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High Electrophilicity at Silicon in η^3-Silane σ-Complexes: Lewis Base Adducts of a Silane Ligand, Featuring Octahedral Silicon and Three Ru−H−Si Interactions

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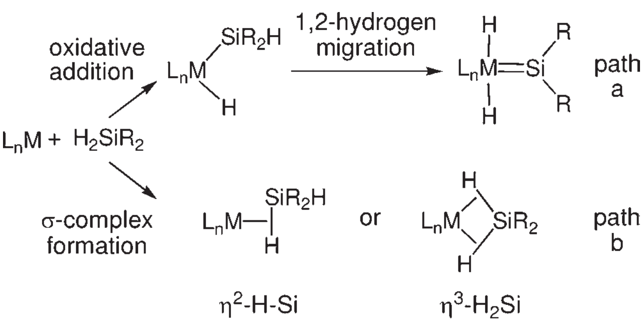
ABSTRACT: New η^3-silane σ-complexes $[PhBP^{Ph}_3]RuH(\eta^3\text{-}H_2SiRR')$ (RR′ = PhMe, Ph$_2$) were synthesized. Lewis bases [THF, 4-(dimethylamino)pyridine, and PMe$_3$] coordinate to the silicon centers of these complexes to form stable adducts. The base adducts, $[PhBP^{Ph}_3]Ru(\mu\text{-}H)_3SiRR'(\text{base})$, feature three nonclassical Ru−H−Si interactions and hexacoordinate silicon centers, as determined by multinuclear NMR spectroscopy, X-ray crystallography, and computational investigations.

Transition-metal-mediated Si−H bond activations are key steps in many catalytic reactions that form bonds to silicon (Si−X; X = C, O, N, Si).[1,2] In recent years, interest has focused on transformations involving two successive Si−H activations that form silylene complexes (L_nMSiRR'),[3] especially since these species may participate as key intermediates in catalytic cycles. This type of silane activation occurs via Si−H oxidative addition[2] to form a silyl complex, followed by 1,2-hydrogen migration[4] to form the silylene complex (Scheme 1, path a). This reaction sequence appears to be important in olefin hydrosilation reactions carried out by cationic ruthenium[5] and iridium[6] silylene complexes. In these mechanisms, the electrophilic silylene ligand interacts directly with the olefin to facilitate Si−C bond formation. Experimental results and DFT calculations indicate that this reactivity requires a cationic metal silylene complex that possesses significant silylenium character.[7] Double Si−H activations have similarly been proposed to account for rhodium-catalyzed hydrosilations of carbonyl compounds.[3c]

Partial Si−H bond activations are also well known and result in nonclassical structures that retain Si···H bonding interactions (σ-complexes).[8] Well-known silane σ-complexes exhibit η^2-HSi coordination, but silanes may also coordinate to a metal center via two M−H−Si interactions, resulting in the η^3-H$_2$Si coordination mode (Scheme 1, path b).[2b] The latter binding mode is not common, with the only reported examples being $([PhBP^{iPr}_3]FeH(\eta^3\text{-}H_2SiArMe)$[9] and $\{(Cy_3P)_2H_2Ru\}_2(\mu\text{-}\eta^3,\eta^3\text{-}SiH_4)$.[10] Little is known regarding the reactivity of η^3-silane complexes, but potential similarities with silylene dihydrides are suggested by a DFT study of olefin hydrosilation reactions catalyzed by a ruthenium silylene dihydride.[11] This investigation characterized a key mechanistic step as involving attack of the olefin onto a silylene ligand possessing two significant Si···H−Ru interactions, suggestive of the formulation $[Cp(PH_3)Ru(\eta^3\text{-}H_2SiH_2)]^+$.

Scheme 1



In attempts to access neutral hydrosilation catalysts with zwitterionic character, ruthenium silylene complexes supported by the tris(diphenylphosphinomethyl)borato ligand ($[PhBP^{Ph}_3]^-$)[3a,12] were targeted. This activity initially involved examination of reactions of $\{[PhBP^{Ph}_3]Ru(\mu\text{-}Cl)\}_2$[13] (**1**) with secondary silanes, which were found to produce the η^3-silane complexes $[PhBP^{Ph}_3]RuH(\eta^3\text{-}H_2SiRR')$ (Scheme 2, RR′ = PhMe, **2a**; RR′ = Ph$_2$, **2b**). As described below, complexes **2a,b** feature highly electrophilic silicon centers and, in this regard, are analogous to metal silylene complexes.[14]

Reactions of **1** with excess PhMeSiH$_2$ (6 equiv) or Ph$_2$SiH$_2$ (20 equiv) in benzene-d_6 led to quantitative formation of **2a,b** (determined by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy). Resonances attributed to chlorosilane byproducts PhMeSiHCl and Ph$_2$SiHCl were observed in the ^{1}H NMR spectra of the reaction mixtures. Compounds **2a,b** were isolated directly from reaction solutions utilizing fluorobenzene as the solvent. Layering the solutions with pentane and storing at −35 °C for 3 days provided pure, yellow crystals of **2a,b** with respective yields of 83 and 76%.

The ^{31}P{^{1}H} NMR spectra for **2a,b** display one singlet, even at −80 °C in toluene-d_8. Similarly, only one hydride resonance was detected for each compound by ^{1}H NMR spectroscopy (−80 to 25 °C). The ^{1}H−^{29}Si HMBC NMR spectra display hydride signals at −7.00 ppm (**2a**, J_{SiH} = 65 Hz, ^{29}Si δ 154 ppm) and −6.41 ppm (**2b**, J_{SiH} = 68 Hz, ^{29}Si δ 141 ppm). Similar ^{29}Si chemical shifts were reported for $[PhBP^{iPr}_3]FeH(\eta^3\text{-}H_2SiArMe)$ (δ 162 ppm, Ar = Ph; δ 160, Ar = Mes).[9] Notably, these ^{29}Si chemical shifts are downfield of those commonly observed for silyl ligands (<90 ppm),[2] while terminal silylene ligands typically

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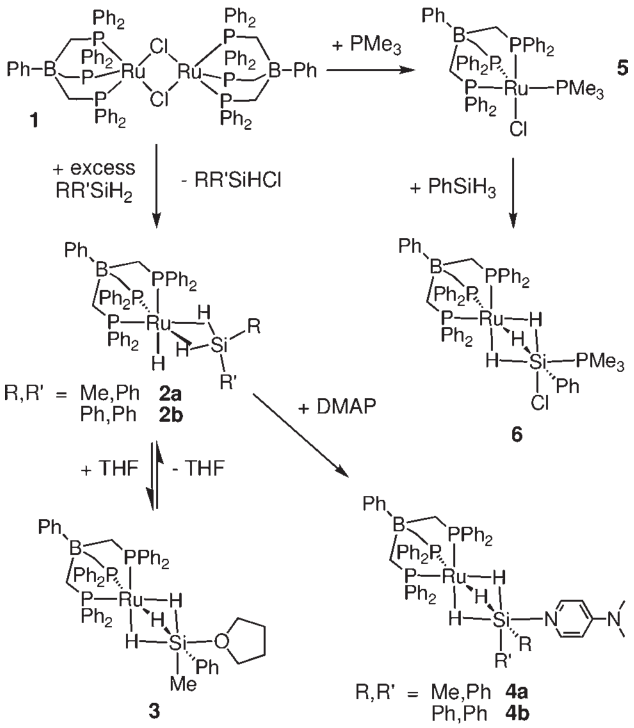
have ^{29}Si NMR resonances >200 ppm.[14] The observed J_{SiH} values represent the average of coupling associated with one classical hydride ligand (J_{SiH} < 10 Hz) and two nonclassical Ru−H−Si interactions. Thus, large $^1J_{SiH}$ values of ca. 95 Hz can be inferred for the nonclassical hydride ligands, indicative of strong Si−H interactions in **2a,b**.[8b,15b,16] Characteristic absorptions in the FTIR spectra of **2a** (1974, 1666 cm^{-1}) and **2b** (1999, 1643 cm^{-1}) provided further evidence for the presence of terminal and nonclassical hydride ligands.[15b]

The molecular structure of **2a** (Figure 1a) exhibits a Ru−H distance (1.56(4) Å) that is typical for a terminal Ru−H bond (ca. 1.6 Å),[17] while the other Ru−H bonds are significantly longer (1.73(4), 1.76(4) Å). The latter hydride ligands are bonded to the silicon center (*d*(Si−H) 1.61(4), 1.66(7) Å); note that complete Si−H oxidative addition results in Si−H distances >2.00 Å.[8,15b] The Si−H distances are closer to those observed for free silanes (ca. 1.48 Å),[18] suggesting weak to moderate activation of the Si−H bonds in **2a**. Interestingly, the Ru−Si distance (2.263(1) Å) is comparable to those of ruthenium silylene complexes (2.181(1)−2.2842(5) Å).[19] Geometry optimization calculations provided a model structure, **2a′**, that is in good agreement with the structure determined by X-ray crystallography.[20]

Scheme 2



The Lewis acidic nature of **2a** is indicated by its formation of the colorless THF adduct **3** (Scheme 2). With equal initial concentrations (20 mM) of **2a** and THF in benzene-d_6, a single, broad Ru−H resonance was observed at −8.5 ppm by ^{1}H NMR spectroscopy. The chemical shift of this resonance is dependent on the concentration of THF, with higher THF concentrations leading to increasingly upfield shifts. At THF concentrations ≥200 mM, a sharp hydride resonance is observed at −9.09 ppm. Thus, complex **3** appears to exist in equilibrium with **2a** and free THF, and this has so far prevented the isolation of **3** as a pure compound. A ^{29}Si HMBC NMR experiment under conditions of excess THF (200 mM THF; 20 mM **3**) provided a ^{29}Si chemical shift of 67 ppm for **3**, nearly 90 ppm upfield from that observed for **2a**. Similarly, base-stabilized silylene complexes exhibit ^{29}Si chemical shifts that are significantly upfield from those of their base-free counterparts.[2,21] A J_{SiH} value of 40 Hz was determined for **3**, which is smaller than that observed for **2a** but large enough to suggest the presence of significant Si−H interactions in **3**. Thus, the Si−H bonds of **2a** appear to be weakened, but not entirely cleaved, upon formation of the THF adduct **3**. This contrasts with results from the DFT study of $[CpRu(PH_3)(\eta^3\text{-}H_2SiH_2)]^+$, in which Ru−H−Si interactions were absent for the Me_2O-stabilized silylene complex, $[CpRu(PH_3)(H)_2SiH_2(OMe_2)]^+$.[11]

Complexes **2a,b** reacted rapidly with 4-(dimethylamino)-pyridine (DMAP) in toluene to form adducts **4a,b** (Scheme 2), isolated as pure white powders in respective yields of 71 and 47%. At room temperature, compounds **4a,b** exhibit a single ^{31}P{^{1}H} NMR resonance (**4a**, 40.5 ppm; **4b**, 39.9 ppm) in benzene-d_6, and the three hydride ligands appear as a single resonance (**4a**, −8.75 ppm; **4b**, −8.45 ppm). The ^{29}Si resonances (**4a**, 30 ppm; **4b**, 31 ppm) are shifted upfield by >100 ppm relative to those of **2a,b**. The ^{1}H{^{31}P} NMR spectra display ^{29}Si satellites for the Ru−H signals, revealing moderately large J_{SiH} values (J_{Si-H} = 42 Hz (**4a**); 43 Hz (**4b**)). Variable-temperature ^{1}H NMR experiments with **4a** (−80 to 25 °C, toluene-d_8) show that the hydride resonance is resolved into three doublets of triplets at −60 °C (δ −8.38, −8.75, −8.97 ppm). Each hydride resonance exhibits similar couplings to *trans* ($^2J_{PH}$ ≈ 42 Hz) and *cis* phosphine ligands ($^2J_{PH}$ ≈ 10 Hz). A ^{29}Si-filtered, ^{1}H{^{31}P} NMR experiment at −60 °C revealed three ^{29}Si-coupled hydride resonances as doublets ($^1J_{SiH}$ = 43, 35, 44 Hz). These coupling constants span a small range, suggesting similar Ru−H−Si interactions for all three hydride ligands in **4a**. This is particularly notable, given that the corresponding η^3-silane complex **2a** possesses only two Ru−H−Si interactions.

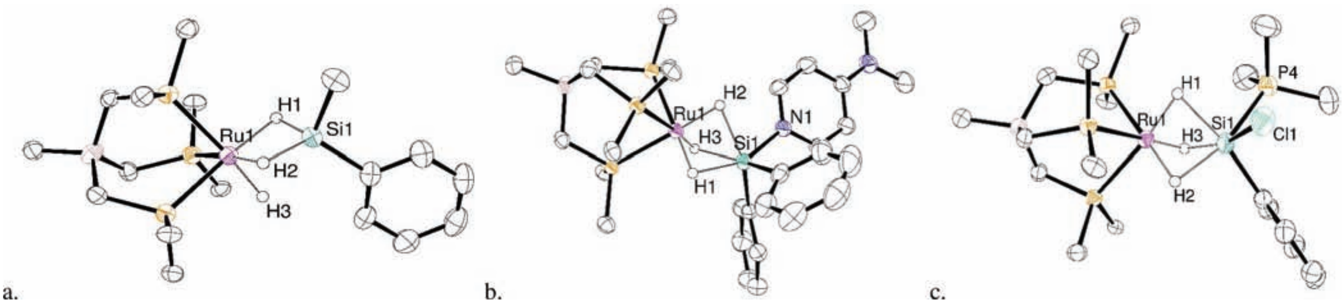


Figure 1. Molecular structures of (a) **2a**, (b) **4b**, and (c) **6**. Thermal ellipsoids set to 50% probability. Non-*ipso* carbon atoms of the $[PhBP^{Ph}{}_3]^-$ ligand and non-hydridic hydrogen atoms are omitted for clarity.

The X-ray structure of **4b** (Figure 1b) reveals octahedral coordination about ruthenium, with three hydride ligands defining a trigonal face that is capped by $SiPh_2(DMAP)$. The silicon center is in a distorted octahedral environment, with each hydride ligand approximately *trans* to one of the terminal substituents at silicon. The shortest Si−H distance (1.82(3) Å) occurs for the hydride ligand *trans* to nitrogen, a consequence of the highly polar Si−N bond. The other Si−H distances (1.98(4), 1.99(3) Å) are near the 2.00 Å limit associated with σ-HSi coordination[8,15b] but well within the observed range for secondary Si−H interactions (<2.4 Å).[15b] The Ru−Si distance is also short (2.2891(8) Å). Structurally related $(R_3P)_3MH_3SiR'_3$ (M = Fe, Ru, Os) complexes are known,[15,22] but **4a,b** are the first examples of this structural motif to include neutral, two-electron donors bonded to silicon.

A complex with a similar structure, $\{[PhBP^{Ph}_3]Ru(\mu\text{-}H)_3Si(Ph)(Cl)(PMe_3)\}$ (**6**), was isolated in 67% yield from the reaction of $[PhBP^{Ph}_3]Ru(PMe_3)Cl$[13] (**5**) with $PhSiH_3$ in THF (Scheme 2). The molecular structure of **6** (Figure 1c), determined by X-ray crystallography, strongly resembles that of **4b**. All of the Si−H distances are short enough to indicate bonding interactions (1.81(4), 1.84(3), 1.91(3) Å), and the Ru−Si distance is quite short (2.2426(10) Å). The NMR data for **6** resemble those of the other base adducts, including a ^{29}Si chemical shift of 9 ppm and an apparent J_{SiH} value of 45 Hz. At −60 °C, the observed $^1J_{SiH}$ values (51, 48, 35 Hz) reflect the presence of three inequivalent Ru−H−Si interactions. Notably, **6** can be considered as the PMe_3 adduct of an η^3-$H_2SiPhCl$ complex.

Given the observed similarities in structure, spectroscopic parameters, and reactivity, it is of interest to compare bonding modes for silylene dihydride and η^3-H_2SiR_2 complexes. Metal silylene complexes feature trigonal planar silicon centers that are strongly Lewis acidic. The latter property results from weak M−Si π-bonding, which compensates poorly for the low coordination number of silicon, especially in cationic complexes.[7,14] The η^3-binding mode is mainly the result of donation from a filled SiH_2 bonding orbital into two lobes of an unoccupied 4d orbital on ruthenium (Figure 2). This donation, coupled with weak π-back-donation from ruthenium to the silane (evident from slight Si−H activation and NBO calculations[23] for **2a′**), depletes electron density from silicon. The LUMOs of **2a,b** result from an out-of-phase combination of a ruthenium 4d orbital and a silicon 3p orbital, with a nodal plane that contains the hydrogen atoms. A similar LUMO was recently reported for a cationic Ni(II) complex ($[(dtbpe)Ni(\mu\text{-}H)SiMes_2][BAr^F_4]$) that possesses one Ni−H−Si three-center, two-electron bond, which results from arrested 1,2-hydrogen migration.[24] Interestingly, LUMOs of this type strongly resemble the π^*-orbital that serves as the electron pair acceptor orbital in silylene complexes.[7,14,25] Thus, the η^3-silane complexes **2a,b** possess a suitable acceptor orbital at the silicon center, even though relatively strong Si−H interactions maintain a four-coordinate, tetrahedral geometry at silicon.

Base adducts **4b** and **6** were investigated using DFT geometry optimization[20] and NBO[23] calculations. In the optimized structures (**4b′** and **6′**), the Ru−H and Si−H distances are slightly longer than those determined by X-ray crystallography, but all three hydride ligands are within bonding distance of silicon (d(Si−H) 1.872, 2.006, 2.059 Å, **4b′**; 1.867, 1.933, 2.076 Å, **6′**). The Ru−H−Si interactions were examined using NBO analysis to assess delocalization of electron density from $\{[PhBP^{Ph}_3]RuH_3\}^{2-}$ to $[SiPh_2(DMAP)]^{2+}$ or $[SiPhCl(PMe_3)]^{2+}$. All of the Ru−H bonds were found to be of relatively low occupancy (1.55−1.60 e^-), with significant electron delocalization onto silicon. Three ruthenium 4d orbitals were found to be of relatively high occupancy (**4b′**, 1.928, 1.925, 1.862 e^-; **6′**, 1.936, 1.932, 1.819 e^-), with the lowest-occupancy orbital for each complex exhibiting slight delocalization onto silicon. Thus, donation from Ru to Si appears to be relatively unimportant for stabilizing the η^3-H_2SiRR'(base) ligand, which is instead stabilized via donation from a Ru−H bond to the silicon center, resulting in a total of three Ru−H−Si three-center, two-electron bonds.

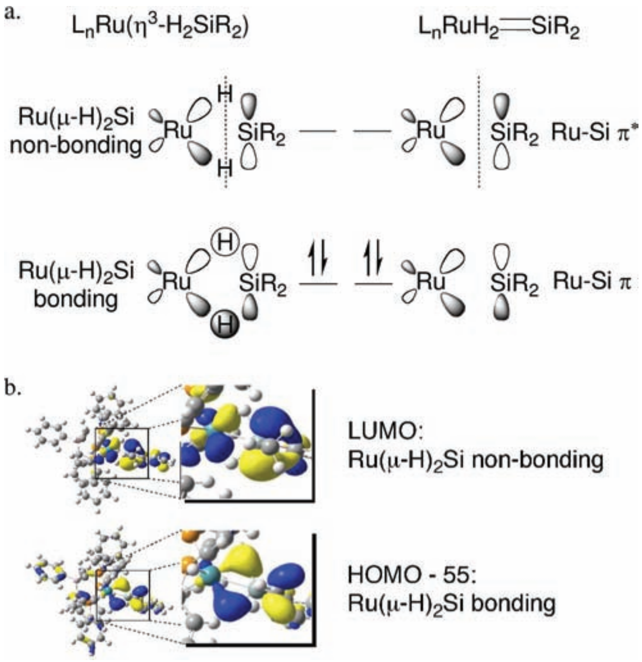


Figure 2. (a) Comparison of frontier molecular orbitals in $Ru(\eta^3\text{-}H_2SiR_2)$ complexes (left) with those of $L_nRuH_2{=}SiR_2$ (right). (b) Computationally determined orbital representations from DFT calculations of **2a′**.

In summary, complexes **2a,b** demonstrate an interesting type of metal-promoted activation for a silane. The partial activation of two Si−H bonds in **2a,b** results in properties similar to those of related silylene dihydride complexes, which result from complete cleavage of two Si−H bonds. Notably, both types of complexes feature an electrophilic silicon center that forms stable adducts with Lewis bases. Previously, intermolecular coordination of Lewis bases to silicon ligands was known only for the formation of base-stabilized silylene complexes (to give four-coordinate silicon). Thus, the base adducts **3**, **4a,b**, and **6** represent the first transition metal complexes to feature neutral, two-electron donors bound to hypercoordinate silicon centers. In the absence of transition metals, hypercoordinate silicon species are generally associated with silanes possessing electron-withdrawing substituents (NR_2, OR, F, and Cl) but have not been observed for silanes featuring only Si−C and Si−H bonds.[26] Interestingly, transition metal complexes with hypercoordinate silicon centers have been proposed as intermediates in catalytic ketone hydrosilations[27] and catalytic Si−H hydrolysis.[28] In these proposed mechanisms, a basic substrate (ketone or water) coordinates directly to the silicon center of a silyl ligand[27] or an η^3-H_2SiR_3 ligand,[28] but the resulting intermediates were not observed. The reaction chemistry of the η^3-silane complexes is currently being explored, within the context of their ability to promote catalytic hydrosilations.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental, spectroscopic, and computational details and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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