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The First Platinum Formyl, a Member of a Series of Hexanuclear Clusters Exhibiting a Rare Structure**

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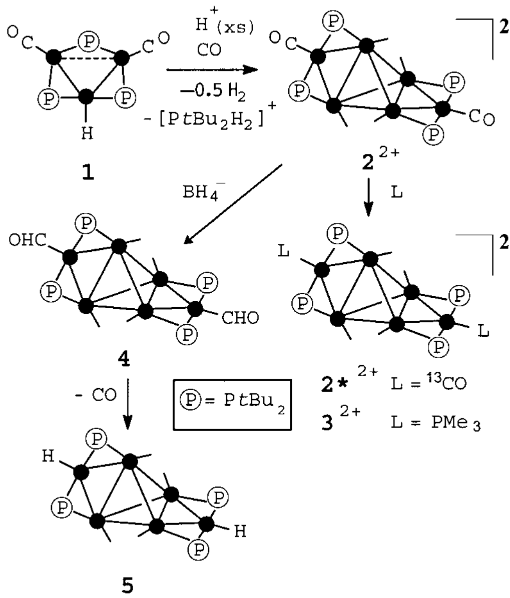
A large number of platinum clusters have been reported in the past decades.[1] Nevertheless, only two hexanuclear structures have been authenticated by X-ray crystallography: the trigonal-prismatic $[\mathrm{Pt_6}(\mu\text{-CO})_6(\mathrm{CO})_6]^{2-}$[2a] and the octahedral $[\mathrm{Pt_6}(\mathrm{CO})_6(\mu\text{-dppm})_3]^{2+}$ (dppm = bis(diphenylphosphanyl)methane).[2b] In addition, the decanuclear $[\mathrm{Fe_4Pt_6}(\mathrm{CO})_{22}]^{2-}$,[3] arising from the orthogonal dimerization of two $[\mathrm{Pt_3}(\mathrm{CO})_3\{\mu_2\text{-Fe}(\mathrm{CO})_4\}_2]^-$ triangles, contains a tetrahedral Pt core, two opposite edges of which are each bridged by another platinum atom. We have discovered a facile route to platinum clusters having this unusual structure.[4] The precursor $[\mathrm{Pt_6}(\mathrm{CO})_6(\mu\text{-P}t\mathrm{Bu_2})_4](\mathrm{CF_3SO_3})_2$ (**2**) was prepared by treating the trinuclear hydrido cluster $[\mathrm{Pt_3}(\mathrm{H})(\mathrm{CO})_2(\mu\text{-P}t\mathrm{Bu_2})_3]$ (**1**)[5] with an excess of triflic acid under a CO atmosphere (Scheme 1).

Figure 1 shows an ORTEP view of the cation $\mathbf{2}^{2+}$, which exhibits overall D_{2d} symmetry.[7] Complex **2** is air-stable, thermally robust (decomp 228 °C), and remains unchanged, even under forcing conditions, in the presence of CO (100 °C, 100 atm, 12 h) or H_2 (80 °C, 90 atm, 6 h). Interestingly, **2** reacts with ^{13}CO to give $[\mathrm{Pt_6}(\mathrm{CO})_4(^{13}\mathrm{CO})_2(\mu\text{-P}t\mathrm{Bu_2})_4](\mathrm{CF_3SO_3})_2$ (**2***), the product of selective substitution of the carbonyl ligands attached to the two "apical" atoms Pt2 and Pt5. A similar remarkable regioselectivity was also observed in the reactions of **2** with $\mathrm{PMe_3}$ or $\mathrm{NaBH_4}$ to give $[\mathrm{Pt_6}(\mathrm{CO})_4(\mathrm{PMe_3})_2(\mu\text{-P}t\mathrm{Bu_2})_4](\mathrm{CF_3SO_3})_2$ (**3**), and $[\mathrm{Pt_6}(\mathrm{CO})_4(\mathrm{CHO})_2(\mu\text{-P}t\mathrm{Bu_2})_4]$ (**4**), respectively. The structures of **2***, **3**, and **4** can be clearly assigned on the basis of elemental analyses and IR and NMR spectra. For example, the four bridging P nuclei are still isochronous and in the ^{31}P{^{1}H} NMR spectrum they give rise to a central singlet (doublet in **3**, $^2J(\mathrm{P}_\mu,\mathrm{P}_\mathrm{term} = 13\ \mathrm{Hz})$ flanked by a complex set of ^{195}Pt satellites, very similar to those observed for **2**. Strong similarities were also observed in the main features of the ^{195}Pt{^{1}H} NMR spectra, which still show only two signals and hence rule out all other possible isomers.



Scheme 1. Synthesis and further reactions of **2**.

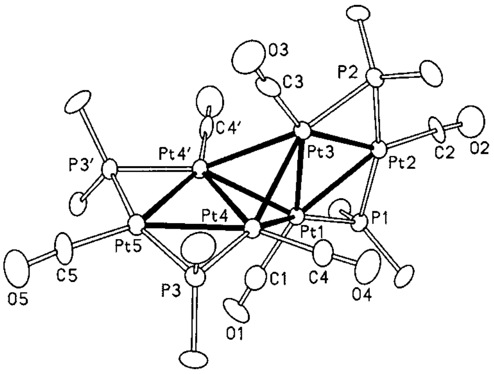


Figure 1. Molecular structure of $\mathbf{2}^{2+}$.[7] Methyl groups are omitted for clarity (thermal ellipsoids at 30% probability; symmetry code: ′ = $x, -y, z$). Selected bond lengths [Å] and angles [°]: Pt1-Pt2 2.758(1), Pt1-Pt3 2.667(1), Pt1-Pt4 2.841(1), Pt2-Pt3 2.762(1), Pt3-Pt4 2.841(1), Pt4-Pt4′ 2.666(1), Pt4-Pt5 2.756(1); Pt3-Pt1-Pt2 61.17(3), Pt1-Pt2-Pt3 57.79(3), Pt1-Pt3-Pt2 61.04(3), Pt3-Pt1-Pt4 62.00 (3), Pt1-Pt3-Pt4 62.00(3), Pt1-Pt4-Pt3 56.00(3), Pt1-Pt4-Pt4′ 62.01(2), Pt3-Pt4-Pt4′ 62.01(2), Pt4′-Pt4-Pt5 61.071(15), Pt4-Pt5-Pt4′ 57.86(3).

Complex **4** is of particular interest, being the first platinum formyl, and its structure was unequivocally confirmed by comparison of its spectra with those of the labeled $[\mathrm{Pt_6}(\mathrm{CO})_4(^{13}\mathrm{CHO})_2(\mu\text{-P}t\mathrm{Bu_2})_4]$ (**4***). In particular, the triplet for the formyl group at $\delta = 18.9$ ($^3J(\mathrm{H,P}) = 14$ Hz) in the ^{1}H NMR spectrum of **4** splits as expected in **4*** (br dt, $^1J(\mathrm{C,H}) = 152$ Hz) for coupling with the adjacent ^{13}C nucleus (Figure 2a, b). The same coupling is exhibited by a doublet at $\delta = 244.6$ for the formyl C atom in the proton-coupled ^{13}C NMR spectrum of **4*** (Figure 2c, d).[6a] Furthermore, a

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[**] We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), Programmi di Interesse Nazionale, 2000–2001, for financial support.

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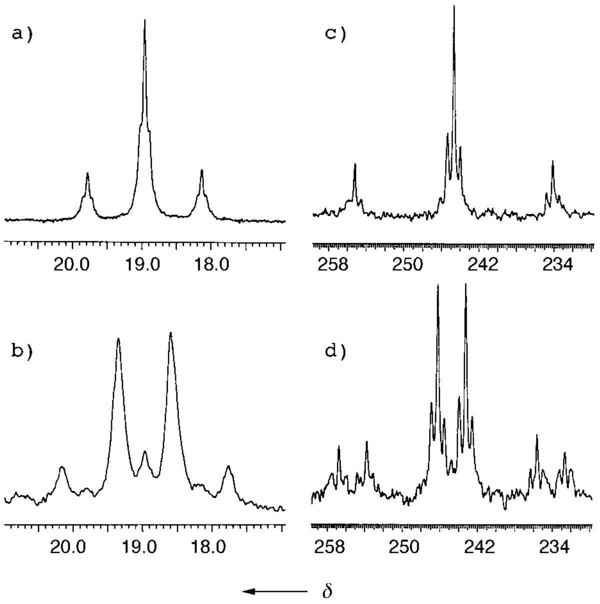

Figure 2. Formyl signals in the ^{1}H NMR spectra of **4** (a) and **4*** (b), and in the proton-decoupled (c) and -coupled (d) ^{13}C NMR spectra of **4***.

$\nu_{C=O}$ band at 1604 cm^{-1} in the IR spectrum of **4** shifts to 1574 cm^{-1} in the spectrum of **4***.[6a]

Metal formyls are suggested to be important intermediates in the metal-catalyzed reduction of carbon monoxide.[6] Complex **4** exhibits relatively high thermal stability (decarbonylation in toluene to give the dihydrido cluster $[Pt_6(H)_2(CO)_4(\mu\text{-}PtBu_2)_4]$ (**5**) occurs in 5 h at 60 °C and in 36 h at room temperature). Finally, to the best of our knowledge, metal diformyls were previously unknown.

Experimental Section

2: CF_3SO_3H (0.4 mL, 4.5 mmol) was added to a red solution of **1** (614 mg, 0.57 mmol; prepared as previously described[5]) in $CHCl_3$ (20 mL). After 2 h the flask was filled with CO (1 atm) and the reaction mixture stirred for 0.5 h; the solvent was evaporated and the residue was suspended in THF/Et_2O. Complex **2** was isolated as a red solid (353 mg, 56 %). Elemental analysis (%) calcd for $C_{40}H_{72}F_6O_{12}P_4Pt_6S_2$: C 21.7, H 3.27; found: C 21.7, H 3.26. **2*** was prepared by dissolving **2** in [D$_6$]acetone under a ^{13}CO atmosphere. After 24 h the solution contained a 1:10 mixture of **2** and **2***. Selected data for **2** [**2***]. ^{31}P{^{1}H} NMR (80.9 MHz, [D$_6$]acetone, 25 °C): $\delta = 383.7$ (s, with ^{195}Pt satellites); ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C): $\delta = 1.62$ (vt, ^3J(H,P) + ^5J(H,P) = 8 Hz); ^{195}Pt{^{1}H} NMR (42.8 MHz, [D$_6$]acetone, 25 °C): $\delta = -4960$ (m, 2 Pt [dm, ^1J(C,Pt) ≈ 1750 Hz]), −3203 (4 Pt); ^{13}C{^{1}H} NMR (50.3 MHz, CH_3CN, 25 °C): $\delta = 206.1$ (weak br s, with satellites, 4 CO), 185.8 (weak br s, with satellites, 2 CO [in [D$_6$]acetone, 185.4, strong t, ^2J(C,P) = 4.7 Hz, with satellites, ^1J(C,Pt) = 1750 Hz, ^2J(C,Pt) = 144 Hz]), 48.5 (s, with satellites, PC), 32.3 (s, CH$_3$); IR (CH_2Cl_2): $\tilde{\nu} = 2089$ (2 CO [2040]), 2056 cm^{-1} (4 CO).

3: PMe$_3$ (8 µL, 0.077 mmol) was added to a solution of **2** (60 mg, 0.027 mmol) in CH_2Cl_2 (2 mL). After 1 h at room temperature, most of the solvent was evaporated; addition of Et_2O (8 mL) caused the precipitation of **3** as an orange powder (44 mg, 70 % yield). Elemental analysis (%) calcd for $C_{44}H_{90}F_6O_{10}P_6Pt_6S_2$: C 22.8, H 3.92; found: C 22.6, H 3.95. Selected spectroscopic data: ^{31}P{^{1}H} NMR (80.9 MHz, CDCl$_3$, 25 °C): $\delta = 337.4$ (d, ^2J(P,P) = 13 Hz, with satellites, μ-P), −13.7 (t, ^2J(P,P) = 13 Hz, with satellites, ^1J(P,Pt) = 3370 Hz, ^2J(P,Pt) = 333 Hz, P$_{term}$); ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): $\delta = 2.46$ (d, ^2J(H,P) = 10.2 Hz, with satellites, ^3J(H,Pt) = 40 Hz, PCH$_3$), 1.50 (vt, ^3J(H,P) + ^5J(H,P) = 7 Hz, CCH$_3$); ^{195}Pt{^{1}H} NMR (42.8 MHz, CDCl$_3$, 25 °C): $\delta = -2914$ (m, 4 Pt), −5218 (m, 2 Pt, ^1J(Pt,P) = 3370 Hz; ^{13}C{^{1}H} NMR (50.3 MHz, CDCl$_3$, 25 °C): $\delta = 45.7$ (s, with satellites, *C*CH$_3$), 32.5 (s, C*C*H$_3$), 25.0 (d, ^1J(C,P) = 38 Hz, with satellites, ^2J(C,Pt) = 54 Hz, PCH$_3$); IR (CDCl$_3$): $\tilde{\nu} = 2030$ cm^{-1}.

4: NaBH$_4$ (44 mg, 1.16 mmol) was added to a solution of **2** (152 mg, 0.0685 mmol) in MeOH (15 mL). Complex **4** precipitated as a violet solid (84 mg, 64 %). Elemental analysis (%) calcd for $C_{38}H_{74}O_6P_4Pt_6$: C 23.7, H 3.88; found: C 23.5, H 3.90. **4*** was prepared as above, starting from **2***. Selected spectroscopic data for **4** [**4***]: ^{31}P{^{1}H} NMR (80.9 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 316.3$ (s, with satellites); ^{1}H NMR (200 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 18.9$ (t, ^3J(H,P) = 14 Hz, with satellites, ^2J(H,Pt) = 332 Hz, CHO [br dt, ^1J(H,C) = 152 Hz, with satellites]), 1.31 (vt, ^3J(H,P) + ^5J(H,P) = 7 Hz, CC*H*$_3$); ^{13}C{^{1}H} NMR (50.3 MHz, CD$_2$Cl$_2$, 25 °C): δ = [244.6 (s) (H coupled: d, ^1J(C,H) = 152 Hz) with satellites, ^1J(C,Pt) = 1062 Hz, ^2J(C,Pt) = 68 Hz]; ^{195}Pt{^{1}H} NMR (42.8 MHz, C$_6$D$_6$, 25 °C): $\delta = -4642$ (m, 2 Pt), −2570 (m, 4 Pt). IR (CD$_2$Cl$_2$): $\tilde{\nu} = 2006$ (C≡O), 1608 [1574] (C=O) cm^{-1}.

5: A violet solution of complex **4** (50 mg, 0.026 mmol) in toluene (2 mL) was heated at 70 °C; the solution became red. After 6 h the solvent was evaporated and the red cluster **5** was suspended in acetone and collected by filtration (27 mg, 56 %). Elemental analysis (%) calcd for $C_{36}H_{74}O_4P_4Pt_6$: C 23.2, H 4.00; found: C 23.3, H 3.98; ^{31}P{^{1}H} NMR (80.9 MHz, C$_6$D$_6$, 25 °C): $\delta = 342.0$ (s, with satellites); ^{1}H NMR (200 MHz, C$_6$D$_6$, 25 °C): $\delta = 1.41$ (vt, ^3J(H,P) + ^5J(H,P) = 7 Hz, CC*H*$_3$), −0.09 (m, with satellites, ^1J(H,Pt) = 1385 Hz, PtH); ^{195}Pt{^{1}H} NMR (42.8 MHz, C$_6$D$_6$, 25 °C): $\delta = -5146$ (m, 2 Pt [dm, ^1J(Pt,H) = 1384 Hz, in the H-coupled spectrum]), −2822 (m, 4 Pt).

Received: March 13, 2001
Revised: May 28, 2001 [Z16768]

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[7] Crystal data for **2**: $C_{40}H_{72}F_6O_{12}P_4Pt_6S_2$, crystal dimensions 0.36 × 0.23 × 0.02 mm^3, space group *C*2/*m* (No. 12), $a = 23.088(2)$, $b = 21.814(2)$, $c = 14.707(1)$ Å, $\beta = 113.93(1)^\circ$, $V = 6770(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.176$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 12.567$ mm^{-3}, $F(000) = 4088$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $T = 293(2)$ K. The intensities of 6137 reflections with $2.3 \leq \theta \leq 25^\circ$ were collected. After correction for Lorentzian, polarization, and absorption effects with the ψ-scan method[8] ($R_{int} = \Sigma | F_o^2 - F_o^2(\mathrm{mean}) | / \Sigma(F_o^2) = 0.0292$), the structure was solved by standard direct and Fourier methods and refined by full-matrix least-squares procedures. The final refinement cycle gave a conventional *R* factor (F_o) of 0.0481, calculated for 3754 observed reflections (322 parameters), and a value of 0.0853 for all 5418 data. 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-159650. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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