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Migration/Redistribution

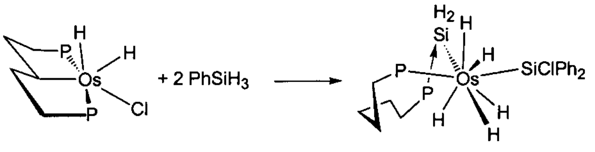
Polyhydrido(silylene)osmium and Silyl(dinitrogen)ruthenium Products Through Redistribution of Phenylsilane with Osmium and Ruthenium Pincer Complexes[**]

Dmitry G. Gusev, Frédéric-Georges Fontaine, Alan J. Lough, and Davit Zargarian**

Transition-metal silylene complexes, silicon analogues of metal carbenes, are reactive species believed to be important intermediates in the industrial synthesis of chloromethylsilanes,[1] the catalytic oligomerization of hydrosilanes,[2] and the redistribution chemistry of organosilanes.[3] The high reactivity of metal silylenes is related to the electron deficiency of the silicon center, which is presumably due to the very weak π bonding between the silicon atom and the transition metal.[4] Consistent with this notion, in most of the complexes reported to date[5] the silylene moiety requires stabilization from coordinating Lewis bases and/or hetero-atom-based substituents (e.g., OR, SR, NR_2),[6] whereas nonstabilized silylene complexes are difficult to isolate.[7]

The tendency of Os and Ru pincer complexes to give coordinatively unsaturated alkylidene and vinylidene products in reactions with alkynes[8a] prompted us to investigate their reactivity towards hydrosilanes with the expectation that addition or 1,2 migration of the Si–H bonds might afford silylene products. Here we describe silylene and silyl complexes obtained from the reaction of $PhSiH_3$ with $[OsH_2Cl\{CH(C_2H_4P\textit{t}Bu_2)_2\}]$ (**1**),[8b] $[OsH_2Cl\{2,6\text{-}(CH_2P\textit{t}Bu_2)_2C_6H_3\}]$ (**2**),[8c] and $[RuHCl\{1,3\text{-}(CH_2P\textit{t}Bu_2)_2\text{-}C_6H_4\}]$ (**3**).[8d]

Addition of 2 equiv of $PhSiH_3$ to **1** in toluene afforded the pentahydrido complex **4** in 83 % yield [Eq. (1), P = P*t*Bu₂]. A



1 **4** (1)

single-crystal X-ray analysis of **4** showed that the Os center adopts an 8-coordinate, dodecahedral geometry consisting of two orthogonal, trapezoidal planes defined by the atoms $Si1,H1_{Os},H5_{Os},P2$ and $Si2,H3_{Os},H4_{Os},H2_{Os}$ (Figure 1, left). The Os–Si distances for the silyl (2.374 Å) and the base-stabilized silylene (2.386 Å) ligand are in the normal range for Os–Si single bonds in hydrido(silyl)osmium complexes (3.34 to 2.49 Å).[9] The anticipated uncertainty associated with locating the hydride ligands in the solid-state structure of **4** prompted a study of its structure using ONIOM (DFT/HF) geometry optimization (Figure 1, right);[10] the closeness of the computational and experimental data indicates that the structure of this complex has been established reliably. Solution NMR data are also consistent with the proposed structure for **4** and show that the hydride ligands are highly fluxional. For example, the averaged OsH_5 resonance did not decoalesce down to −100 °C (^1H NMR, $[D_8]$toluene) and its

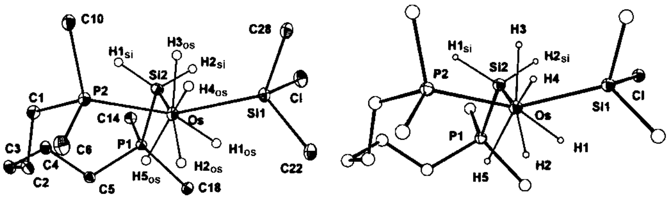


Figure 1. Partial experimental (left) and calculated (right) structures of **4** with the methyl groups and the co-crystallized toluene molecule omitted for clarity. Key experimental parameters [Å, deg]: Os-Si1 2.3739(8), Os-Si2 2.3857(8), Os-P2 2.4044(8), P1-Si2 2.361(1); P1-Si2-Os 120.29(3), P2-Os-Si1 140.63(3), P2-Os-Si2 100.96(3), Si1-Os-Si2 104.84(3), $H1_{Si}$-Si2-$H2_{Si}$ 102.9(19), H_{Si}-Si2-Os (av.) 120.2(14). Calculated parameters [Å, deg]: Os-Si1 2.417, Os-Si2 2.409, Os-P2 2.454, P1-Si2 2.363, Si1···H1 2.071, Si2···H3 2.246, Os-H1–Os-H5 1.638, 1.635, 1.670, 1.642, 1.653; P1-Si2-Os 124.3, P2-Os-Si1 142.2, P2-Os-Si2 99.8, Si1-Os-Si2 101.3, $H1_{Si}$-Si2-$H2_{Si}$ 101.0, H_{Si}-Si2-Os (av.) 120.9, H2···H5 1.883 (the shortest H···H separation).

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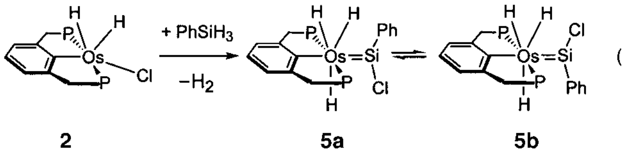
average relaxation time $T1_{min}$ was long (215 ms at −20 °C and 300 MHz), which is typical of polyhydrides with no short H···H contacts.

Evidently, complex **1** and two molecules of $PhSiH_3$ have undergone a series of redistribution reactions culminating in the net hydrogenation of the Os–C bond and the generation of one silyl, one base-stabilized silylene, and five hydride ligands. Complex **4** is the first compound bearing a base-stabilized SiH_2 ligand. We have briefly probed the relative stability of the P→Si interaction in the presence of other Lewis bases. Thus, addition of 1 equiv of NEt_3 to a C_6D_6 solution of **4** reduced the intensities of the ^{31}P resonances attributed to the P nuclei coordinated to the SiH_2 moiety ($\delta = 14.5$ ppm) and the Os center ($\delta = 56.6$ ppm), and gave rise to two new resonances at $\delta = 27.4$ and 50.3 ppm (conversion ca. 50 %). The chemical shift of one of the new resonances is very close to that of the uncoordinated bis(di-*tert*-butylphosphanyl)pentane ligand ($\delta = 27.7$ ppm in C_6D_6), indicating that this ligand is monodentate in the resulting complex. Similar observations were made when 1 equiv of PCy_3 was reacted with **4**: new ^{31}P resonances emerged at $\delta = 27.5$, 48.9, and −4.9 ppm (conversion ca. 80 %); decoupling experiments have allowed us to assign the latter resonance to the $Cy_3P \rightarrow SiH_2$ moiety. These preliminary observations demonstrate that good Lewis bases can displace the $PtBu_2$ group, thereby generating new donor-stabilized SiH_2 complexes.

To better understand the influence of the ligand on the reactivity of **1,** we investigated the reaction of $PhSiH_3$ with complex **2,** a direct analogue of **1** that has a pincer ligand with a more rigid backbone. In this case, the trihydrido(silylene) product **5** was obtained in 60 % yield [Eq. (2), $P = PtBu_2$].



(2)

Complex **5** undergoes a slow decomposition at room temperature, both in the solid and in solution, as evident from a gradual color change from yellow to dark brown. The thermal instability of **5** prevented crystallographic characterization, but NMR spectra collected at low temperature using samples prepared at −70 °C established the identity of the product as a trihydrido(silylene) complex that exists as two rotamers in solution, as described below. In addition, a computational study using the ONIOM (DFT/HF) methodology supported the structural assignments for both isomers (the optimized structure of **5a** is shown in Figure 2).

The $^{31}P\{^1H\}$ NMR spectrum of the isolated solid showed a single resonance ($\delta = 85.7$ ppm), whereas the $^{29}Si\{^1H\}$ NMR spectrum showed two triplets (6:1 signal intensity ratio) in a chemical shift region characteristic of silylenes ($\delta = 239.3$ (**5a**) and 246.5 ppm (**5b**), $^2J_{PSi} = 9.4$ Hz). Two sets of resonances were also observed in the hydride region of the ^1H NMR spectrum (1:2 intensity ratio within each set), implying two different trihydrido substructures. We interpret these observations to indicate that **5** is a silylene complex with a plane of symmetry that renders the two phosphorus nuclei equivalent; the rotation of the silylene moiety about the Os–Si bond gives rise to two rotamers, which were assigned the structures **5a** and **5b** on the basis of the difference NOE spectra. For example, isomer **5a** showed a strong NOE between the SiPh and the H2/H3 signals, whereas no NOE was detected between the signals for the *ortho* hydrogen atoms of SiPh and H1 (numbering according to Figure 2). In contrast, a strong NOE was detected in isomer **5b** between the *ortho* hydrogen atoms of SiPh and H1. The NOE experiments also indicated a slow exchange at −70 °C between **5a** and **5b**: irradiation of the H1 resonance of one isomer resulted in a partial saturation transfer to the corresponding hydride resonance of the other. Integration of the hydride signals allowed us to determine that the **5b**/**5a** equilibrium has a small ΔG (−0.7 kcal mol^{-1}); consistent with this, the computational study showed a very small energy difference (−0.01 kcal mol^{-1}) between the two isomers.

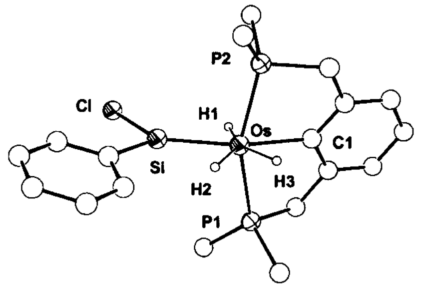
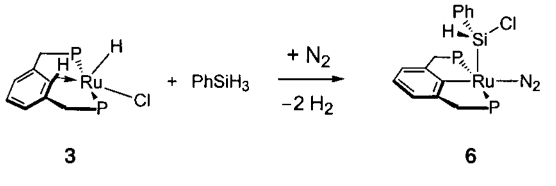


Figure 2. Partial calculated structure of **5a** with the methyl groups omitted for clarity. Key parameters [Å, deg]: Os-Si 2.281, Os-C1 2.171, Os-P1 2.387, Os-P2 2.394, Os-H1 1.670, Os-H2 1.641, Os-H3 1.651, H2···H3 1.652; P1-Os-P2 157.3, Si-Os-C1 161.9, Si-Os-H1 82.4, Si-Os-H2 63.9, C1-Os-H1 79.9, C1-Os-H3 74.3, H2-Os-H3 60.2.

The different reactivities of **1** and **2** underline the importance of the auxiliary ligand in determining the course and outcome of the reaction with $PhSiH_3$. We have also probed the importance of the metal atom by reacting $PhSiH_3$ with **3**, the Ru analogue of **2** that displays an agostic interaction between the central C–H moiety and the Ru center. This reaction gave the dinitrogen(silyl) complex **6** in 75 % yield [Eq. (3), $P = PtBu_2$]. The identity of **6** was established by spectroscopic studies and X-ray crystallography (Figure 3), as described below.



(3)

The IR spectrum of complex **6** features strong N≡N and Si–H stretches at 2142 and 2105 cm^{-1}, respectively. The presence of the Si–H group was also evident from the NMR spectra, which showed a ^1H signal ($\delta = 5.37$ ppm, d, $^3J_{PH} =$

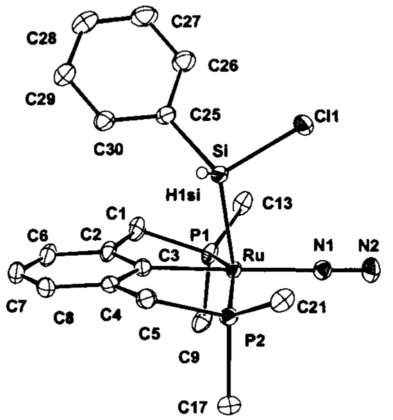


Figure 3. Partial experimental structures of **6** with the methyl groups omitted for clarity. Key parameters [Å, deg]: Ru-C3 2.068(3), Ru-Si 2.2821(7), Ru-N1 2.014(2), Ru-P1 2.3512(7), Ru-P2 2.3632(7), N1-N2 1.099(3); P1-Ru-P2 157.35(3), C3-Ru-Si 78.23(7), C3-Ru-N1 178.5(1), Si-Ru-N1 100.33(7).

17.7 Hz) featuring the anticipated Si satellites ($^1J_{SiH} = 206$ Hz) and a $^{29}Si\{^1H\}$ signal with the appropriate multiplicity ($\delta = 31.5$ ppm, t, $^2J_{PSi} = 24$ Hz). The asymmetric nature of this silyl ligand renders the CH_2 and $PtBu_2$ groups inequivalent in the NMR spectra of **6**. According to the X-ray data, the geometry around Ru in **6** is square-pyramidal with the silyl ligand occupying the apical position; the absence of a ligand *trans* to the silyl moiety is presumably responsible for the very short Ru–Si bond (2.282 Å). The Ru–N (2.014 Å) and N≡N (1.099 Å) distances are similar to the corresponding distances in related neutral dinitrogen complexes: $[RuH(N_2)\{CH(C_2H_4PtBu_2)_2\}]$ (1.965/1.117 Å),[11a] $[RuH_2(N_2)\{\kappa^3(P,P,P)\text{-}PhP(C_3H_6PCy_2)_2\}]$ (2.005/1.093 Å),[11b] and $[(PPh_3)_2RuH(\mu\text{-}H_3)Ru(N_2)(PPh_3)_2]$ (2.003/1.086 Å).[11c]

A comparison of the reactivities observed for complexes **2** and **3** provides some insight into the mechanism of their reactions with $PhSiH_3$. The following sequence of steps can be envisaged: 1) addition of $PhSiH_3$ to **2**/**3** generates the initial silyl ligand $PhSiH_2$ and releases H_2; 2) a redistributive SiH/MCl exchange gives the 16-electron intermediate [(PCP-ligand)$MH_2(PhSi(H)Cl)$]; 3) the Os^{IV} intermediate undergoes a 1,2 migration of SiH to give the trihydrido(silylene) complex **5**, whereas its Ru counterpart loses H_2 to give the dinitrogen(silyl) complex **6**. The difference in the reactivities of **2** and **3** is presumably due to the weaker Ru–H bonds (compared to Os–H bonds) and the prevalence of the +2 oxidation state in the chemistry of Ru complexes stabilized by phosphanes.

In summary, the described reactions of $PhSiH_3$ with complexes **1**–**3** have provided an opportunity to study the direct and unassisted conversion of a hydrosilane to transition-metal silylene derivatives, a transformation believed to be important in many catalytic processes involving organosilicon compounds.[12] The spontaneous silyl-to-silylene conversions observed here are rather rare, though they can be induced by photolysis[13] or assisted by Lewis acids.[14] On the other hand, silylene formation by Si–SiR_3 migrations has been observed with Rh^I,[15] Ir^I,[16] and Ni^{II}[17] systems. The transformations with the Os complex **1** are even more interesting, since they involve complex redistribution reactions that convert two molecules of $PhSiH_3$ to the silyl ligand Ph_2SiCl and the unprecedented parent silylene moiety SiH_2.

Experimental Section

Spectroscopic data for compounds **4**–**6** are given below; all other information pertaining to the synthetic and computational work is provided in the Supporting Information. Complete crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. CCDC-190307 (**4**) and CCDC-190308 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Complex **4**: elemental analysis calcd for $C_{33}H_{63}ClOsP_2Si_2\cdot$toluene (895.811): C 53.63, H 7.99; found: C 53.61, H 8.40. IR (Nujol): $\tilde{\nu}(\nu_{SiH}, \nu_{OsH}) = 2079, 2066, 2001, 1913\ cm^{-1}$. NMR (20 °C, C_6D_6, J in Hz): ^1H NMR: $\delta = -9.70$ (ddt, $^2J_{HP} = 5.9$, $^3J_{HP} = 8.1$, $^3J_{HH} = 1.6$, 5H, OsH_5), 1.00 (d, $^3J_{HP} = 12.9$, 18H, CH_3), 1.16 (d, $^3J_{HP} = 12.3$, 18H, CH_3), 1.1–1.8 (m, 10H, CH_2), 4.74 (dd, $^2J_{HP} = 19.0$, $^3J_{HP} = 3.0$, $^1J_{HSi} = 179.3$, SiH_2), 7.12, 7.30, 8.34 ppm (m, 10H, Ph). $^{13}C\{^1H\}$ NMR: $\delta = 14.0$ (d, $J_{CP} = 21.7$, CH_2), 20.3 (s, CH_2), 21.0 (d, $J_{CP} = 17.7$, CH_2), 22.9 (d, $J_{CP} = 1.6$, CH_2), 29.6 (dd, $J_{CP} = 8.5, 10.2$, CH_2), 29.4 (s, CH_3), 30.0 (s, CH_3), 34.6 (d, $J_{CP} = 17.1$, PC), 35.3 (d, $J_{CP} = 20.7$, PC), 127.0 (s, CH), 127.5 (s, CH), 135.4 (s, CH), 151.5 ppm (d, $J_{CP} = 2.7$, C). $^{31}P\{^1H\}$ NMR: $\delta = 56.6$ ($^2J_{PSi} = 27.8$), 14.5 ppm ($^1J_{PSi} = 44.6$). $^{29}Si\{^1H\}$ NMR: $\delta = 30.4$ (dd, $^3J_{SiP} = 2.8$, $^2J_{SiP} = 27.8$), -67.4 ppm (dd, $^2J_{SiP} = 5.5$, $^1J_{SiP} = 44.7$).

Complex **5**: IR (Nujol): $\tilde{\nu}(\nu_{OsH}) = 2177, 2089, 1870\ cm^{-1}$. NMR (−70 °C, $[D_8]$toluene, J in Hz): ^1H NMR: $\delta = -7.50$ (**5a**), -7.34 (**5b**) (br, 2H, OsH_2), -6.98 (**5b**) (t, $^2J_{HP} = 11.4$, OsH), -6.33 ppm (**5a**) (t, $^2J_{HP} = 13.8$, OsH). $^1H\{^{31}P\}$ NMR: $\delta = 1.01$ (s, 18H, CH_3), 1.18 (s, 18H, CH_3), 3.24 (d, $^2J_{HH} = 15.9$, 2H, CH_2), 3.41 (d, $^2J_{HH} = 15.9$, 2H, CH_2), 7.0–7.3 (m, 6H, Ar), 8.66 ppm (d, $^2J_{HP} = 7.5$, 2H, Ph). $^{31}P\{^1H\}$ NMR: $\delta = 85.7$ ppm (s). $^{13}C\{^1H\}$ NMR: $\delta = 29.2$ (br, CH_3), 34.0 (vt, $^vJ = 10.5$, PC), 35.9 (vt, $^vJ = 12.0$, PC), 42.8 (vt, $^vJ = 14.8$, CH_2), 120.0 (vt, $^vJ = 7.8$, CH, Ar), 123.3 (s, CH, Ar), 132.4 (s, CH, Ph), 128.8 (s, CH, Ph), 135.2 (s, CH, Ph), 149.3 (vt, $^vJ = 8.5$, C, Ar), 149.9 (s, C, Ph), 155.2 ppm (t, $^2J_{CP} = 3.7$, RuC). $^{29}Si\{^1H\}$ NMR: $\delta = 239.3$ (**5a**), 246.5 ppm (**5b**) (t, $^2J_{SiP} = 9.4$).

Complex **6**: elemental analysis calcd for $C_{30}H_{49}ClN_2P_2RuSi$ (664.29): C 54.24, H 7.43, N 4.22; found: C 53.90, H 7.64, N 4.02. IR (Nujol): $\tilde{\nu} = 2142\ (\nu_{N=N})$, $2105\ cm^{-1}\ (\nu_{SiH})$. NMR ($[D_8]$toluene, J in Hz): ^1H NMR: $\delta = 5.37$ ppm (d, $^3J_{HP} = 17.7$, $^1J_{HSi} = 206$, SiH). $^1H\{^{31}P\}$ NMR: $\delta = 0.90, 0.94, 1.20, 1.42$ (s, 36H, CH_3), 2.56 (d, $^2J_{HH} = 16.4$, 1H, CH_2), 2.78 (d, $^2J_{HH} = 16.4$, 1H, CH_2), 3.09 (d, $^2J_{HH} = 16.7$, 1H, CH_2), 3.73 (d, $^2J_{HH} = 16.7$, 1H, CH_2), 6.9–7.1 ppm (m, 8H, Ar). $^{31}P\{^1H\}$ NMR: $\delta = 74.8, 80.7$ ppm (d, $^2J_{PP} = 217$). $^{13}C\{^1H\}$ NMR: $\delta = 30.5, 30.6, 32.1, 32.9$ (d, CH_3), 35.3 (d, $^1J_{CP} = 21.9$, CH_2), 36.3 (d, $^1J_{CP} = 19.3$, CH_2), 35.0, 36.6, 37.5, 38.1 (d, PC), 121.9 (d, $^3J_{CP} = 17.0$, CH, Ar), 122.5 (d, $^3J_{CP} = 16.7$, CH, Ar), 124.2 (s, CH, Ar), 126.5, 127.8, 135.6 (s, CH, Ph), 144.6 (d, $^3J_{CP} = 2.3$, SiC, Ph), 156.0 (m, C, Ar), 178.1 ppm (t, $^2J_{CP} = 2.9$, RuC). $^{29}Si\{^1H\}$ NMR: $\delta = 31.5$ ppm (t, $^2J_{SiP} = 24$).

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Asbestos Decontamination

Soil Fungal Hyphae Bind and Attack Asbestos Fibers**

Elena Martino, Laura Prandi, Ivana Fenoglio, Paola Bonfante, Silvia Perotto, and Bice Fubini**

Once a major issue in occupational health and safety, asbestos has now become a general environmental problem.[1] Several mountain areas—from the western Alps in Italy to the Sierra Nevada in the USA—are rich in asbestos and asbestiform minerals, and many defunct asbestos industries and mines have left substantial amounts of asbestos fibers on the abandoned sites. Exposure to airborne asbestos fibrils causes a severe pneumoconiosis (asbestosis) and malignancies such as bronchogenic carcinoma and pleural mesothelioma.[2–4] The decontamination of asbestos fibers dispersed over wide areas of soil and in waters obviously requires a different approach from what was proposed for asbestos localized in buildings.[5] The fibers cannot be removed but have to be inactivated in situ without damaging the environment. New, environmentally friendly techniques are thus required for

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