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Formation and X-ray Crystal Structure Determination of the Novel Triplatinum Cluster $[(Ph_3P)Pt(\mu\text{-}SiC_{12}H_8)]_3$ from Reaction of Silafluorene with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$

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*Summary: Reaction of silafluorene ($H_2SiC_{12}H_8$) with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ in C_6D_6 (or C_7D_8) provided the trinuclear complex $[(Ph_3P)Pt(\mu\text{-}SiC_{12}H_8)]_3$ (**3**). The structure of **3**, which exhibits a nonplanar Pt_3Si_3 core, was confirmed by X-ray crystallography.*

Oxidative addition reactions of primary and secondary hydrosilanes with late-transition-metal precursors have provided a variety of structural motifs.[1] Formal insertion of the metal center into the Si−H bond initially provides a complex with the general formula $L_nM(H)\text{-}SiR_3$. With primary and secondary hydrosilanes, residual protons at the bound silicon center (SiR_3, where R can be H) provide additional sites of reactivity that can give rise to dinuclear or higher order metal clusters.

Examples of different complexes that can be generated from Si−H bond activation reactions involving primary and secondary hydrosilanes with platinum centers are shown in Figure 1. Mononuclear complexes containing one silyl group (**A**)[2] or two silyl groups at platinum (**B**)[3] where only one Si−H bond has been reacted with a metal have been reported. In addition, dinuclear complexes containing bridging silylene moieties (**C**)[3a,b,4] as well as dinuclear species having nonclassical Pt···H···Si interactions (**D**)[2b,4g,5] have been prepared. More recently, a trinuclear platinum cluster containing a bridging silylene group has been isolated (**E**).[6] Dinuclear and especially trinuclear complexes containing Pt and Si are quite rare.

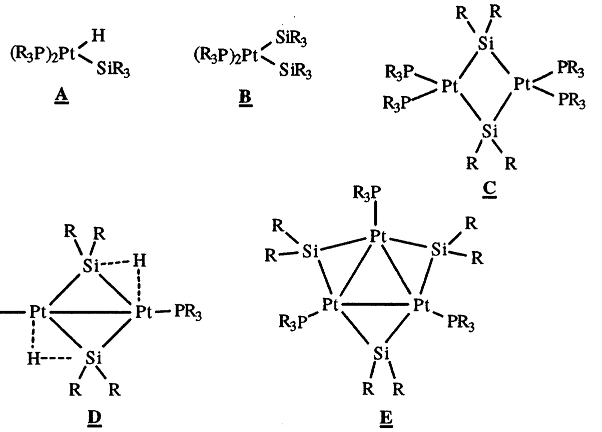

Figure 1. Examples of complexes formed from Si−H bond activation reactions involving primary and secondary hydrosilanes with Pt−phosphine precursors.

Herein, we report the synthesis of a triplatinum cluster containing a bridging silafluorenyl unit ($SiC_{12}H_8$) by starting from the secondary arylhydrosilane silafluorene ($H_2SiC_{12}H_8$)[7] and the Pt(0) precursor $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$. To the best of our knowledge, this is the first example of a trinuclear platinum complex containing bridging silylene units formed from mononuclear silicon and platinum precursors.

Reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with ($H_2SiC_{12}H_8$) (ca. 1:1 ratio) initially provided the oxidative addition product $(Ph_3P)_2Pt(H)[Si(H)C_{12}H_8]$ (**1**) in quantitative yield by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Complex **1** was characterized in solution only (C_6D_6 or C_7D_8).[8] After approximately 15 min the NMR signals for **1** disappeared. During the initial 15 min period a new broad resonance (ca. 20 ppm) intensified in the $^{31}P\{^1H\}$ spectrum. Low-temperature NMR experiments suggest that this species is the dinuclear complex **2**, which will be described in more detail in a full paper.[9]

The reaction mixture was continuously monitored by NMR spectroscopy over a period of several hours. After

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[8] Complex **1** was not isolated. Selected spectroscopic data for **1**: $^{31}P\{^1H\}$ NMR (C_7D_8, 202 MHz) δ 34.2 (d with Pt satellites, $^1J_{PtP}$ = 1877 Hz, $^2J_{PtP}$ = 7 Hz, P trans to Si), 33.9 (br s with Pt satellites, $^1J_{PtP}$ = 2533 Hz); ^1H NMR (C_7D_8, 500 MHz) δ 5.1 (m, 1H, SiH), −1.72 (dd with Pt satellites, 1H, Pt−H, $^1J_{PtH}$ = 956 Hz, $^2J_{PH}$ (trans) = 156 Hz, $^2J_{PH}$ (cis) = 21 Hz).

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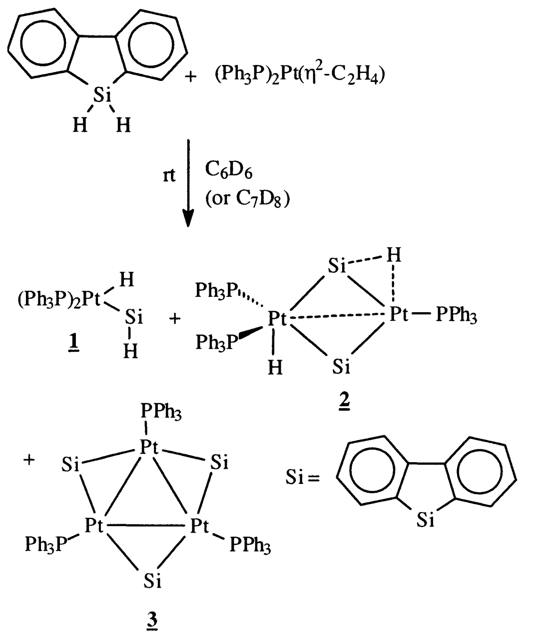
Scheme 1



approximately 2.5−3 h an additional new resonance appeared in the ^{31}P{^{1}H} NMR spectrum at ca. 70 ppm as a singlet with a complex Pt satellite pattern.[10] This resonance was assigned to the trinuclear Pt complex **3**.[11] Scheme 1 summarizes the products observed from reaction of silafluorene with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$.

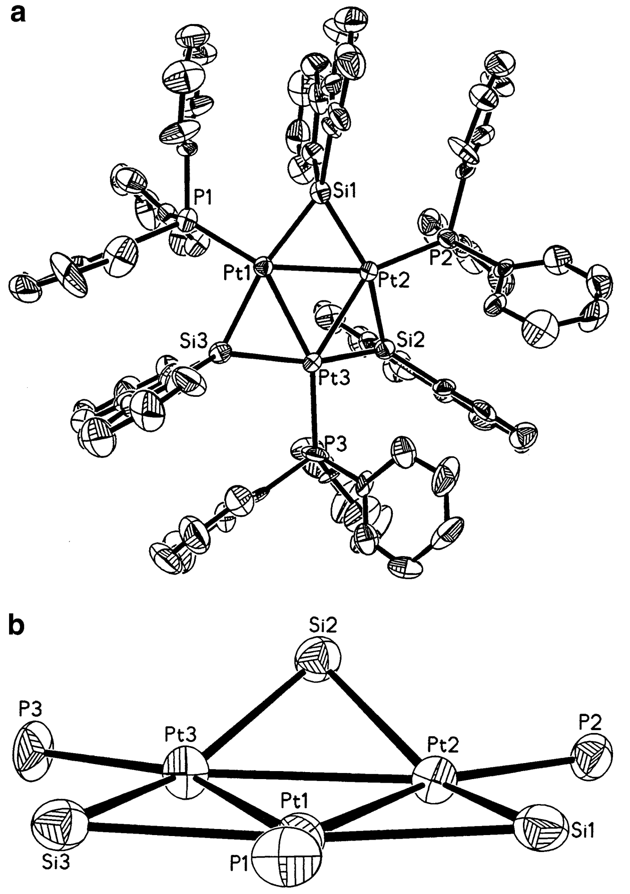


Figure 2. (a, top) Top view of the molecular structure of $[(Ph_3P)Pt(\mu\text{-}SiC_{12}H_8)]_3$ (**3**) (50% probability). (b, bottom) Side view of the molecular structure of **3** showing core $P_3Pt_3Si_3$ atoms only. Selected bond distances (Å) and angles (deg): Pt(1)−Pt(2) = 2.7080(11), Pt(1)−Pt(3) = 2.7114(11), Pt(2)−Pt(3) = 2.7033(11), Pt(1)−P(1) = 2.240(6), Pt(2)−P(2) = 2.238(5), Pt(3)−P(3) = 2.277(5), Pt(1)−Si(1) = 2.374(6), Pt(1)−Si(3) = 2.388(6), Pt(2)−Si(1) = 2.348(6), Pt(2)−Si(2) = 2.346(6), Pt(3)−Si(2) = 2.344(6), Pt(3)−Si(3) = 2.355(6); Pt(2)−Pt(1)−Pt(3) = 59.84(3), Pt(2)−Pt(3)−Pt(1) = 60.02(3), Pt(3)−Pt(2)−Pt(1) = 60.14(3), Pt(2)−Si(1)−Pt(1) = 69.99(17), Pt(3)−Si(2)−Pt(2) = 70.44(17), Pt(3)−Si(3)−Pt(1) = 69.74(17).

The structure of **3** was confirmed by X-ray crystallography (Figure 2).[12] Although the quality of the structural data for **3** does not permit a detailed discussion, it provides information for the basic features of the molecule. Each Pt in the triangular Pt core is bridged by a silafluorenylidene moiety, and one PPh_3 ligand is bound to each Pt center. The central Pt_3Si_3 core is nonplanar (Figure 2b). One silicon (Si2) lies above the plane defined by the remaining Pt_3Si_2 atoms by approximately 1 Å. In addition, one phosphorus atom (P1) also lies above that plane by nearly 0.4 Å, whereas the other two phosphorus centers lie in the same plane as the Pt_3Si_2 atoms. The unsymmetrical nature found in the solid-state structure of **3** may be due to packing forces. The Pt−Pt−Pt angles are acute, as a result of the triangular arrangement of the Pt_3 core (59−60°). The Pt−Si distances (2.34−2.38 Å) fall in the range[1] for other known Pt−Si complexes and are similar to those in the related structure $[(Me_3P)Pt(\mu\text{-}SiPh_2)]_3$.[6] The Pt−Pt distances are in the expected range (2.70−2.71 Å) for Pt−Pt single bonds in triangular platinum systems.[13,14] Due to the quality of the crystallographic data, the presence of a terminal or bridging

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(9) Two distinct resonances were observed in the ^{31}P{^{1}H} NMR spectrum at 17 (d) and 31 (t) ppm in a 2:1 ratio, each with two sets of Pt satellites. The ^{29}Si{^{1}H} NMR spectrum showed two peaks at 146 (t) and 154 (d) ppm, indicating two different silicon sites. In addition, the ^{1}H NMR spectrum exhibited two hydride signals at ca. −5 (t, with Pt satellites) and 2 ppm (d, Pt satellites not resolved). The data were obtained at 223 K and are consistent with an unsymmetrical environment about the two Pt centers in **2**. Precedence for a directly related unsymmetrical palladium dimer has recently been published; see: Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi, J.-C.; Yamamoto, T. *Organometallics* **1998**, *17*, 4929.

(10) The satellite pattern observed in the ^{31}P{^{1}H} NMR spectrum for **3** is in good agreement with a calculated spectrum for the related triplatinum complex $Pt_3(\mu\text{-}CO)_3(PCy_3)_3$; see: Moor, A.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chim. Acta* **1981**, *48*, 153.

(11) Silafluorene (73 mg, 0.40 mmol) and $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (250 mg, 0.33 mmol) were added to C_6D_6 (1.5 mL) and C_6H_6 (3.5 mL), resulting in a clear, amber red solution. After several hours, red crystals of **3** had precipitated, which were separated. Addition of hexane (8 mL) to the mother liquor resulted in precipitation of an additional crop of **3**. The solid was dried under vacuum for 2 h to give **3** (64 mg, 30%). Selected NMR data for **3**: ^{31}P{^{1}H} NMR (C_7D_8, 202 MHz) δ 70.5 (s with Pt satellites, $^{1}J_{PtP}$ = 3338 Hz, $^{2}J_{PtP}$ = 421 Hz, $^{3}J_{PP}$ = 80 Hz); ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.40 (d, $^{3}J_{HH}$ = 7.6 Hz), 7.06 (t, $^{3}J_{HH}$ = 7.3 Hz), 6.95−6.87 (m), 6.07 (t, $^{3}J_{HH}$ = 7.6 Hz) ArH; ^{29}Si{^{1}H} NMR (C_7D_8, 99 MHz) δ 269 ($^{1}J_{PtSi}$ = 934 Hz). Anal. Calcd for $C_{90}H_{69}P_3Pt_3Si_3\cdot 2C_6H_6$: C, 59.21; H, 3.95. Found: C, 59.32; H, 4.11.

(12) Crystals of **3** were obtained by slow evaporation from d_8-toluene solution. Crystallographic data for **3**: $C_{90}H_{69}P_3Pt_3Si_3\cdot C_7D_8$, monoclinic, space group $P2_1/n$, T = 223(2) K, a = 9.8929(2) Å, b = 14.4094(2) Å, c = 55.0754(9) Å, β = 92.649(1)°, V = 7842.7 (2) Å^3, Z = 4, μ = 8.834 mm^{-1}, $F(000)$ = 3920, ρ_{calcd} = 1.698 g cm^{-3}. Final residual values: R_F = 11.2% for 11 672 reflections ($I > 2\sigma(I)$) and $R_w(F^2)$ = 21.6% for 13 184 reflections and 919 parameters. Crystallographic data for structure **3** have been be deposited with the Cambridge Structural Data Base dep #CCDC 196309.

(13) For a recent review see: Imhof, D.; Venanzi, L. M. *Chem. Soc. Rev.* **1994**, *23*, 185.

(14) See for example: Bender, R.; Braunstein, P.; Dedieu, A.; Ellis, P. D.; Huggins, B.; Harvey, P. D.; Sappa, E.; Tiripicchio, A. *Inorg. Chem.* **1996**, *35*, 1223.

hydride could not be confirmed. When d_2-silafluorene was utilized as the reactant, the ^{2}H NMR spectrum did not show resonances for either bridging or terminal metal deuterides.

Trinuclear complexes of Pt containing bridging carbonyl,[13] nitrile, or phosphido[14] ligands are well-known, but those that incorporate silyl substituents are uncommon. For example, Osakada et al. recently prepared the triplatinum complex $[(Me_3P)Pt(\mu\text{-}SiPh_2)]_3$ in 28% yield from thermolysis of the preformed mononuclear complex $(Me_3P)_2Pt(SiPh_2H)_2$ at 100 °C.[6] Unlike Osakada's Pt_3-Si_3 system, the current triplatinum–μ-silylene complex (**3**) was generated at room temperature. To the best of our knowledge, the only other known Pt_3 system incorporating a silicon-containing substituent is a triplatinum complex with a terminal silyl group, $-Si(OSiMe_3)_3$, which was synthesized by reaction of the preexisting triplatinum cluster $[Pt_3(Ph)(\mu\text{-}PPh_2)_3(PPh_3)_2]$ with $HSi(OSiMe_3)_3$.[15] Both complexes were structurally characterized by X-ray crystallography. Trinuclear complexes of other transition metals with bridging silylene units are particularly rare.[16]

Further studies are in progress with other constrained secondary hydrosilanes to determine if such silicon systems will generate trinuclear or higher order polynuclear clusters as well as their mechanism of formation.

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Supporting Information Available: Figures giving selected NMR spectroscopic data and tables giving crystallographic data for **3**, including crystal data and structure refinement details, atomic coordinates, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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