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Isolation and Characterization of Neutral Platinum Silylene Complexes of the Type $(R_3P)_2Pt{=}SiMes_2$ (Mes = 2,4,6-Trimethylphenyl)

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Unlike the analogous transition-metal carbene complexes, silylene complexes ($L_nM{=}SiR_2$) are extremely rare and poorly understood.[1] Nonetheless, such species have generated considerable interest since they appear to be involved in numerous transformations of organosilicon compounds.[2] For this reason, many synthetic efforts have targeted the isolation and study of complexes featuring silylene ligands. In recent years, these efforts have culminated in the syntheses of a number of transition metal compounds containing sp^2-hybridized silicon.[3] For the most part these compounds are cationic, having been obtained via an "anion-abstraction" method.[3a,4] Even among the limited number of silylene complexes known, a rich variety of bonding modes and reactivities have been observed. Of particular interest are neutral silylene complexes of the type $(R_3P)_2M{=}SiR_2$ (M = Pd, Pt), which have historically been the primary focus of speculation regarding catalytic silylene intermediates.[5] In this communication, we describe isolation of the first neutral silylene complexes of this type and initial reactivity studies with them.

Photolysis of a mixture of $Mes_2Si(SiMe_3)_2$[6] and $Pt(PCy_3)_2$[7] in hexanes resulted in a green, supersaturated solution of the silylene complex $(Cy_3P)_2Pt{=}SiMes_2$ (**1**; Scheme 1). After workup, this complex was isolated in 54% yield as green microcrystals. Similarly, red solutions of $(^iPr_3P)_2Pt{=}SiMes_2$ (**2**) were quantitatively produced from $Pt(P^iPr_3)_3$[7] and $Mes_2Si(SiMe_3)_2$ in benzene-d_6 (by ^1H and ^{31}P NMR spectroscopy), but removal of solvent resulted in complete conversion back to $Pt(P^iPr_3)_3$, along with a variety of unidentified silicon-containing products. Complex **1** is stable indefinitely in the solid state, but decomposes in solution over several days to $Pt(PCy_3)_2$ and uncharacterized silicon-containing compounds. For sparingly soluble **1**, a long accumulation time was required to observe the ^{29}Si NMR resonance (δ 358; J_{SiP} = 112 Hz), which confirmed the presence of the silylene ligand.[3] For the soluble complex **2** the ^{29}Si NMR signal was more readily observed, at δ 367 (J_{SiP} = 107 Hz; J_{SiPt} = 2973 Hz). For comparison, the only other platinum silylene complexes to be reported have ^{29}Si shifts of δ 309, for [*trans*-$(Cy_3P)_2(H)Pt{=}Si(SEt)_2$][$BPh_4$],[3c] and δ 338, for [$(^iPr_2PCH_2CH_2P^iPr_2)(H)Pt{=}SiMes_2$][$MeB(C_6F_5)_3$].[8]

X-ray quality crystals of **1** were grown from dilute (<0.04 M) reaction solutions. The molecular structure is shown in Scheme 1. The Pt−Si bond distance of 2.210(2) Å is the shortest yet reported, and is about 6% shorter than typical Pt−Si single bonds (2.30−2.40 Å).[1a,b] For comparison, the Pt−Si distance in [*trans*-$(Cy_3P)_2(H)PtSi(SEt)_2$][BPh_4] is 2.270(2) Å, but note that the latter complex was characterized as being "Fischer-like", with significant Si−S, but very little Pt−Si, π-bonding.[3c] The summation of angles about Si, 359.8(6)°, confirms the presence of a planar, sp^2-hybridized silicon atom, and the angles about platinum also sum within experimental error to 360°. The least-squares plane of the silylene ligand (including Pt, Si, and the two *ipso* carbons) and the coordination plane of platinum (Si, Pt, P, P) intersect at a dihedral angle of 68.6°, which is not optimal for Pt-to-Si π-donation. This deviation appears to result from the sterically hindered environment about the Pt−Si bond, as the expected dihedral angle of 90° is observed in structures of the related germylene and stannylene complexes $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$[9] and $(^iPr_2PCH_2CH_2P^iPr_2)PdSn[CH(SiMe_3)_2]_2$,[10] respectively.

Initial reactivity studies show that **1** quantitatively transfers its silylene group to water and alcohols via insertion into O−H bonds (Scheme 1). Thus, addition of ROH (R = H, Me, Et) to **1** resulted in the clean formation of $Pt(PCy_3)_2$ and the corresponding silane $Mes_2Si(OR)H$. No intermediates were observed while monitoring the reaction of **1** with ethanol at −60 °C (by ^1H and ^{31}P NMR spectroscopy in toluene-d_8). Related reactivity was previously reported for the base-stabilized silylene complex $[Cp^*(Me_3P)_2RuSiPh_2(NCMe)]^+$, which was presumed to dissociate acetonitrile prior to reaction with an alcohol.[11] This reactivity contrasts with what has been observed for $(^iPr_2PCH_2CH_2P^iPr_2)PdSn[CH(SiMe_3)_2]_2$, which reversibly adds H_2O across the Pd−Sn bond to form a palladium hydride species.[12] Reactions of **1** with various phosphines ($^iPr_2PCH_2CH_2P^iPr_2$, $Ph_2PCH_2CH_2PPh_2$, and PMe_3, in excess) led to PCy_3- and $SiMes_2$-displacement, with formation of the corresponding PtL_4 complex (quantitative by ^{31}P NMR spectroscopy). In these processes, the displaced silylene ligand is observed to decompose to a number of species (but not significant amounts of $Mes_2Si{=}SiMes_2$).

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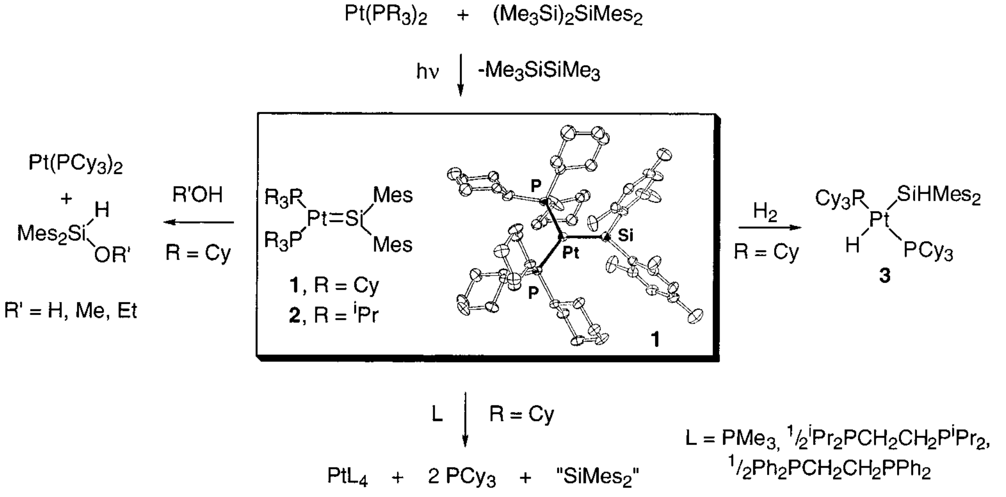
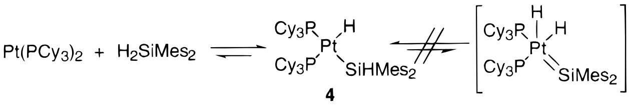
Scheme 1



Hydrogen (1 atm) reacts with a benzene solution of **1** over 2 days to form *trans*-$(Cy_3P)_2Pt(H)(SiHMes_2)$ (**3**, Scheme 1; by ^1H and ^{31}P NMR spectroscopy). With this slow conversion there is competing decomposition of **1** via loss of the silylene ligand to produce *trans*-$(Cy_3P)_2PtH_2$ (ca. 50%; *without* formation of Mes_2SiH_2). At higher temperatures (refluxing benzene-d_6), **3** is hydrogenated to *trans*-$(Cy_3P)_2PtH_2$ and Mes_2SiH_2. In contrast to the germylene complex $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$,[13] the addition of hydrogen to **1** is irreversible. Complex **3** is fluxional in solution as observed by variable-temperature ^{31}P NMR spectroscopy. At −29 °C, two doublets (δ 26.9, $J_{PtP} = 2632$ Hz, $J_{PP} = 346$ Hz; δ 33.6, $J_{PtP} = 2715$ Hz) are observed which, upon heating, broaden and coalesce to a singlet (δ 28.9, $J_{PtP} = 2707$ Hz) at 91 °C. The PtH and SiH ^1H NMR shifts are also temperature dependent; however, coalescence is obscured by the Cy resonances. This behavior is consistent with restricted rotation about the Pt−Si bond ($\Delta G^{\ddagger} = 15.8(4)$ kcal/mol). The mechanism of hydrogen addition to **1** could involve oxidative addition to the platinum center, followed by migration of hydride to the silylene ligand, or direct addition of hydrogen to the Pt═Si double bond. At this point the mechanism is unknown, but it is interesting to note that whereas the trans silyl hydride is formed by this reaction, the oxidative addition of Mes_2SiH_2 to $Pt(PCy_3)_2$ exclusively gives *cis*-$(Cy_3P)_2Pt(H)(SiHMes_2)$ (**4**). The *cis*-complex **4** isomerizes slowly to **3** at 90 °C, where its decomposition is more rapid ($t_{1/2}$ = ca. 45 min).

Interestingly, the PtH and SiH hydrogens of **4** undergo rapid exchange with a rate constant of 23(4) Hz (27 °C), as determined by ^1H NMR EXSY experiments. Given the stability of silylene ligands in this system, it seemed possible that this exchange could occur via an α-H migration process (eq 1). However, a reductive elimination−oxidative addition couple could also account for this observation. An intermolecular mechanism was suggested by the ^1H NMR EXSY spectrum, which contains cross-peaks corresponding to the exchange of ^{195}PtH hydrogens with complexes of **4** containing other Pt isotopes. More significantly, EXSY experiments revealed the exchange of PtH hydrogens with the SiH hydrogens of *free* H_2SiMes_2 (25 equiv), also with a rate constant of 23(4) Hz. In addition, ^{31}P EXSY NMR experiments provided a similar rate for phosphorus exchange. This exchange process was shown to be intramolecular based on the absence of cross-peaks between phosphorus signals in **4** and free PCy_3 in the ^{31}P EXSY spectra. Thus, hydrogen exchange in *cis*-$(Cy_3P)_2Pt(H)(SiHMes_2)$ occurs via the rate-determining reductive elimination of silane, which does not require prior phosphine dissociation. These results are consistent with our recent observation that hydrogen appears not to migrate to platinum in 4-coordinate $(^iPr_2PCH_2CH_2P^iPr_2)Pt(Me)SiHMes_2$, whereas the 3-coordinate cation $[(^iPr_2PCH_2CH_2P^iPr_2)PtSiHMes_2]^+$ rapidly converts to $[(^iPr_2PCH_2CH_2P^iPr_2)(H)Pt═SiMes_2]^+$.[8]



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Supporting Information Available: Synthetic details and characterization data for new compounds; crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **1** (16 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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