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Communications

A $Pt^{III}{}_2Si_2$ Four-Membered Cycle and a Dinuclear Platinum Complex Bridged by a Cyclodisiloxane Ring

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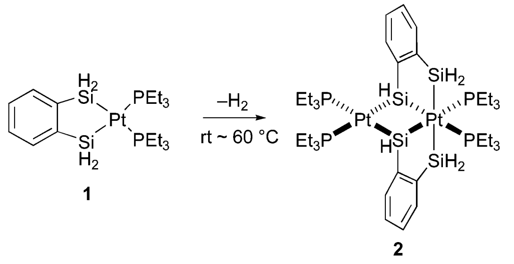
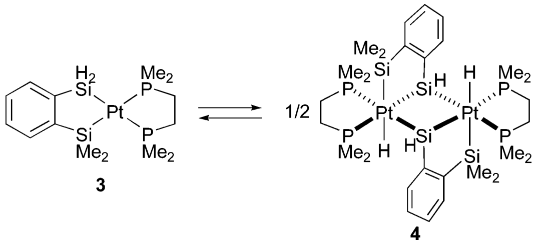
*Summary: Thermolysis of an equilibrium mixture of {1,2-C_6H_4-($SiMe_2$)(SiH_2)}Pt(dmpe) (**3**; dmpe = 1,2-bis(dimethylphosphino)ethane) and its dimer **4** afforded a novel dinuclear complex consisting of a Pt_2Si_2 four-membered cycle with formal Pt^{III} centers as well as a small amount of an unexpected dinuclear Pt^{II} complex bridged by a cyclodisiloxane ring.*

The chemistry of silyl and silylene transition-metal complexes has rapidly grown during the last two decades, and a number of novel structures have been elucidated.[1] Hydrosilanes are the most widely used silyl precursors for these complexes. The reactions of dihydrosilanes (H_2SiR_2, R = organic groups, etc.) and trihydrosilanes (H_3SiR) with transition-metal complexes often generate a more diverse range of products than those of monohydrosilanes ($HSiR_3$) because dihydro- and trihydrosilanes have more than one reactive Si−H bond and/or are less sterically hindered than monohydrosilanes; for example, dihydro- and trihydrosilanes can easily form multinuclear complexes.[1,2]

Scheme 1



Scheme 2



We have been studying the reaction of chelating hydrosilanes such as 1,2-bis(silyl)benzenes[3] and bis(2-silylphenyl)silane,[4] which have dihydrosilyl and/or trihydrosilyl groups, with group 10 transition-metal complexes. The chelating effects in addition to the characteristics of dihydro- and trihydrosilanes mentioned above make the chemistry of these hydrosilanes very unique. The reaction of 1,2-$C_6H_4(SiH_3)_2$ with $Pt(PEt_3)_3$ gives the expected bis(silyl)platinum(II) complex **1**, while complex **1** easily dimerizes with hydrogen elimination to form the mixed-valent $Pt^{II}Pt^{IV}$ complex **2** (Scheme 1).[5] On the other hand, the similar bis(silyl)platinum(II) complex **3**, derived from 1,2-C_6H_4-($SiMe_2H$)(SiH_3) and Pt(dmpe)(PEt_3)$_2$, has proved to be in equilibrium with another type of dimer **4** (Scheme 2).[6] During the formation of complex **2**, several transient species were observed by NMR spectroscopy, although their structures could not be identified. We thought that a complex similar to complex **4** could be a possible intermediate for the formation of complex **2** from **1** and, therefore, thermolysis of an equilibrium mixture of complexes **3** and **4** was examined. In this paper, we report two unexpected dinuclear complexes formed from a mixture of **3** and **4**.

Monitoring the thermolysis of an equilibrium mixture of complexes **3** and **4** at 80 °C or higher by ^{31}P NMR spectroscopy

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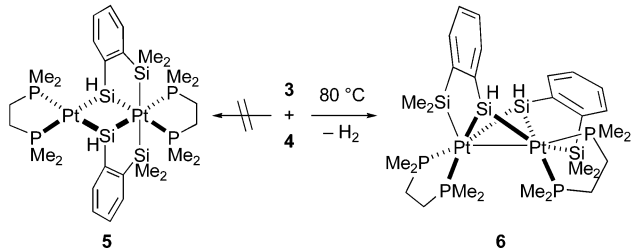
Scheme 3



showed the emergence of four new signals. The new signals have equal intensities, and each of the signals is accompanied by two sets of platinum satellites, suggesting the formation of a new dinuclear platinum complex with four phosphorus atoms in different environments. Another experiment on a larger scale afforded light orange crystals in 65% yield. Single-crystal X-ray analysis disclosed that the new complex is not the mixed-valent $Pt^{II}Pt^{IV}$ complex **5**, which is similar to complex **2**, but complex **6**, which has an unprecedented structure (Scheme 3 and Figure 1).[7] Complex **6** has a puckered $(PtSi)_2$ four-membered cycle, each Pt center of which is bound to three silicon atoms and is formally Pt^{III}.[8] Complex **6** is the first example of a $(PtSi)_2$ four-membered cycle with formal Pt^{III} centers. We have reported that the formation of the tetrakis(silyl)platinum(IV) complex $\{1,2\text{-}C_6H_4(SiMe_2)(SiH_2)\}_2Pt^{IV}(dmpe)$ is much slower than that of $\{1,2\text{-}C_6H_4(SiH_2)_2\}_2Pt^{IV}(PEt_3)_2$, probably because of the steric repulsion between the methyl groups on the silicon and phosphorus atoms in the former complex.[6] A similar steric repulsion in complex **5** is probably, at least in part, the reason for the selective formation of complex **6**.

There are more than 20 examples of $(PtSi)_2$ four-membered cycles that have been structurally characterized by single-crystal X-ray analysis.[5−6,9,10] These complexes can be classified into two categories by the diagonal Si−Si and Pt−Pt distances. Complexes belonging to one category (category A) have short diagonal Si−Si distances (2.55−2.88 Å) and long diagonal Pt−Pt distances (3.66−4.05 Å). On the other hand, complexes belonging to the other category (category B) have long diagonal Si−Si distances (3.84−3.97 Å) and short diagonal Pt−Pt distances (2.68−2.74 Å). However, complex **6** belongs to neither of the two categories; diagonal Si−Si (3.0219(12) Å) and Pt−Pt (2.9947(2) Å) distances in **6** are between those of categories A and B.

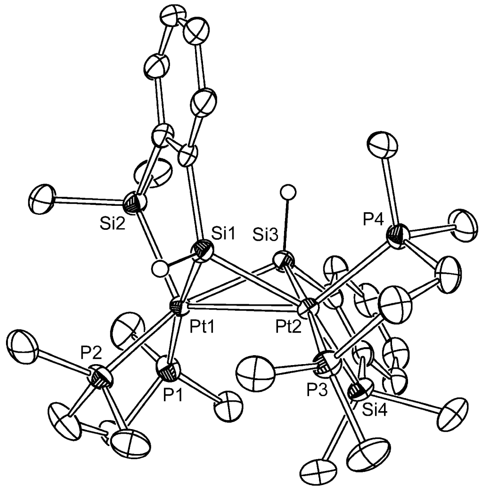
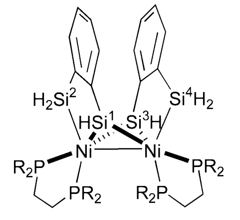
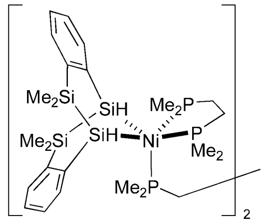


Figure 1. Molecular structure of complex **6** (50% probability ellipsoids). Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−Pt2 = 2.9947(2), Pt1−Si1 = 2.3676(9), Pt1−Si2 = 2.3757(10), Pt1−Si3 = 2.3486(9), Pt2−Si1 = 2.3777(9), Pt2−Si3 = 2.3370(9), Pt2−Si4 = 2.4095(9), Pt1−P1 = 2.3353(9), Pt1−P2 = 2.3149(9), Pt2−P3 = 2.3260(9), Pt2−P4 = 2.2733(9), Si1•••Si3 = 3.0219(12), Si2•••Si3 = 3.2723(13); Pt1−Si1−Pt2 = 78.26(2), Pt1−Si3−Pt2 = 79.45(2), Si1−Pt1−Si2 = 82.28(3), Si1−Pt1−Si3 = 79.70(3), Si1−Pt1−P1 = 171.29(3), Si1−Pt1−P2 = 92.40(3), Si1−Pt2−Si3 = 79.72(3), Si1−Pt2−Si4 = 145.69(3), Si1−Pt2−P3 = 97.59(3), Si1−Pt2−P4 = 108.19(3), Si2−Pt1−Si3 = 87.68(3), Si2−Pt1−P1 = 106.42(3), Si2−Pt1−P2 = 111.51(3), Si3−Pt1−P1 = 99.97(3), Si3−Pt1−P2 = 158.24(3), Si3−Pt2−Si4 = 81.93(3), Si3−Pt2−P3 = 175.80(3), Si3−Pt2−P4 = 95.98(3), Si4−Pt2−P3 = 98.80(3), Si4−Pt2−P4 = 102.34(3).



7 (R = Me or Et)



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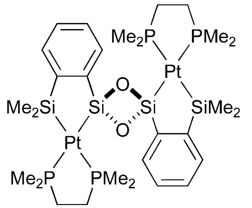

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The structure of complex **6** is somewhat similar to that of dinuclear nickel complexes **7** having formal Ni^{III} centers, which were obtained from the reaction of $1,2\text{-}C_6H_4(SiH_3)_2$ and $Ni(dmpe)_2$ or $Ni(depe)(PEt_3)_2$ (depe = 1,2-bis(diethylphosphino)ethane).[3c] In complexes **7**, two $[1,2\text{-}C_6H_4(SiH_2)(\mu\text{-}SiH)]$ ligands are symmetrically bound to the nickel centers and the structures are C_2-symmetric. On the other hand, in complex **6** two $[1,2\text{-}C_6H_4(SiMe_2)(\mu\text{-}SiH)]$ ligands are unsymmetrically bound to the platinum centers. In complexes **7**, the $Si^1\cdots Si^4$ and $Si^2\cdots Si^3$ distances are short (2.685(1)−2.7049(9) Å) and are comparable to the longest Si−Si single bond,[11] while no short Si•••Si contact is found in **6** (Si2−Si3 = 3.2723(13) Å). As previously reported,

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[7] Crystal data for $6\cdot C_6H_6$: $C_{34}H_{60}P_4Pt_2Si_4$, $M_r = 1095.27$, monoclinic, space group $P2_1/c$ (No. 14), $a = 14.9570(9)$ Å, $b = 15.2972(10)$ Å, $c = 18.6367(12)$ Å, $\beta = 96.8210(10)°$, $V = 4233.9(5)$ Å^3, $Z = 4$, $\mu = 6.861$ mm^{-1}, $T = 153(2)$ K, R1 = 0.0208 for 8381 observed reflections with $I > 2\sigma(I)$ from 9353 unique reflections, wR2 = 0.0507, GOF = 1.027.

[8] One of the reviewers suggested that the electron counting can also be done by considering the bridging μ-SiHAr group as a neutral 2e donor and the $SiMe_2Ar$ group as an anionic 2e donor. This would give formal Pt^{I} centers.

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[10] CSD, version 5.27, November 2005.

[11] Wieberg, N.; Schuster, H.; Simon, A.; Peters, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 79.

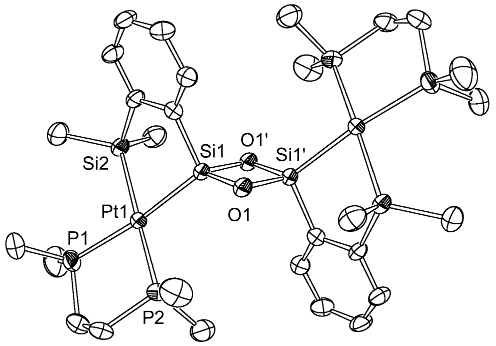

Figure 2. Molecular structure of complex **9** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−Si1 = 2.3364(18), Pt1−Si2 = 2.3772(15), Pt1−P1 = 2.314(2), Pt1−P2 = 2.3103(16), Si1−Si1′ = 2.433(2), Si1−O1 = 1.684(4), Si1−O1′ = 1.710(4); Si1−Pt1−Si2 = 78.22(6), Si1−Pt1−P1 = 173.25(4), Si1−Pt1−P2 = 98.39(6), Si2−Pt1−P1 = 97.50(6), Si2−Pt1−P2 = 174.39(5), P1−Pt1−P2 = 85.44(6), Si1−O1−Si1′ = 91.6(2), O1−Si1−O1′ = 88.4(2).

the reaction of Ni(dmpe)$_2$ with 1,2-$C_6H_4(SiMe_2H)(SiH_3)$ did not afford a complex similar to **6** or **7** but gave complex **8** having Si−Si bonds, which may be produced through an intermediate similar to **7**.[3c] On the other hand, no Si−Si bond formation has been observed in the reaction of 1,2-$C_6H_4(SiMe_2H)(SiH_3)$ with platinum(0) phosphine complexes.

During the thermolysis of an equilibrium mixture of complexes **3** and **4**, we occasionally observed the formation of a small quantity of a solid precipitate, whose structure was confirmed by single-crystal X-ray analysis to be the dinuclear Pt^{II} complex **9** having a cyclodisiloxane core (Figure 2).[12,13] The Si⋯Si distance (2.433(2) Å) of the cyclodisiloxane ring in **9** is similar to observed distances in related examples (2.31−2.47 Å).[10]

Isolated examples of cyclodisiloxanes are limited, and compound **9** is the first example of a transition-metal-bound cyclodisiloxane. The cyclodisiloxanes so far reported have been prepared by the oxidation of disilenes[14] or oxadisilirane[15] or dimerization of unstable silanone intermediates.[16] Therefore, the mechanism of the formation of compound **9** from the platinum-substituted dihydrosilane **3** or its dimer **4** is quite interesting. Attempts to determine the oxygen source (O_2, H_2O, ...) and to clarify the mechanism of the formation of compound **9** are underway.

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Supporting Information Available: Text giving experimental details and spectroscopic data for complex **6** and a CIF file giving X-ray crystallographic data. This material is available free of charge via the Internet at http:/pubs.acs.org.

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(12) Single crystals of **9** (∼1 mg) were obtained when the thermolysis was conducted in a NMR tube. Attempts to obtain compound **9** in large quantities under various conditions have not been successful so far. Therefore, this compound was characterized only by X-ray analysis.

(13) Crystal data for **9**: $C_{28}H_{52}O_2P_4Pt_2Si_4$, $M_r = 1047.13$, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.8853(13)$ Å, $b = 10.2640(9)$ Å, $c = 11.3562(13)$ Å, $\alpha = 98.945(10)°$, $\beta = 109.916(8)°$, $\gamma = 97.737(10)°$, $V = 942.06(19)$ Å^3, $Z = 1$, $\mu = 7.708$ mm^{-1}, $T = 223(2)$ K, R1 = 0.0273 for 3097 observed reflections with $I > 2\sigma(I)$ from 3505 unique reflections, wR2 = 0.0631, GOF = 1.001.

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