechanism over options proposed by Ojima, Zheng and Chan.[5] Although a structurally characterized rhodium silylene has thus far remained elusive, experimental work by Kühn, Herrmann, and co-workers corroborates the DFT results, and provides strong supporting evidence that rhodium silylenes are key intermediates in HS catalysis.[6]

Beyond the relevance to HS catalysis, the reactivity, structure and bonding of an isolable rhodium silylene is of great fundamental interest. Following the isolation of donor-stabilized complexes of Ru and Fe,[7] synthetic methods were developed

in order to access reactive silylenes for a host of transition metals.[8] Tilley and colleagues have shown that α-H migration from Si to a metal center (a 1,2-shift) can be promoted by abstraction of either a methide (CH$_3^-$) or hydride (H$^-$) ligand with B(C$_6$F$_5$)$_3$, generating silylenes from silyl complexes of Pt[9] and Ir (Scheme 1a).[10] Such α-H migration processes could be reason-
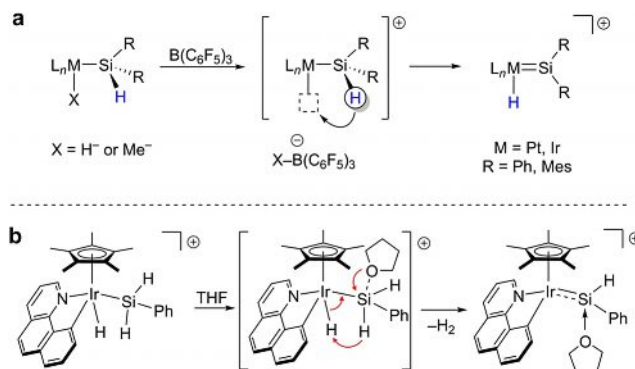
Scheme 1. a) α-H migration of Si—H promoted by B(C$_6$F$_5$)$_3$. b) Spontaneous generation of Ir silylene upon THF coordination and subsequent H$_2$ loss.

ably expected to serve as a promising route to rhodium silylenes, given the ubiquity of rhodium silyl hydride complexes that can be easily prepared by standard oxidative addition reactions. Along these lines, Sadow and colleagues employed this method to generate the cationic Rh^{III} silylene [{κ^3-N,Si,C-PhB(Ox^{Me2})(Ox^{Me2}SiHPh)Im^{Mes}}Rh(H)CO][HB(C$_6$F$_5$)$_3$] (Ox^{Me2} = 4,4-dimethyl-2-oxazoline; Im^{Mes} = 1-mesitylimidazole) from the addition of B(C$_6$F$_5$)$_3$ to the neutral rhodium silyl hydride {PhB(Ox^{Me2})$_2$Im^{Mes}}RhH(SiH$_2$Ph)CO. Comprehensive NMR spectral data provided evidence for a silylene Si atom that was stabilized by coordination from a borate-linked oxazoline donor.[11] These results show promise that directed α-H migration and related strategies may lead to the isolation and structural characterization of catalytically important rhodium silylenes.

Rhodium complexes bearing phosphinimine donors as part of a monoanionic ^{R}NNN ligand set, (^{R}NNN = 2,5-[R$_2$P = N(4-iPrC$_6$H$_4$)]$_2$N(C$_4$H$_2$)$^-$, R = Ph, iPr) have recently been shown to have a propensity to enact cooperative bond activation of H$_2$ and CO.[12] The ylidic nature of the P—N bond results in strongly basic N donors capable of stabilizing electrophilic metals and main group functionalities.[13] Following the recognition that silylenes are defined by the pronounced Lewis acidity of the Si atom,[8] precursor Rh silyl hydride complexes bearing a strongly-donating ligand set were targeted. Toluene solutions of (^{iPr}NNN)Rh(COE) (**1**-COE) and 1 equivalent of PhSiRH$_2$ (R = H, Ph) were stirred for 1 hour at ambient temperature leading to Si—H oxidative addition, along with concomitant loss of COE (Scheme 2). Recrystallization of the red-orange solids at −35 °C from pentane gave analytically pure (^{iPr}NNN)Rh(H)SiHRPh (R = H, **2**-SiH$_2$Ph; Ph, **2**-SiHPh$_2$) in 91 and 94 % yield, respectively. The solid-state structures of **2** confirmed the presence of both rhodium hydride and silyl groups. Hydride ligands for **2**-SiH$_2$Ph and **2**-SiHPh$_2$ were also characterized by ^{1}H NMR spectroscopy as doublets at $\delta = -14.28$ ($^1J_{H-Rh} = 25.6$) and $\delta = -13.68$

[a] C. S. MacNeil, Prof. Dr. P. G. Hayes
Canadian Centre for Research in Advanced Fluorine Technologies (C-CRAFT)
Department of Chemistry and Biochemistry, University of Lethbridge
4401 University Drive W, Lethbridge, T1K 3M4 (Canada)
E-mail: p.hayes@uleth.ca

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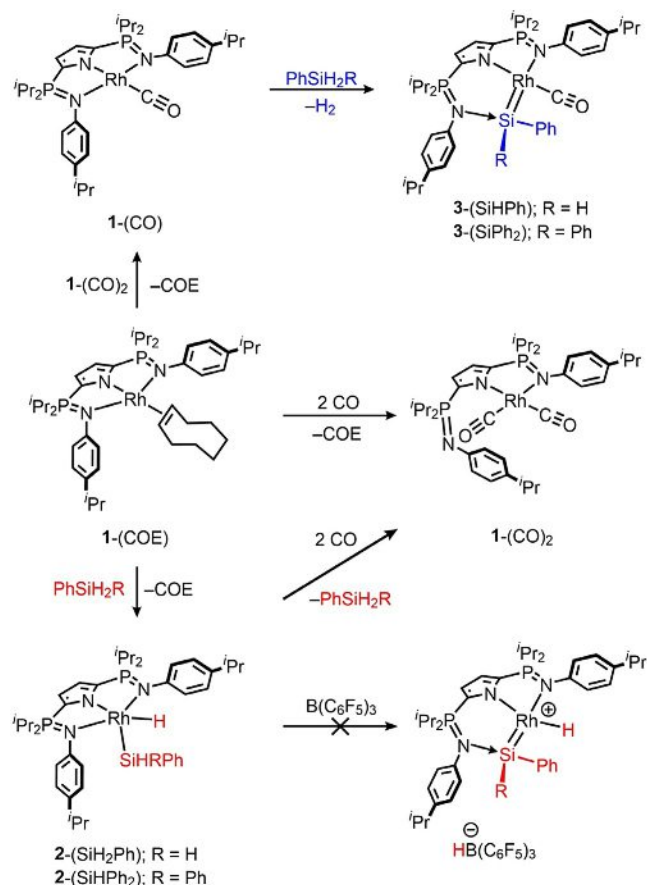
Scheme 2. Formation of rhodium(I) silylenes by a dehydrogenative process, and rhodium(III) silyl hydrides by oxidative addition of silanes.

phinimine donor capable of stabilizing a Lewis acidic silylene Si.

Reaction of **1**-CO and PhSiH$_3$ in benzene at 50 °C for 3 hours afforded a product that has two equal intensity peaks at $\delta = 53.0$ and $\delta = 43.5$ in its ^{31}P NMR spectrum.[14] The latter resonance was not consistent with a free phosphinimine, but was similar to a recently reported phosphinimine-borane-stabilized metalated formamide.[12a] Examination of the ^{1}H NMR spectrum revealed a sharp singlet at $\delta = 4.47$, which disappeared upon exposure to reduced pressure, suggesting the evolution of H$_2$ gas. Cases in which silylene formation occurs with spontaneous H$_2$ loss are rare;[15] a recent example from Djukic and co-workers highlighted the role of an exogeneous donor (THF) in promoting such H$_2$ extrusion (Scheme 1 b).[16] A diagnostic silicon-bound hydrogen was identified as a doublet of doublets ($^2J_{H-Rh} = 5.4$ Hz, $^3J_{H-P} = 5.8$ Hz) at $\delta = 5.90$. When decoupled from ^{31}P, this resonance collapses into a doublet with well-resolved ^{29}Si satellites ($^1J_{H-Si} = 183$ Hz). A polarization transfer experiment (^{1}H→^{29}Si) indicated a single ^{29}Si environment as a doublet of doublet of doublets (ddd) at $\delta = 54.6$ (Figure 1 b), a marked downfield shift compared to both **2**-SiH$_2$Ph ($\delta = -8.3$) and the previously mentioned Rh^{III} silylene described by Sadow (vide supra) ($\delta = 6.6$).[11] The ^{29}Si nucleus is coupled to two chemically-unique ^{31}P nuclei ($^2J_{Si-P} = 10$ Hz and $^3J_{Si-P} = 2.6$ Hz), consistent with a phosphinimine-stabilized Rh^I silylene.

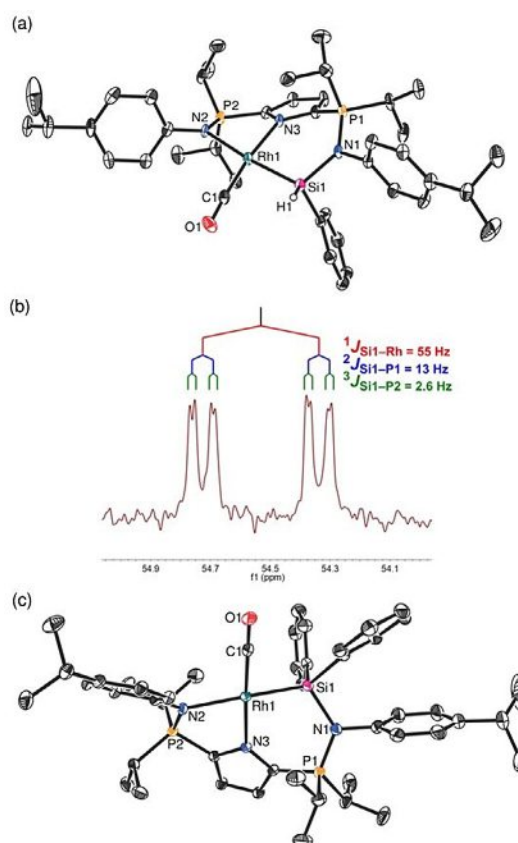**Figure 1.** a) Thermal ellipsoid plot (30% probability) of **3**-SiHPh with hydrogens omitted for clarity. b) ^{29}Si NMR (139 MHz) spectrum of **3**-SiHPh in [D$_6$]benzene at 298 K. c) Thermal ellipsoid plot (30% probability) of **3**-SiPh$_2$ with hydrogens omitted for clarity.

($^1J_{H-Rh} = 26.1$ Hz), respectively. The ^{29}Si NMR spectrum of **2**-SiH$_2$Ph features two unique overlapping doublets ($^1J_{Si-Rh} = 27.5$ Hz, $^1J_{Si-Rh} = 27.7$ Hz) at $\delta = -8.0$ and $\delta = -8.1$, presumably the result of two rotamers that interconvert slowly on the NMR timescale via rotation about the Rh–Si bond (Figure S6).

With silyl hydride complexes **2**-SiH$_2$Ph and **2**-SiHPh$_2$ in hand, attempts to generate Rh silylenes via H$^-$ abstraction using B(C$_6$F$_5$)$_3$, in line with work by Tilley and Sadow, were conducted.[9–11] Specifically, a stirring bromobenzene-d_5 solution of **2**-SiH$_2$Ph was combined with 1 equivalent of B(C$_6$F$_5$)$_3$, forming the anticipated hydridoborate anion [HB(C$_6$F$_5$)$_3$]$^-$, as confirmed by ^{11}B and ^{19}F NMR spectroscopy. However, the expected metal-containing cation arising from α-H migration from Si to Rh was not observed (^{1}H and ^{31}P NMR spectra indicated formation of multiple products). Exhaustive efforts to isolate a Rh silylene species from this mixture proved unsuccessful.

Recognizing that the ^{iPr}NNN ligand platform had previously demonstrated cooperative activity with Rh toward small molecules,[12] we sought a method by which silylene formation could be mediated by a hemilabile phosphinimine donor. With this goal in mind, and the knowledge that (^{iPr}NNN)Rh(CO)$_2$ (**1**-(CO)$_2$) exhibits a κ^2-N,N bound ^{iPr}NNN ligand, it was postulated that combinations of **1**-CO and/or **1**-(CO)$_2$ with silanes might lead to oxidative addition products featuring a pendant phos-

Notably, the observed ^{29}Si chemical shift is comparable to well-known base-stabilized Ru silylenes [Cp*(PiPr$_3$)RuH$_2$(SiPh$_2$·DMAP)]$^+$ (DMAP = 4-Dimethylaminopyridine) ($\delta = 68.5$) and [Cp*(PiPr$_3$)RuH$_2$(SiPh$_2$·NHMePh)]$^+$ ($\delta = 55.7$) reported by Tilley and colleagues.[17]

Recrystallization of the purported silylene complex from pentane at $-35\,^\circ$C provided single yellow crystals suitable for X-ray diffraction analysis. The solid-state structure (Figure 1a) confirmed the compound's identity as κ^2-N,N(^{iPr}NNN)(CO)Rh=SiHPh (**3**-SiHPh), a rare H-substituted silylene,[18] and to the best of our knowledge, the first example of an isolated Rh$^{\rm I}$ silylene derived from a hydrosilane. The Rh$^{\rm I}$—Si bond distance of 2.262(1) Å is the shortest yet observed. The N—Si contact between the phosphinimine N atom and the Lewis acidic silylene Si is 1.834(3) Å, 0.12 Å longer than N—Si bonds reported for stable N-heterocyclic silylene complexes of rhodium [1.711(2)–1.714(3) Å].[19]

In order to ascertain the generality of the above reaction, Ph$_2$SiH$_2$ was combined with **1**-CO to give the anticipated diphenylsilylene κ^2-N,N(^{iPr}NNN)(CO)Rh=SiPh$_2$ (**3**-SiPh$_2$) and H$_2$. The X-ray crystal structure of **3**-SiPh$_2$ (Figure 1c) is isostructural to **3**-SiHPh with only minor geometrical deviations (Rh—Si = 2.2702(7), N—Si = 1.842(2) Å). For both **3**-SiHPh ($\tau_4 = 1.0$) and **3**-SiPh$_2$ ($\tau_4 = 0.97$) the geometry at Si is tetrahedral. The ^{29}Si NMR spectrum revealed one resonance centered at $\delta = 51.4$ (dd), consistent with the connectivity established by X-ray diffraction analysis. Deuterium labelling experiments conducted with Ph$_2$SiD$_2$ exclusively produced D$_2$ gas (Figure S27), which was detected by ^{2}H NMR spectroscopy, thus confirming that the silane is the source of liberated H$_2$. When the reaction was repeated using a 1:1 mixture of Ph$_2$SiH$_2$ and Ph$_2$SiD$_2$, no H–D was observed, thus implying H$_2$ loss occurs via an intramolecular process.

In an effort to understand the nature of the Rh—Si interactions in complexes **3**, a DFT study was conducted at the BP86/6-31G(d,p) level of theory using a polarized SDD effective core potential for Rh. Geometry optimizations reproduced Rh—Si and Si—N bond lengths within 0.02 and 0.07 Å, respectively. Inspection of the Kohn-Sham orbitals obtained for both **3**-SiHPh and **3**-SiPh$_2$ revealed HOMOs corresponding to a nonbonding Rh d_{z^2} orbital consistent with a d^8 square planar Rh$^{\rm I}$ center. The LUMOs for both species were delocalized over the ^{iPr}NNN scaffold. While Rh→CO backbonding interactions of π-symmetry were observed, our DFT analyses do not support the presence of substantial Rh→Si π bonding, such as those reported previously for iridium silylenes.[13,14] Notably, Djukic and co-workers found that coordination of THF to an Ir=SiHPh moiety resulted in a 30% reduction of the π character in the Ir—Si interaction.[16] We therefore reason that the stronger σ-donor abilities of the phosphinimine in **3**, compared to THF, may account for the diminished double bond character in this system. A comparison of the natural atomic charge on Si in **3**-SiHPh, with that in the base-free (PNP)Ir(H)=SiHMes (PNP = [N(2-PiPr$_2$-4-Me-C$_6$H$_3$)$_2$]$^-$), reported by Tilley,[10] indicated similar values ($+1.19$ $cf.$ $+1.03$, respectively), which is perhaps at odds with this hypothesis.

In an effort to glean insight into the mechanism of silylene formation attempts were undertaken to generate **3**-SiHPh and **3**-SiPh$_2$ following a complementary route. When either **2**-SiH$_2$Ph or **2**-SiHPh$_2$ were combined with excess CO gas, immediate formation of **1**-(CO)$_2$ was observed, along with reductive elimination of the corresponding silane (Scheme 2). Accordingly, the relative thermochemistry of **1**-CO and **1**-(CO)$_2$ was investigated using DFT gas-phase calculations that demonstrated **1**-CO is destabilized by 13.8 kcal mol^{-1} relative to **1**-(CO)$_2$. To further probe mechanistic questions, and to contrast the reactivity of **1**-COE and **1**-CO, each complex was also allowed to react with the tertiary silane Ph$_3$SiH. Unsurprisingly, Si—H oxidative addition, along with concurrent release of COE, prevailed in the former case, leading to the Rh$^{\rm III}$ silyl hydride (^{iPr}NNN)Rh(H)SiPh$_3$ (**4**). By contrast, at elevated temperatures with Ph$_3$SiH over multiple days, **1**-CO slowly transformed into an asymmetric product, characterized by equal intensity resonances in the ^{31}P NMR spectrum ($\delta = 76.2$ and 42.9), which we propose to be the zwitterionic compound κ^2-N,N-(H-^{iPr}NNN)(CO)RhSiPh$_3$ (**5**), the result of deprotonation of the putative rhodium hydride in κ^2-N,N-(^{iPr}NNN)(CO)Rh(H)SiPh$_3$ by the internal phosphinimine base.[20] Unfortunately, under all tested experimental conditions complex **5** decomposed at a rate that was competitive with its formation, thereby rendering further study impossible. Nonetheless, these data suggest that following Si—H oxidative addition, Rh—H deprotonation by the free phosphinimine, subsequent α-H migration from Si to Rh, and finally H$_2$ loss (NH and Rh—H)/phosphinimine coordination to Si, is a plausible pathway for silylene formation. Alternatively, it is possible that direct phosphinimine coordination to Si would create a 5-coordinate Si intermediate from which H$_2$ loss (Rh—H and Si—H) is facile.

By leveraging hard–soft interactions between ligand and metal,[21] rhodium silylenes can be accessed directly from commercially-available silanes. Thermochemical analysis using DFT suggests the observed reactivity stems from the energetic disparity of a hard nitrogen-donor ligand set and the soft Rh$^{\rm I}$ center. The neutral rhodium silylenes, which were synthesized on a preparative scale, allow for further studies into structure, bonding and reactivity. For example, preliminary results indicate that **3**-SiHPh reacts with B(C$_6$F$_5$)$_3$ by an H$^-$ abstraction sequence, possibly providing access to the cationic rhodium silylyne [κ^2-N,N-(^{iPr}NNN)(CO)Rh≡SiPh][HB(C$_6$F$_5$)$_3$], the synthesis and chemistry of which is currently being explored.

Crystallographic Data

CCDC 1901814–1901817 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Conflict of interest

The authors declare no conflict of interest.

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[18] A survey of the literature returned the following hydrogen-substituted transition metal silylenes: a) [Cp*(*i*Pr$_3$P)(H)$_2$Os=SiH(trip)][B(C$_6$F$_5$)$_4$] and b) [Cp*(*i*Pr$_3$P)(H)$_2$Ru=Si(H)Ph·Et$_2$O][B(C$_6$F$_5$)$_4$] see: P. B. Glaser, T. D. Tilley, *J. Am. Chem. Soc.* **2003**, *125*, 13640–13641; c) [Cp*(*i*Pr$_3$P)(H)Os=SiH(trip or dmp) see: P. G. Hayes, C. Beddie, M. B. Hall, R. Waterman, T. D. Tilley, *J. Am. Chem. Soc.* **2006**, *128*, 428–429; d) [(Et$_3$P)$_3$(H)$_2$Ir=Si(H)(dmp)][B(C$_6$F$_5$)$_4$] see: R. S. Simons, J. C. Gallucci, C. A. Tessier, W. J. Youngs, *J. Organomet. Chem.* **2002**, *654*, 224–228; e) [PhBP$_3$](H)$_2$Ir=SiH(trip) see: J. D. Feldman, J. C. Peters, T. D. Tilley, *Organometallics* **2002**, *21*, 4065–4075; f) Cp*(*i*Pr$_2$MeP)(H)Ru=SiH(trip or dmp) see: P. G. Hayes, R. Waterman, P. B. Glaser, T. D. Tilley, *Organometallics* **2009**, *28*, 5082–5089; g) Cp*(CO)$_2$(H)W=Si(H){C(SiMe$_3$)$_3$} see: T. Watanabe, H. Hashimoto, H. Tobita, *Angew. Chem. Int. Ed.* **2004**, *43*, 218–221; *Angew. Chem.* **2004**, *116*, 220–223; h) Cp′(CO)$_2$(H)W=SiH{C(SiMe$_3$)$_3$}; (Cp′=η^5-C$_5$Me$_4$Et) see: T. Watanabe, H. Hashimoto, H. Tobita, *J. Am. Chem. Soc.* **2006**, *128*, 2176–2177; i) Cp′(CO)(H)Ru=SiH{C(SiMe$_3$)$_3$} see: M. Ochiai, H. Hashimoto, H. Tobita, *Angew. Chem. Int. Ed.* **2007**, *46*, 8192–8194; *Angew. Chem.* **2007**, *119*, 8340–8342; j) [Cp*(*i*Pr$_3$P)(H)$_2$Ru=SiH(Mes)][CB$_{11}$H$_6$Br$_6$ or B(C$_6$F$_5$)$_4$] see: M. E. Fasulo, M. C. Lipke, T. D. Tilley, *Chem. Sci.* **2013**, *4*, 3882–3887, and M. E. Fasulo, P. B. Glaser, T. D. Tilley, *Organometallics* **2011**, *30*, 5524–5531; k) [(PNP)(H)Ir=SiH(Mes)][B(C$_6$F$_5$)$_4$]; see reference [10b]; l) [(PNP)(H)Ir=SiH(trip or dmp)][B(C$_6$F$_5$)$_4$]; see reference [10a]; m) Cp*(*i*Pr$_2$MeP)Fe(H)Si=H(trip or dmp) see: P. W. Smith, T. D. Tilley, *J. Am. Chem. Soc.* **2018**, *140*, 3880–3883; n) Cp(CO)$_2$Mn=SiH(2-Me$_2$NCH$_2$C$_6$H$_4$), MeCp(CO)$_2$Mn=SiH(2-Me$_2$NCH$_2$C$_6$H$_4$), Cp(CO)$_4$Fe=SiH(2-Me$_2$NCH$_2$C$_6$H$_4$) and Cp(CO)$_5$Cr=SiH(2-Me$_2$NCH$_2$C$_6$H$_4$); see reference [15f]; o) Cp*(μ-*P*,*N*-2-NMe$_2$-3-*P*iPr$_2$-indene)(H)$_2$Ru=SiHPh]$^+$ X$^-$ (X = SO$_3$CF$_3$, B(C$_6$F$_5$)$_4$), Cp*(μ-2-NMe$_2$-3-*P*iPr$_2$-indenide)(H)$_2$Ru=SiHPh and [Cp*(μ-1-*P*iPr$_2$-2-NMe$_2$-indene)(H)$_2$Ru=SiHPh]$^+$ X$^-$ (X = SO$_3$CF$_3$, B(C$_6$F$_5$)$_4$; see: M. A. Rankin, D. F. MacLean, G. Schatte, R. McDonald, M. Stradiotto, *J. Am. Chem. Soc.* **2007**, *129*, 15855–15864.

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