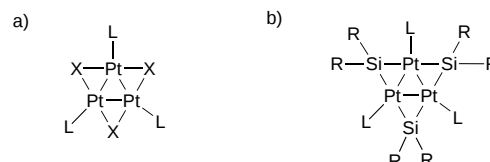


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- [16] Physical data: M.p. > 350 °C; ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): δ = 8.78 (s, 1H; H-10), 8.67 (s, 2H; H-5, H-15), 3.95 (m, 4H; H-2a, H-18a), 3.83 (q, 4H; H-3a, H-17a), 3.65 (m, 4H; H-8a, H-12a), 1.87 (t, 6H; H-2b, H-18b), 1.74 (t, 6H; H-3b, H-17b), 1.71 (s, 6H; H-7a, H-13a), 1.64 (t, 6H; H-8b, H-12b); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 140.1, 138.0, 136.8, 136.0, 134.9, 131.5, 129.9, 129.1, 95.6 (C-10), 93.2 (C-5, 15), 21.1, 20.2, 20.1, 19.3, 17.8, 11.9; MALDI/TOF MS (%) *m/z*: 1186.53 (100), calcd for C₆₆H₇₈N₈¹⁰²Ru₂: 1186.45; IR (KBr): $\tilde{\nu}$ = 2962 (CH), 2927 (CH), 2896 (CH), 1610, 1450, 1059, 822 cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max}[nm](ε) = 336 (103295), 393 (59071), 521 (15481); elemental analysis calcd (%) for C₆₆H₇₈N₈Ru₂: C 66.87, H 6.63, N 9.45; found: C 66.93, H 6.69, N 9.50.
- [17] X-ray data: C₆₆H₇₈Ru₂N₈, crystals were obtained by slow diffusion of methanol in dichloromethane; crystal dimensions 0.40 × 0.38 × 0.10 mm, monoclinic *P*2₁/*c*, *a* = 14.2080(8), *b* = 13.6160(8), *c* = 16.1907(7) Å, β = 113.322(3)°, *V* = 2876.3(3) Å³, *Z* = 2; ρ_{calcd} = 1.369 g cm⁻³, μ(Mo) = 5.73 cm⁻¹. The measurement of the reflection intensities was carried out on an Enraf-Nonius Kappa-CCD diffractometer (*T* = 112(2) K, MoK_α radiation λ = 0.71073 Å); φ and ω scans with κ offsets; 2θ_{max} = 55°; 15324 measured reflections (*R*_{int} = 0.053). The structure was solved with direct methods and refined with *F*² against all independently observed reflections (4507); heavy atoms with anisotropic, H atoms with isotropic temperature factors; *R*1 = 0.0957, *wR*2 = 0.2476 (for *I* > 2σ(*I*); total number of parameters 351, Δρ_{max} = 1.051 e Å⁻³, Δρ_{min} = -0.553 e Å⁻³. The programs used for solving and refinement of the structure were SHELXS-97 and SHELXL-97 (G. M. Sheldrick, University of Göttingen) respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141388. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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A Triangular Triplatinum Complex with Electron-Releasing SiPh₂ and PMe₃ Ligands: [{Pt(μ-SiPh₂)(PMe₃)₃}]³⁺*

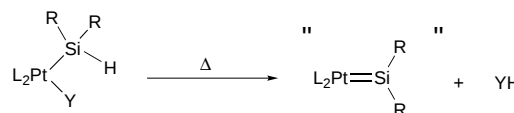
Kohtaro Osakada,* Makoto Tanabe, and Tomoaki Tanase

Triangular complexes composed of three zerovalent transition metal centers are among the most extensively studied cluster compounds. The trinuclear Pt⁰ complexes reported so far contain bridging CO or CNR ligands, which have significant π-acceptor character and stabilize complexes with low-valent metal centers (Scheme 1a).^[1] Organosilyl ligands



Scheme 1. Triangular trinuclear complexes of platinum: a) known complexes, where X = CO, CNR, or other neutral ligands; b) target complexes with organosilyl ligands.

have not been commonly used as ligands for these cluster compounds, partly because of the mismatched coordination of a ligand having a significant σ-donor character and negligible π-acceptor capability with electron-rich metal centers. The electronic state and structure of Pt⁰ complexes with organosilyl ligands would be of significant interest, but they have not yet been prepared.^[2–3] Since the target structure in Scheme 1b is a trimeric form of a platinum–silylene complex, a synthetic approach that uses such species as precursors might be successful. Owing to their intrinsic instability,^[4,5] mononuclear platinum–silylene complexes were obtained only by using well-designed precursors; however, they were postulated to arise by α-elimination from dialkyl- or diarylsilyl complexes of platinum (Scheme 2).^[6,7] We chose a diaryl-



Scheme 2. Postulated formation of mononuclear platinum–silylene complexes by α-elimination.

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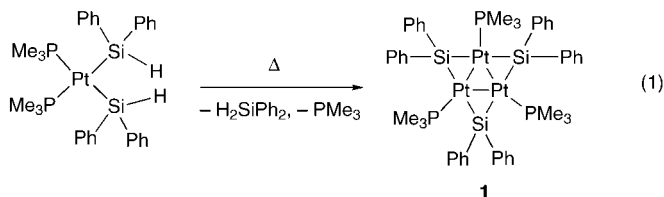
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silylplatinum complex as the precursor for a trinuclear Pt⁰ cluster with bridging silylene ligands.

Heating [Pt(SiHPh₂)₂(PMe₃)₂]^[8] at 100 °C gave **1**, which was isolated as red crystals [Eq. (1)].^[9] The accompanying formation of H₂SiPh₂ and a smaller quantity of HSiPh₃ was



observed during the reaction. The reaction mixture also contained [(Me₃P)₂Pt(Ph₂SiOSiPh₂)] (**2**), which can be attributed to the reaction of adventitious oxygen with a disilene Pt complex generated in situ.^[10] Figure 1 shows the molecular

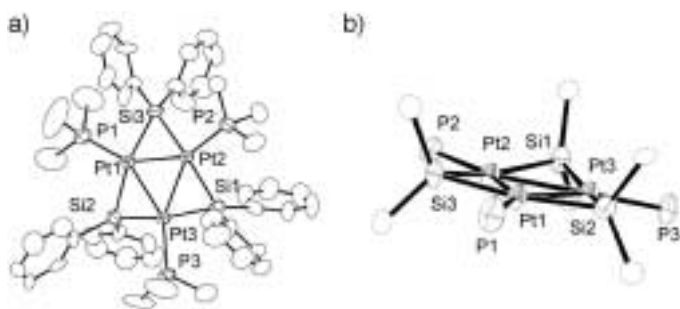


Figure 1. a) Top view and b) side view of the X-ray structure of **1**. Selected bond lengths [Å] and angles [°]: Pt1–Pt2 2.716(1), Pt1–Pt3 2.713(1), Pt2–Pt3 2.697(1), Pt1–P1 2.243(5), Pt2–P2 2.226(5), Pt3–P3 2.247(4), Pt1–Si2 2.364(5), Pt1–Si3 2.357(5), Pt2–Si1 2.355(5), Pt2–Si2 2.345(5), Pt3–Si3 2.343(5), Pt3–Si1 2.337(5); Pt1–Pt2–Pt3 60.17(3), Pt2–Pt3–Pt1 60.27(3), Pt3–Pt1–Pt2 59.57(3), Pt1–Pt2–Si2 55.1(1), Pt2–Pt1–Si2 54.5(1), Pt2–Pt3–Si1 55.2(1), Pt3–Pt2–Si1 54.6(1), Pt1–Pt3–Si3 55.0(1), Pt3–Pt1–Si3 54.5(1), Si2–Pt1–Si3 167.0(2), Si1–Pt2–Si2 163.4(2), Si3–Pt3–Si1 164.1(2), Si2–Pt1–P1 94.0(2), Si3–Pt1–P1 98.0(2), Si1–Pt2–P2 95.0(2), Si2–Pt2–P2 94.9(2), Si1–Pt3–P3 94.6(2), Si3–Pt3–P3 96.6(2), Pt1–Si2–Pt2 70.4(1), Pt2–Si3–Pt3 70.5(1), Pt2–Si1–Pt3 70.2(1).

structure of **1**, as determined by X-ray crystallography.^[11] The three Pt centers form a triangle with Pt–Pt distances of 2.697–2.716 Å and Pt–Pt–Pt angles of 59.6–60.3°. The metal–metal distances are similar to those in analogous trinuclear Pt⁰ complexes with bridging CNR and CO ligands and suggest the presence of Pt–Pt bonds. Interaction between transition metals with d¹⁰ configurations was proposed to account for the structure and electronic state of multinuclear complexes of Pd⁰, Pt⁰, and Cu^I. The acute Pt–Si–Pt angles (70.0–70.4°) and the almost perpendicular orientation of the phenyl substituents with respect to the coordination plane are similar to other silylene-bridged transition metal complexes.

The satellite signals of the PMe₃ hydrogen atoms in the ¹H NMR spectrum exhibit both three- and four-bond Pt–H coupling (³J_{Pt,H} = 43, ⁴J_{Pt,H} = 25 Hz). The ³¹P{¹H} NMR spectrum (Figure 2) exhibits long-range ³¹P–¹⁹⁵Pt and ³¹P–³¹P coupling. The presence of significantly stable Pt–Pt bonds, confirmed from the crystallographic and spectroscopic data, seems to be more consistent with Pt⁰ rather than the alternative Pt^{II} formulation.^[12]

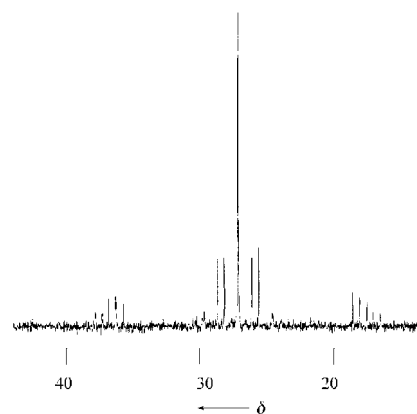


Figure 2. ³¹P{¹H} NMR spectrum of **1** (160 MHz at 25 °C in [D₆]benzene).

Complex **1** contains SiPh₂ and PMe₃ ligands, both of which are strongly electron donating, and is expected to have a unique electronic state. Modeling the electronic state of **1** by extended Hückel molecular orbital calculations on the C_{3v} model complex [Pt₃(PH₃)₃(μ-SiH₂)₃] (**I**) gave results that were consistent with the above structure.^[13] The electronic structure of **I** was consistent with the proposed 42-valence-electron cluster in which three Pt centers are bound with metal–metal bonds, in a similar manner to that observed in [Pt₃(PH₃)₃(μ-CN₃)₃] (**II**).^[14, 15] The Pt–Pt bond overlap population in **I** (0.24) is comparable to that in **II** (0.20), whereas the energy of the HOMO is higher than that of the isocyanide complex **II** due to significant mixing of Si p orbitals.

Experimental Section

1: A solution of [Pt(SiHPh₂)₂(PMe₃)₂] (405 mg, 0.57 mmol) in toluene (20 mL) was heated for 24 h at 100 °C. The color of the solution changed from yellow to dark red. Analysis of the solution by ¹H NMR spectroscopy showed the formation of H₂SiPh₂ and a smaller amount of HSiPh₃. After evaporation of the solvent, hexane was added to the residue. This resulted in separation of an orange solid, which was repeatedly recrystallized from toluene/hexane to afford **1** as red crystals (96 mg, 28%). Cooling the hexane filtrate obtained after separation of **1** yielded **2** as pale yellow crystals (34%).

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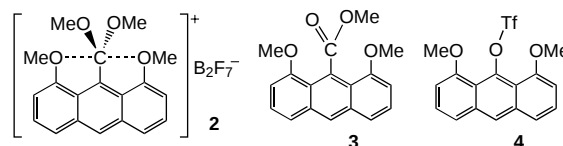
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- [10] Complex **2** gave satisfactory elemental analyses, NMR data, and X-ray crystallographic results. Analogous complexes $[(\text{dppe})\text{Pt}(\text{R}_2\text{SiO-SiR}_2)]$ ($\text{R} = \text{Me}$, $i\text{Pr}$) were prepared by reaction of O_2 with disilene Pt complexes $[(\text{dppe})\text{Pt}(\text{R}_2\text{SiSiR}_2)]$ ($\text{dppe} = 1,2$ -bis(diphenylphosphanyl)ethane): E. K. Pham, R. West, *J. Am. Chem. Soc.* **1989**, 111, 7667; E. K. Pham, R. West, *Organometallics* **1990**, 9, 1517.
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- [12] Pt^{II} and Pd^{II} complexes with a stable metal-metal bond are unknown. X-ray photoelectron spectroscopy (XPS) was applied to **1** and related Pt complexes to obtain more direct evidence for the valency of the metal centers. Complex **1** shows peaks at 72.3 and 75.6 eV (due to $4f_{7/2}$ and $4f_{5/2}$ states, respectively). The peak positions, however, are negligibly different to those of the triangular Pt^0 complex $[\text{Pt}_3(2,6\text{-Me}_2\text{-C}_6\text{H}_3\text{CN})_6]$ (72.2 and 75.5 eV) and the mononuclear Pt^{II} complex $[\text{Pt}(\text{SiHPh}_2)_2(\text{PMe}_3)_2]$ (72.3 and 75.7 eV). These data and the NMR data of the complexes did not provide additional useful information for determining the valence of Pt in **1**.
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- [15] The molecular orbital diagram is available as Supporting Information.

Synthesis of a Versatile Tridentate Anthracene Ligand and its Application for the Synthesis of Hypervalent Pentacoordinate Boron Compounds (10-B-5)**

Makoto Yamashita, Yohsuke Yamamoto, Kin-ya Akiba,* and Shigeru Nagase

Hypervalent pentacoordinate boron compounds (10-B-5)^[1] have been postulated as transition states in $\text{S}_{\text{N}}2$ -type reactions at a boron atom. For example, the reaction of the $[\text{BH}_3\text{-CO}]$ complex with NMe_3 ^[2] as well as the intramolecular bond switch at the boron atom in compounds bearing a van Koten type ligand^[3] have been reported. There has been only one report of isolable hypervalent boron compounds (10-B-5 and 12-B-6),^[4] but the compounds bearing tridentate pyridine diol ligand(s) were characterized by ^1H , ^{13}C , ^{19}F , and ^{11}B NMR spectra in solution. The X-ray analysis of the compounds has not been reported. Here we report the synthesis and X-ray structures of 1,8-dimethoxy-9-borylanthracene (**1a-c**, see Scheme 2): the first fully characterized hypervalent 10-B-5 compounds.

Recently, we reported the synthesis and the X-ray structure of the hypervalent five-coordinate carbon compound (10-C-5) **2** through the use of an 1,8-dimethoxy-9-anthracenyl ligand.^[5] Ester **3** was synthesized from the 9-OTf derivative **4** (OTf = trifluoromethanesulfonate) by carbon monoxide insertion in



methanol mediated by $[\text{Pd}(\text{PPh}_3)_4]$. However, several attempts to synthesize **1** from **4** were not successful. Thus, we designed a novel versatile precursor 1,8-dimethoxy-9-bromoanthracene (**8**). The synthetic pathway for **8** is illustrated in Scheme 1. After conversion of 1,8-dimethoxy-9-hydroxyanthracene (**5**)^[6] into the corresponding phosphate (**6**), reaction conditions for the reduction of **6** and the subsequent treatment of the resulting anion **7** with $\text{BrCF}_2\text{CF}_2\text{Br}$ to yield **8** were examined (Table 1). Only the 9-H compound was obtained using Birch reduction conditions (entry 1) and only a trace amount of **8** was obtained by using lithium naphthalenide (entry 2). Fortunately, the reduction of **6** with lithium 4,4'-di-

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