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A Fischer-Type Silylene Complex of Platinum: [*trans*-$(Cy_3P)_2(H)Pt{=}Si(SEt)_2$]$BPh_4$

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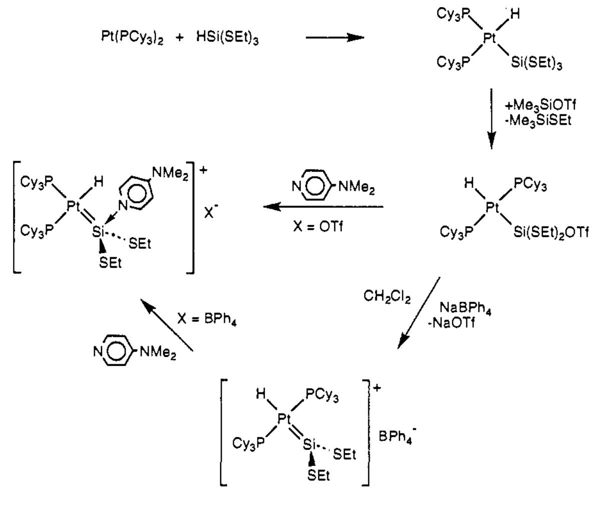
Since the discovery of transition-metal carbene complexes, $L_nM{=}CR_2$, in the early 1960s,[1] chemists have pursued possible synthetic routes to the congeneric silicon compounds, $L_nM{=}SiR_2$ (silylene complexes). Interest in silylene complexes intensified as it became clear that the carbene derivatives could play important roles in synthesis.[2] Indeed, silylene complexes have often been invoked as unobserved intermediates in proposed mechanisms.[3] However, attempted syntheses of silylene complexes have met with little success, despite development of routes to well-defined germylene, stannylene, and plumbylene analogs.[4] Significant advances occurred in 1987, when separate reports described the base-stabilized complexes $(CO)_4Fe{=}Si(O^tBu)_2[OP(NMe_2)_3]$ and $[Cp^*(PMe_3)_2Ru{=}SiPh_2(NCMe)]^+BPh_4^-$ ($Cp^* = \eta^5\text{-}C_5Me_5$).[5,6] A number of related adducts containing tetrahedral silicon are now known.[7]

The marked difficulty encountered in obtaining base-free silylene complexes raises questions concerning the fundamental nature of metal–silylene bonding interactions and highlights the necessity for defining the structural and electronic properties of these elusive species. The recent isolation of stable, base-free silylene complexes of the type $Cp^*(PMe_3)_2Ru{=}Si(SR)_2^+$ [8] and dynamic studies of their acetonitrile adducts[9] suggest that thiolate groups have a stabilizing influence on the silylene ligand, perhaps via 3p–3p π-donation from sulfur to silicon.[10] However, structural information has remained unavailable for these compounds. More recently, we have established the presence of a planar, sp^2-hybridized silicon center in a complex with two transition metals, $Cp^*(PMe_3)_2Ru{-}Si(STol\text{-}p)Os(CO)_4$ (Tol = tolyl).[11] In search of new transition-metal silylene complexes which could be structurally characterized, we have turned our attention to platinum derivatives. Such systems should also yield more information on known catalytic processes, since platinum provides many of the most widely used catalysts for transformations of organosilicon compounds.[3]

Scheme I



The starting square-planar platinum silyl complex is obtained by oxidative addition of $HSi(SEt)_3$ to $Pt(PCy_3)_2$ (Cy = cyclohexyl), as shown in Scheme I. The resulting product has *cis* stereochemistry (by ^1H and ^{31}P NMR spectroscopy), but it is quantitatively isomerized to the *trans* geometry upon photolysis (3 h, 450-W Hg lamp) or heating (over ca. 8 h at 65 °C in benzene-d_6).[12] *cis*-$(Cy_3P)_2Pt(H)Si(SEt)_3$ reacts with trimethylsilyl triflate, Me_3SiOTf ($OTf = OSO_2CF_3$), in a pentane/diethyl ether solution over 3 days to produce the silyl complex *trans*-$(Cy_3P)_2Pt(H)Si(SEt)_2OTf$ in 57% yield. The latter triflate derivative has inequivalent methylene protons that appear in the ^1H NMR spectrum at room temperature as overlapping multiplets centered at δ 3.30 (benzene-d_6). These resonances coalesce at 40 °C, probably by a mechanism involving dissociation of the triflate anion to transiently produce the silylene complex $[(Cy_3P)_2(H)Pt{=}Si(SEt)_2]^+OTf^-$, in which the methylene hydrogens are equivalent. Related behavior has been observed for the ruthenium complex $Cp^*(PMe_3)_2RuSi(SEt)_2OTf$, for which the diastereotopic methylene hydrogens coalesce at 21 °C (toluene-d_8 solution).[8] The labile triflate group in *trans*-$(Cy_3P)_2Pt(H)Si(SEt)_2OTf$ is displaced in benzene-d_6 by the neutral two-electron donor (dimethylamino)pyridine (DMAP), to afford the donor-

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(12) Selected data are as follows. *cis*-$(PCy_3)_2(H)PtSi(SEt)_3$: $^{31}P\{^1H\}$NMR (benzene-d_6, 121.5 MHz, 23 °C) δ 39.31 (mult with ^{195}Pt satellites as dd for each P, $J_{PPt} = 6454$ Hz, $J_{PP} = 33$ Hz, and $J_{PPt} = 4409$ Hz, $J_{PP} = 33$ Hz), IR (Nujol, CsI, cm^{-1}) 2088 m (PtH). *trans*-$(PCy_3)_2(H)PtSi(SEt)_3$: $^{31}P\{^1H\}$NMR (benzene-d_6, 121.5 MHz, 23 °C) δ 39.61 (s with ^{195}Pt satellites, $J_{PPt} = 2646$ Hz); IR (Nujol, CsI, cm^{-1}), 2010 w (PtH). *trans*-$(PCy_3)_2(H)PtSi(SEt)_2OTf$: $^{31}P\{^1H\}$ NMR (benzene-d_6, 121.5 MHz, 23 °C) δ 40.61 (s with ^{195}Pt satellites, $J_{PPt} = 2561$ Hz); IR (Nujol, CsI, cm^{-1}) 2058 w (PtH). *cis*, $[(PCy_3)_2(H)Pt(Si(SEt)_2DMAP)]$ [OTf]: $^{31}P\{^1H\}$ NMR (dichloromethane-d_2, 121.5 MHz, 23 °C) δ 39.97 (d with ^{195}Pt satellites, $J_{PPt} = 2561$ Hz, $J_{PP} = 15$ Hz), 38.50 (d with ^{195}Pt satellites, $J_{PPt} = 2022$, Hz, $J_{PP} = 15$ Hz); IR (dichloromethane, KBr, cm^{-1}), 2060 w (PtH). *trans*-$[(PCy_3)_2(H)Pt{=}Si(SEt)_2][BPh_4]$: $^{31}P\{^1H\}$ NMR (dichloromethane-d_2, 121.5 MHz, 23 °C) δ 51.51 (s with ^{195}Pt satellites, $J_{PPt} = 2279$ Hz), IR (dichloromethane, KBr, cm^{-1}), 2010 w (PtH).

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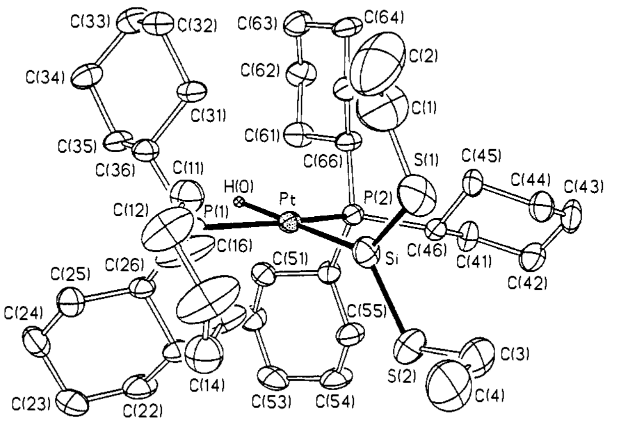


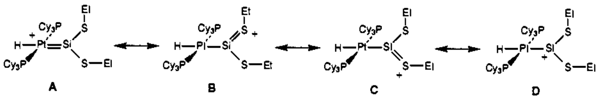
Figure 1. Structure of the cation in $[(Cy_3P)_2(H)Pt{=}Si(SEt)_2]BPh_4{\cdot}CH_2Cl_2$.

stabilized silylene complex [*trans*-$(Cy_3P)_2(H)Pt{=}Si(SEt)_2$-(DMAP)]OTf as the kinetic product. During crystallization of this compound from dichloromethane/diethyl ether, rearrangement to the *cis* isomer occurred (Scheme I).

The title compound was formed in the reaction of *trans*-$(Cy_3P)_2$-$Pt(H)Si(SEt)_2OTf$ with $NaBPh_4$ in dichloromethane (Scheme I). Precipitation of NaOTf produces a solution of the cationic silylene complex, which was crystallized from dichloromethane/diethyl ether in 56% yield. NMR spectra for the compound are consistent with the structure shown in Scheme I, with *trans* hydride and silylene ligands. Of most interest is the ^{29}Si chemical shift of 308.65 ppm, which is dramatically downfield-shifted from that for the triflate *trans*-$(Cy_3P)_2Pt(H)Si(SEt)_2OTf$, 89.69 ppm. Such low-field chemical shifts are found for the previously reported base-free silylene complexes $Cp^*(PMe_3)_2Ru{=}Si(SR)_2^+$, and low-field ^{13}C shifts are also associated with related carbene complexes.[2] The $^1J_{PtSi}$ coupling constant for the silylene complex (1558 Hz) is lower than the $^1J_{PtSi}$ value for the triflate derivative (1825 Hz), implying that the $Si(SEt)_2OTf$ ligand, being a better σ-donor, interacts more with the Pt 6s orbital than does $Si(SEt)_2$.[13]

The structure of [*trans*-$(Cy_3P)_2(H)Pt{=}Si(SEt)_2]^+$, shown in Figure 1, reveals a square-planar coordination geometry for platinum.[14] There are no short interionic or ion–solvent interactions in the solid state. Planarity of the silylene fragment (Si is only 0.04 Å out of the PtS_2 plane) and the summation of angles at silicon (359.9°) reflect sp^2 hybridization.[15] The plane of the silylene ligand is rotated 76° out of the least-squares plane of platinum donor atoms, implying that π-donation from the d_{xy} orbital, rather than from the somewhat lower-energy d_{xz} level, contributes more to the molecular bonding. This "perpendicular" orientation is observed for most square-planar platinum carbene complexes (exceptions occur when the carbene group is constrained as part of a metallacycle).[16] As in the latter cases, this geometry appears to result largely from steric interactions between the silylene substituents and bulky phosphine ligands.[16,17] Scheme II gives the principal resonance structures for [*trans*-$(Cy_3P)_2$-$(H)PtSi(SEt)_2]^+$.

Scheme II



The Pt–Si bond length, 2.270(2) Å, is short in comparison with those in related complexes such as *trans*-$(Cy_3P)_2Pt(H)Si$-$(SEt)_3$ (2.379(1) Å)[9] and *trans*-$(Cy_3P)_2Pt(H)SiH_3$ (2.382(3) Å).[18] The Si–S distances (2.092(4) and 2.074(4) Å) are also short, since Si–S bonds in $Cp^*(PMe_3)_2Ru{-}Si(SR)XY$ complexes generally fall in the range 2.17–2.20 Å,[6,9,11] and the Si–S distances in *trans*-$(Cy_3P)_2Pt(H)Si(SEt)_3$ average to 2.17 Å. The Si–S bond shortening observed for the silylene complex may be ascribed to the lower coordination number for silicon and some degree of π-bonding. The presence of some π-bonding is suggested by acute dihedral angles between the Si–S–C and SiS_2 planes of 9.9 and 10.7°. This results in roughly *cis* and *trans* orientations for the ethyl groups relative to the Pt atom in the solid-state structure, as depicted in Scheme II. However, since the integrity of these orientations is not upheld in dichloromethane solution down to −80 °C, there must be rapid rotation about the Si–S bonds. This contrasts with observations for analogous platinum carbenes, such as $(Ph_3P)_2(I)Pt{=}C(SMe)_2$, for which the rotational barrier about the C–S bonds is high enough for distinct rotamers to be observed at room temperature.[19]

Preliminary computational results based on the Fenske–Hall method[20] suggest that the low-coordinate silicon atom is stabilized more by π-donation from the sulfur atoms than by donation from platinum. While significant overlap exists between the silylene *p* orbital and orbitals of appropriate symmetry on the platinum and sulfur centers, only Si–S (and not Si–Pt) π-bonds are populated. An overlap population of 0.43 electrons per sulfur atom, or 0.86 electrons total, exists between the unhybridized silylene p orbital and the sulfur lone pairs. The computational results therefore suggest that the structure is best described as containing a low-valent silicon center stabilized primarily by π-interactions with the sulfur lone pairs and much less by π-bonding to platinum. In order to more quantitatively describe the bonding of this system, a correlated method such as MCSCF will be necessary.[21] These calculations are in progress.

Initial reactivity studies show that [*trans*-$(Cy_3P)_2(H)Pt{=}$ $Si(SEt)_2]^+BPh_4^-$ does not bind acetonitrile in dichloromethane solution but does bind the stronger base DMAP. We are currently focusing on defining the chemical properties of this complex as they pertain to known and potential catalytic cycles.

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Supplementary Material Available: Experimental procedures and characterization data for complexes, tables of crystal, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates (17 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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[14] Crystal data for [*trans*-$(Cy_3P)_2(H)Pt{=}Si(SEt)_2][BPh_4]{\cdot}CH_2Cl_2$: $C_{66}H_{99}BCl_2P_2PtS_2Si$, triclinic, $P\bar{1}$, $a = 11.567(2)$, $b = 14.510(2)$, and $c = 20.034(3)$ Å, $\alpha = 76.29(1)°$, $\beta = 87.71(1)°$, $\gamma = 83.27(1)°$, $V = 3244.0(9)$ Å^3, $Z = 2$. Of 11 117 reflections collected (Mo Kα, 2θ(max) = 50°, 233 K), 10 784 were independent and 6931 were observed. $R(F) = 4.49$ and $R_w(F) = 5.05$.

[15] Selected angles (deg): Pt–Si–S(1) 130.3(2), Pt–Si–S(2) 122.5(1), S(1)–Si–S(2) 107.1(2).

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