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COMMUNICATION

Silylene-Assisted Hydride Transfer to CO_2 and CS_2 at a $[P_2Si]Ru$ Pincer-Type Complex

Matthew T. Whited,*[a] Jia Zhang,[a] Senjie Ma,[a] Binh D. Nguyen,[a] and Daron E. Janzen[b]

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The synthesis and characterization of base-stabilized and base-free pincer-type bis(phosphine)/silylene $[P_2Si]Ru$ complexes are reported. The base-free complex readily reduces CO_2 and CS_2 via silylene-assisted hydride transfer, affording structurally distinct products with silicon-to-ruthenium formate and dithioformate bridges.

Compared with their ubiquitous metal carbene congeners, metal silylenes ($M{=}SiR_2$) are much less common, due in part to the reactivity of the highly electrophilic *sp*^{2} silicon center. Nevertheless, transition-metal silylene complexes have been implicated in several important catalytic processes, with the silylene either participating directly or acting as a supporting ligand.[1] Moreover, base-free metal silylenes also exhibit a number of unusual modes of reactivity that may yet find application in catalysis, including reversible migration of X-type ligands to silicon,[2] hydrosilylation of polar and nonpolar multiple bonds by hydride transfer from a metal,[3] [2+2] and [2+4] cycloadditions across the M=Si bond,[4] insertion into Si–H bonds of H-substituted silylenes,[5] redistribution of silicon substituents,[6] and halogen radical abstraction.[7]

The variety of distinct modes of metal silylene reactivity suggests that new, cooperative catalysis may be enabled by appropriately designed silylene complexes. As part of a research program focused on developing metal/silicon cooperative approaches to small-molecule activation,[8] our research group has worked to develop multidentate ligand scaffolds capable of supporting silyl and silylene donors as reactive central elements in a pincer-type environment.[9] Several examples of modification of M–Si single bonds within $[P_2Si]M$ environments have been reported,[10] and such processes are frequently reversible, suggesting that incorporating the silicon donor into a pincer environment may be beneficial for catalysis. However, a similar range of processes has not been demonstrated for pincer-type metal silylenes. In principle, chelation through strong donors should help stabilize the reactive M=Si bond, allowing possible elucidation of new reactions occurring at a $M^{\delta-}{=}Si^{\delta+}$ façade and better integration into catalysis. However, only two pincer-type silylene complexes have been previously characterized (Chart 1).[11] Ozerov's platinum complex was unstable, readily undergoing metal-to-silicon migration of various X-type ligands. Previous work in our laboratory also implicated pincer-type silylene intermediates at rhodium.[9]

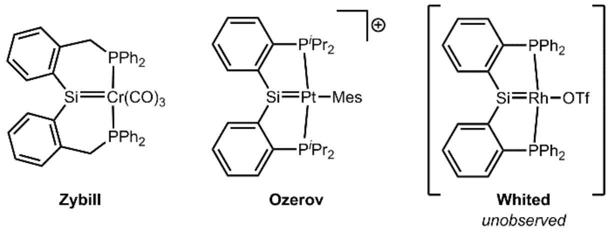

Chart 1. Complexes with base-free silylene donors incorporated into a pincer framework

The preparation and isolation of a pincer-type late-metal silylene complex would allow detailed reactivity studies, with the goal of utilizing ambiphilic $M^{\delta-}{=}Si^{\delta+}$ complexes as intermediates in cooperative processes.[12] In this Communication, we report the preparation of a series of pincer-type $[P_2Si]$ ruthenium hydride complexes, including a base-stabilized and base-free silylene. The base-free complex reduces CO_2 and CS_2 via silicon-assisted hydride transfer from ruthenium to the heteroallene..

Previous results from our laboratory[9, 13] and others[14] have shown that dihydrosilanes will react with metal halides or pseudohalides to form halosilyl metal complexes. To avoid this potential complication, ruthenium hydride precursors were targeted. Metalation of the bis(phosphine)/dihydrosilyl pincer-type proligand $[^{Ph}P_2Si]H_2$ (**1**) with $Ru(H)_2(CO)(PPh_3)_3$ led to quantitative conversion (by ^{31}P NMR spectroscopy) to the

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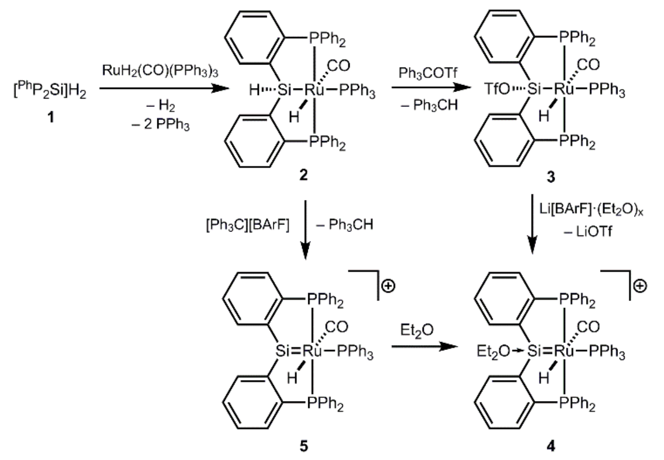
[a] *Department of Chemistry, Carleton College, Northfield, MN 55057, USA*
E-mail: mwhited@carleton.edu
[b] *Department of Chemistry and Biochemistry, St. Catherine University, St. Paul, MN 55105, USA*

Electronic Supplementary Information (ESI) available: Synthesis procedures and characterization data all reported compounds, computational details for complex **5(comp)**, Crystallographic data for **2**, **3**, and **7-B$_{12}$Cl$_{12}$**. CCDC 1566072–1566074. See DOI: 10.1039/x0xx00000x hydrosilyl ruthenium hydride complex ($^{Ph}P_2Si^H$)Ru(H)(CO)(PPh_3) (**2**) with loss of H_2 and 2 equiv of PPh_3 (Scheme 1). Previous work by Tilley and others has shown the utility of triflatosilyl complexes as precursors to silylenes and their reactive equivalents,[9a, 15] and it was found that **2** could be converted to its triflatosilyl derivative (**3**) by reaction with trityl triflate.



Scheme 1. Synthesis of [P_2Si]Ru silyl and silylene complexes

Complex **2** exhibits a number of key spectroscopic handles supportive of its formulation as shown in Scheme 1, including prominent infrared bands associated with Si–H and C≡O stretching modes (ν_{SiH} = 2024 cm^{-1}, ν_{CO} = 1942 cm^{-1}), and a ^{29}Si chemical shift consistent with an *sp*^{3}-hybridized hydrosilyl metal complex (δ 47.3 ppm).[16] Although the Si–H stretching mode is at slightly lower energy than is typical for hydrosilanes,[17] it is quite similar to those reported by Kono *et al.* for related ruthenium complexes.[18] No Si–*H* signal is observed for **2** by ^{1}H NMR spectroscopy, though the chemical shift (δ 6.65 ppm) was confirmed by a ^{1}H/^{29}Si HMQC experiment, showing that the signal is hidden under aromatic C–*H* peaks. The silicon hydride was also located in the Fourier difference map in the crystal structure of **2** and refined freely.

Table 1. Key structural and spectroscopic data for silyl and silylene complexes **2**–**5**

	2	**3**	**4**^{b}	**5**^{b}
∑∠Si^a	329.0(2)°	338.9(3)°	--	--
$d_{Ru–Si}$ (Å)	2.379(1)	2.318(1)	--	--
δ ^{29}Si (ppm)	47	115	151	278
$^2J_{SiP(trans)}$ (Hz)	83	110	112	108
ν_{CO} (cm^{-1})	1942	1965	1955	1979

^{a} ∑∠Si = sum of bond angles around silicon, excluding H (**2**) or OTf (**3**). ^{b} No structural data available for complexes **4** and **5.**

Though complexes **2** and **3** exhibit grossly similar spectroscopic features, there are key differences that are consistent with the different electronic properties engendered by triflate versus hydride. For instance, complex **3** exhibits a ^{29}Si chemical shift that is significantly downfield from that of **2**, and silicon shows a stronger two-bond coupling to the *trans*-PPh_3 ligand, presumably due to a stronger Ru/Si interaction (Table 1). The carbonyl ligand also shows a higher-energy stretching mode due to reduced backbonding from Ru, as expected when the electron-withdrawing triflate is introduced. A comparison of crystal structures obtained for **2** and **3** shows a shorter Ru–Si bond and greater *sp*^{2} character for silicon in **3** (Table 1 and Figure 1).[19]

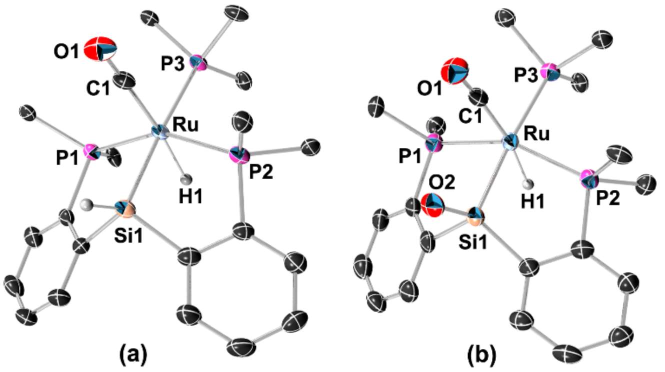
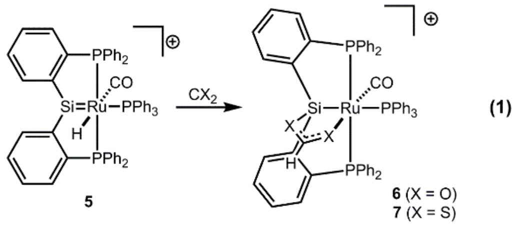


Fig. 1 Crystal structures of (a) **2** and (b) **3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms (except for Ru and Si hydrides) and portions of the triflate and phosphine phenyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: Ru–Si1, 2.3787(10); Ru–P1, 2.3347(9); Ru–P2, 2.3309(10); Ru–P3, 2.4261(9); Ru–C1, 1.895(4); Ru–H1, 1.60(3); C1–O1, 1.151(4); Si1–Ru–P3, 175.69(3); P1–Ru–P2, 153.45(3); Si1–Ru–H1, 80.1(12). For **2**: Ru–Si1, 2.3175(14); Ru–P1, 2.3454(14); Ru–P2, 2.3356(14); Ru–P3, 2.4304(13); Ru–C1, 1.894(5); Ru–H1, 1.62(5); C1–O1, 1.150(6); Si1–Ru–P3, 174.14(5); P1–Ru–P2, 154.66(5); Si1–Ru–H1, 77.5(18).

Initial attempts to prepare a base-free silylene complex focused on triflate abstraction from **3** using Li[BArF]·(Et_2O)$_x$ (BArF = B(C_6F_5)$_4^-$).**[15b]** However, the product **4-BArF** exhibited a ^{29}Si chemical shift (δ 150.7 ppm) more consistent with a base-stabilized than base-free silylene, and ^{1}H NMR revealed the presence of diethyl ether (1 equiv) bonded to silicon (see ESI). Alternatively, the base-free silylene complex, [$^{Ph}P_2Si$=]Ru(H)(CO)(PPh_3) (**5**), could be prepared as a bright yellow solid via hydride abstraction with trityl BArF in non-donor solvents such as dichloromethane, bromobenzene, and fluorobenzene. The reaction was found to proceed most cleanly in fluorobenzene and **5** was unstable over extended periods in dichloromethane, suggesting possible chlorine radical abstraction by the silylene.[7] ^{29}Si NMR spectroscopy confirmed the base-free silylene formulation presented in Scheme 1 (δ 278 ppm).[1b] Also consistent with this formulation, it was found that **4** could be cleanly prepared by addition of Et_2O to a solution of **5**.

Thus far, we have been unable to obtain crystals of **5** suitable for X-ray crystallographic analysis. However, the structure of **5** was probed with density functional theory (DFT), revealing an acute Si–Ru–H bond angle (50°) and close Si···H contact (1.78 Å) as expected for a highly electrophilic cationic silylene hydride,[5c] as well as a short Ru–Si bond (2.243 Å). The Ru–*H* signal observed in the ^{1}H NMR spectrum of **5** reveals parameters similar to those of **2**–**4** (δ –7.89 (t, $^2J_{HP}$ = 15.3 Hz)), though no coupling to the bound PPh_3 was resolved. No ^{29}Si satellites were observed and ^{29}Si/^{1}H coupling was not resolved for the hydride signal by a ^{29}Si-filtered ^{1}H NMR experiment, suggesting that J_{SiH} is less than ca. 20 Hz. The coordination environment of **5** is unusual in that most ruthenium silylene complexes lacking heteroatom stabilization of the silylene utilize Cp* ligands. The closest geometric analogues to **5** are Peters's neutral, six-coordinate Ru(II) silylenes supported by tripodal tris(phosphino)silyl ligands.[20] Ongoing structural and computational studies are aimed at determining the precise structure and bonding description of **5**.



(1)

Exposure of **5** to CO_2 (1 atm) results in a lightening of the solution, loss of the ruthenium hydride resonance observed by ^1H NMR spectroscopy, and appearance of a new singlet at 6.42 ppm, indicating the possible presence of a formate. The carbonyl stretching frequency red-shifts by 24 cm^{-1} to 1955 cm^{-1}, indicative of increased backbonding from ruthenium, and a new intense infrared signal is observed at 1577 cm^{-1}. Additionally, the ^{29}Si NMR resonance moves to 118 ppm, similar to that of the silicon nucleus in triflatosilyl complex **3**. Together, these findings suggest a net cooperative insertion of CO_2, with transfer of hydride from ruthenium to CO_2 and formation of an O–(CH)–O bridge from silicon to ruthenium (Eq 1). Such a formulation is confirmed by reaction of **2** with $^{13}CO_2$, causing the formate C–*H* NMR signal to split into a doublet ($^1J_{HC}$ = 232 Hz) and the symmetric OCO stretch of the bridging formate to shift to 1538 cm^{-1}. Use of $^{13}CO_2$ also allows observation of the formate carbon by $^{13}C\{^1H\}$ NMR (δ 171.6 (d, $^3J_{CP}$ = 8 Hz)). The observation of three-bond coupling to PPh_3 but not the phosphines of the $[P_2Si]$ ligand appears be an unusual manifestation of Karplus's rule by an inorganic system,[21] since the C–O–Ru–P dihedral angle should be ca. 180° (maximum coupling) for to PPh_3 ligand but 90° (minimum coupling) to the phosphines of the $[P_2Si]$ ligand.

An analogous reaction of **5** with CS_2 to affords the bridging dithioformate **7**, which exhibits a carbonyl stretch (ν_{CO} = 1973 cm^{-1}) slightly blue-shifted from that of **6**, presumably due to weaker S→Ru (versus O→Ru) π donation and resultantly weaker backbonding into the CO ligand. The dithioformate C–*H* resonance observed by ^1H NMR spectroscopy is also shifted significantly downfield from the analogous proton in **6** (δ 9.61 ppm), but the ^{29}Si NMR resonance of **7** is nearly identical to that of **6**. Crystals of **7** suitable for X-ray diffraction were ultimately obtained by replacement of BArF with the highly crystalline dodecachlorododecaborate dianion ($B_{12}Cl_{12}^{2-}$) (Figure 2).[22] Consistent with the ^{29}Si NMR data, the silicon center in **7** is pyramidalized to about the same extent as that in **3** ($\sum\angle Si$ = 335.6(2)°). The bridging formate and dithioformate modes found in **6** and **7** represent unusual structural motifs. Tobita has reported a similar structure resulting from the hydrosilylation of arylisocyanates at a neutral ruthenium silylene hydride complex.[3a] Roper has also reported a related bridging acetate complex that was obtained by reaction of a chlorosilyl ruthenium complex with thallium acetate.[23]

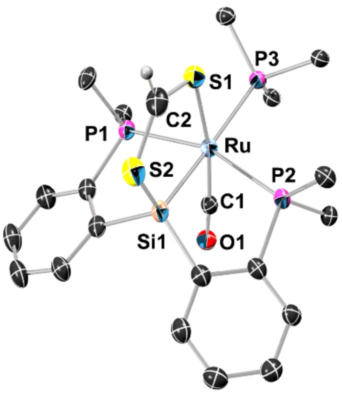
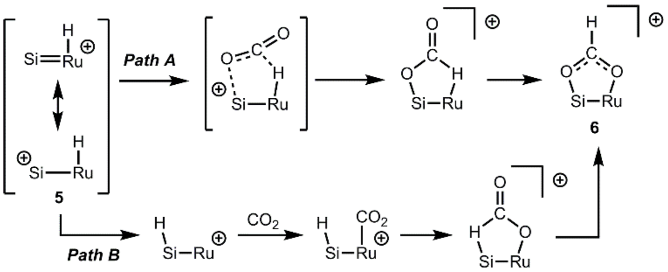


Fig. 2. Crystal structure of cation portion of **7-$B_{12}Cl_{12}$** with thermal ellipsoids at the 50% probability level. Hydrogen atoms (except for dithioformate C–H) and portions of the phosphine phenyl groups have been omitted for clarity. Selected bond lengths (Å): Ru–Si1, 2.3285(11); Ru–P1, 2.3749(10); Ru–P2, 2.4250(10); Ru–P3, 2.5080(10); Ru–C1, 1.876(4); Ru–S1, 2.3939(10); Si1–S2, 2.2310(13); C1–O1, 1.145(4).

The simplest mechanistic option for formation of **6** and **7** would involve cooperative hydride transfer to carbon with concomitant O–Si or S–Si bond formation (Scheme 2, Path A). Alternatively, 1,2-hydrogen migration to silicon could precede CO_2 or CS_2 binding, followed by hydride transfer directly from silicon (Scheme 2, Path B). At this point, we favour Path A because CO_2 is a weak ligand that typically binds in a stable fashion only to electron-rich metal complexes.[24] Path A is also analogous to Hazari's NH-assisted CO_2 insertion into an iridium hydride.[25] The analogy to Hazari's acid-assisted pathway is reinforced by the fact that ether-stabilized complex **4**, with its less electrophilic silicon center, does not react with CO_2 and CS_2, even at elevated temperature.

We considered an alternative mechanism involving direct CO_2/CS_2 insertion into Ru–H, but such an option requires prior dissociation of PPh_3 from the 18-electron complex to allow coordination of the heteroallene. For hydrosilyl complex **2**, phosphine exchange does not occur at ambient temperature and is sluggish at 80 °C (see ESI). Although analogous studies could not be conducted on **5** due to its instability toward Lewis bases, it is expected by analogy that the facile reaction of **5** with CO_2/CS_2 (the CS_2 reaction is instantaneous at ambient temperature) does not require PPh_3 dissociation.



Scheme 2. Possible pathways for CO_2 reduction at silylene **5** (n.b., only the Si/Ru/H core of complex **5** is depicted).

Comparison of the observed reactivity of **5** with the ArNCO and ArNCS reactions of Tobita's neutral silylene hydride[3a] introduces several further points of interest. Firstly, although Tobita's complex performs hydrosilylation of ArNCO, it has not been reported to react with CO_2 or CS_2. Thus, the observed reactivity of **5** may derive partly from the high electrophilicity of the cationic complex. Secondly, Tobita's complex cleaves the C=S bond in mesityl isothiocyanate, whereas **5** simply hydrosilylates CS_2. At this point, the origins of such divergent reactivity are unclear.

In conclusion, we have presented the synthesis of a series of pincer-type $[P_2Si]Ru$ complexes with varying substitution at silicon, including diethyl-ether-stabilized and base-free silylene complexes. The complexes provide unusual examples of pincer ligands incorporating silylene donors, and the base-free silylene participates in stoichiometric hydrosilylation of CO_2 and CS_2. These findings show how the reactivity of a metal hydride can be modulated by a proximal Lewis acid, a feature we intend to exploit as we explore silicon/metal cooperative reactivity with an eye toward catalysis.

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There are no conflicts of interest to declare.

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