1612 *J. Am. Chem. Soc.* **1993,** *115,* 1612-1613

Triangular Platinum(II) Cluster Complexes $[Pt_3(CH_3COO)_4(cdoH)_2(cdoH_2)]$ and $[Pt_3(CH_3COO)_4(dmgH)_2(dmgH_2)]$ ($cdoH_2$ = cyclohexanedionedioxime and $dmgH_2$ = dimethylglyoxime)

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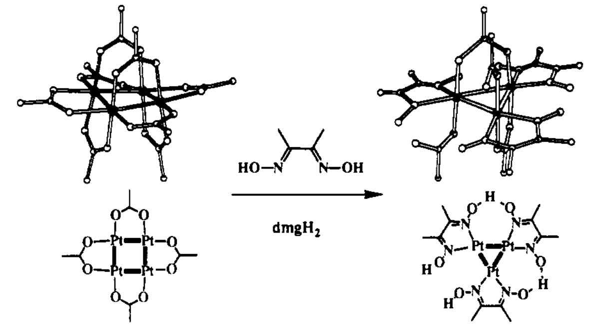
Received November 16, 1992

Platinum cluster complexes with Pt–Pt bonds are known for various oxidation states. Many of them are low-valent platinum cluster.[1-3] Tervalent platinum also forms dimeric cluster complexes[4] or compounds such as platinum blue in a Pt(II)/Pt(III) mixed valence state.[5] Until now divalent platinum clusters have been limited to the tetranuclear octaacetato complex $[Pt^{II}_4(\mu\text{-}CH_3COO)_8]$ (**1**).[6] Recently, we reported that the acetate ligands in **1** which are in the plane of the square-planar Pt cluster core are labile, whereas the out-of-plane ligands are inert to substitution. Thus, we prepared derivatives of the type $[Pt^{II}_4(\mu\text{-}CH_3COO)_4(\mu\text{-}RCOO)_4]$.[7] In this paper, we report new Pt(II) cluster complexes having a novel triangular core.

We found that **1** undergoes a cluster core transformation into a triangular cluster upon reaction with oxime ligands such as cyclohexanedionedioxime ($cdoH_2$) or dimethylglyoxime ($dmgH_2$). The transformation is associated with in-plane ligand substitution (Scheme I, $dmgH_2$ reaction depicted).

Scheme I. Cluster Core Transformation from the Square-Planar to Triangular-type Associated with the In-Plane Ligand Substitution[a]



$Pt_4(CH_3COO)_8$ (**1**) $Pt_3(CH_3COO)_4(dmgH)_2(dmgH_2)$ (**2b**)

[a] The drawings underneath show only the cluster core and the in-plane ligands.

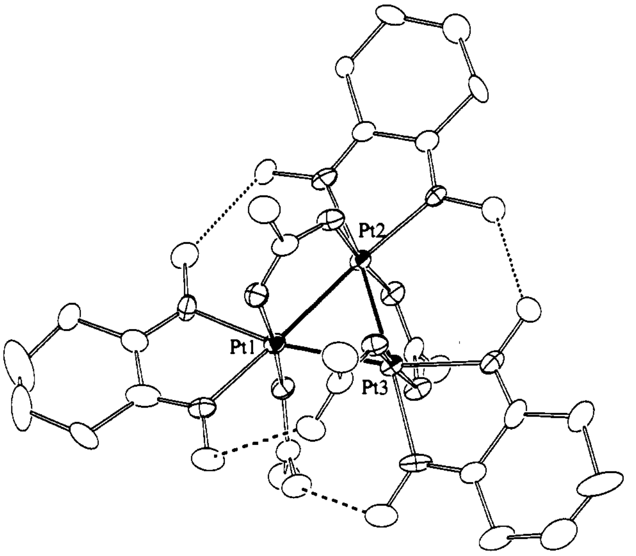
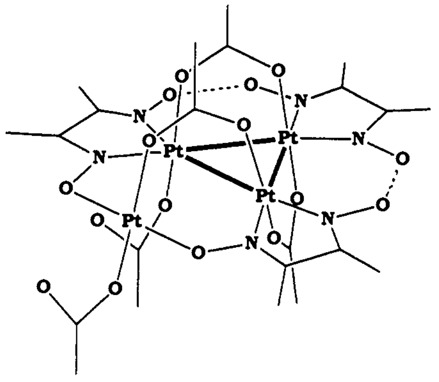


Figure 1. ORTEP drawing of $[Pt_3(CH_3COO)_4(cdoH)_2(cdoH_2)]$ (**2a**) in **2a**·$2CH_3CN$. Dotted and dashed lines show the O–H–O hydrogen bond. Carbon atoms with elongated ellipsoids in the cyclohexane rings are disordered.

Chart I



In the case of the reaction of **1** with $cdoH_2$, red-brown crystalline solid $[Pt_3(CH_3COO)_4(cdoH)_2(cdoH_2)]$ (**2a**)[8] was isolated from the reaction mixture by means of silica gel chromatography. Recrystallization from CH_2Cl_2/CH_3CN yielded a good quality of single crystals of **2a**·$2CH_3CN$. The ORTEP drawing of **2a** in Figure 1[9] shows that this compound is a cluster complex with an isosceles triangle of Pt atoms [Pt(1)–Pt(2) = 2.542(1), Pt(2)–Pt(3) = 2.529(1), Pt(1)–Pt(3) = 2.605(1) Å].[10,11] Three chelating cdo

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(8) Anal. Calcd for $Pt_3O_{14}N_6C_{26}H_{40}$: C, 25.07; H, 3.24; N, 6.75. Found: C, 25.33; H, 3.28; N, 6.59. FABMS: 1246 (calcd MW = 1245.7). NMR data in $CDCl_3$: ^1H, δ 1.73 (b, 6 H, CH_2CH_2), 1.81, 1.86 (s, 6 H, CH_3), 2.97 (m, 6 H, CH_2N), 12.08 (s, 2 H, NO*H*, which are not involved in the hydrogen bond); ^{13}C, δ 21.29, 21.34, 21.42 (CH_2CH_2), 21.68 (CH_3), 25.69, 25.77, 25.84 (CH_2N), 149.94, 151.22, 156.03 (N=*C*), 179.55, 192.06 (*C*OO); ^{195}Pt, δ 1020.0, 1047.8 (vs K_2PtCl_4 in D_2O), J_{AB} = 7671 Hz, suggesting the presence of a Pt–Pt bond.

(9) X-ray analysis of **2a**·$2CH_3CN$. Crystal data: $[Pt_3(CH_3COO)_4(cdoH)(cdoH_2)]\cdot 2CH_3CH = Pt_3O_{14}N_8C_{30}H_{46}$, triclinic, space group $P\bar{1}$, a = 12.376(3), b = 16.898(5), and c = 11.782(4) Å, α = 109.08(2), β = 112.68(2), γ = 102.12(2)°, V = 982(1) Å^3, Z = 2. With the use of 6332 unique reflections ($I > 3\sigma(I)$) collected at room temperature with Mo Kα (λ = 0.71069 Å) radiation up to 2θ = 55.1° on a Rigaku AFC 5R diffractometer, the structure was solved by the conventional heavy-atom method and refined by full matrix least squares with anisotropic temperature factors for non-hydrogen atoms to a final R value of 5.2%.

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ligands are coordinated in the plane of the cluster core. The cdo ligands of **2a** interact via two O–H–O hydrogen bonds (O···O = 2.47(2) and 2.51(2) Å), shown in dotted lines. The out-of-plane coordination sites are occupied by four acetate ligands. Two act as bridging ligands between Pt(1) and Pt(2) and between Pt(2) and Pt(3), and the remaining two are coordinated in a unidentate fashion to Pt(1) and Pt(3). No direct bridge exists between Pt(1) and Pt(3) (long Pt–Pt bond), but the two O(cdo)–H–O(CH_3COO) hydrogen-bonded bridges are shown in dashed lines. If the Pt–Pt bond is included, the coordination geometry around each Pt is a distorted octahedron. The ^{1}H-, ^{13}C-, and ^{195}Pt-NMR spectra[8] of **2a** show that the solid-state structure is retained in a solution state.

On the other hand, the reaction of **1** with $dmgH_2$ gave two kinds of red-brown crystalline solids in the same procedure, $[Pt_3(CH_3COO)_4(dmgH)_2(dmgH_2)]$ (**2b**)[12] and $[Pt_4(CH_3COO)_5(dmgH)_3]$ (**3b**).[13] Yields of **2b** and **3b** were approximately 5 and 75%, respectively, under our experimental conditions. The ^{1}H-, ^{13}C-, and ^{195}Pt-NMR spectra of compound **2b**[12] allow unambigous assignment of a triangular cluster structure very similar to **2a**.

The preliminary X-ray structure of **3b**[14] is shown schematically in Chart I. This compound is tetranuclear and consists of two units, a triangular cluster core very similar to that in **2b** and a mononuclear unit with square planar geometry. There are no Pt–Pt bonds between the units, and the in-plane coordination sites of the triangular core are all occupied by the dmg ligands. The structure shows the partial removal of one Pt from the tetranuclear cluster core of **1**. When one Pt atom in the mononuclear unit and the unidentate acetate attached to the Pt atom are removed from the structure **3b**, a residual structure is essentially the same as **2b**. Disposition of the four out-of-plane acetates in **1** remains almost unchanged in **3b**. In actual fact, **3b** converts to **2b** in acetone solution in the presence of an excess of free $dmgH_2$ ligand in a 4–5% yield under conditions similar to those in the reactions between **1** and the oximes. These facts may suggest that **2b** is formed via **3b**, although details are not certain at this moment. In the case of the $cdoH_2$ reaction, a tetranuclear compound corresponding to **3b** was detected as only a very weak chromatographic band. The transformation mechanism is now being studied.

When **1** is allowed to react with $cdoH_2$ or $dmgH_2$, in-plane ligand substitution takes place initially, as evidenced by the fact that the in-plane coordination sites in **2a**, **2b**, and **3b** are all occupied by the oxime ligands. The incoming oxime ligands take up a chelate coordination mode rather than the bridge coordination of acetates in **1**. Because of the steric demands of the bulky oxime ligands at the in-plane sites, one Pt in the square planar cluster of **1** is pushed out from the core to yield the triangular cluster. The oxidation state of Pt atoms in the products **2a**, **2b**, and **3b** remains in the +2 state. To our knowledge, the present complexes are the first compounds with triangular Pt(II) cluster cores, although similar triangular cluster cores are known for low-valent Pt.[1,2]

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (Nos. 02303006 and 04241102) from the Ministry of Education, Science, and Culture, Japan.

Supplementary Material Available: Tables of crystallographic data, experimental conditions, atomic positional and thermal parameters, and interatomic distances and bond angles for $\mathbf{2a}\cdot 2CH_3CN$ (10 pages); tables of observed and calculated structure factors (43 pages). Ordering information is given on any current masthead page.

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[10] EHMO calculation for the triangular model compound $[Pt_3(HCOO)_4(glyH)_2(glyH_2)]$ ($glyH_2$ = glyoxime) showed clearly the presence of three Pt–Pt single bonds between neighboring Pt atoms in the triangle. The calculation was carried out in a way similar to that reported previously for **1**.[7]

[11] Palladium(II) acetate, $Pd_3(CH_3COO)_6$, also has triangular structure, although it has no direct Pd–Pd bond (Skapski, A. C.; Smart, M. L. *J. Chem. Soc., Chem. Commun.* **1970**, 658).

[12] Anal. Calcd for $Pt_3O_{14}N_6C_{20}H_{34}$: C, 20.57; H, 2.94; N, 7.20. Found: C, 21.47; H, 3.13; N, 6.93. FABMS: 1168 (calcd MW = 1167.6). NMR data (JEOL JNM-GSX-270 FT NMR spectrometer) in $CDCl_3$: ^{1}H, δ 1.79, 1.85 (s, 6 H, acetate-CH_3), 2.35, 2.40, 2.40 (s, 6 H, dmg-CH_3), 12.22 (s, 2 H, NO*H*, which are not involved in the hydrogen bond); ^{13}C, δ 12.77, 12.94, 13.16 (dmg-*C*H_3), 21.25, 21.62 (acetate-*C*H_3), 149.31, 150.33, 155.59 (N=*C*), 179.58, 192.07 (*C*OO); ^{195}Pt, δ 1035.1 (2 Pt), 1038.7 (1 Pt) (vs K_2PtCl_4 in D_2O).

[13] Anal. Calcd for $Pt_4O_{16}N_6C_{22}H_{36}$: C, 18.61; H, 2.49; N, 5.92. Found: C, 18.67; H, 2.55; N, 5.54. FABMS: 1420 (calcd MW = 1421.0).

[14] Crystal data: $Pt_4(CH_3COO)_5(dmgH)_3 = Pt_4O_{16}N_6C_{22}H_{36}$, triclinic, space group $P\bar{1}$, a = 12.106(3), b = 16.229(2), and c = 11.752(2) Å, α = 95.39(1), β = 115.37(1), γ = 97.81(2)°, V = 2036.8(7) Å^3, Z = 2, current R = 7.8%. A unidentate acetate attached to the Pt atom in the mononuclear unit is disordered except for the donor oxygen.

Solution EPR Spectra of Reactive 1,5- and 1,6-Biradicals

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Received December 3, 1992

Biradicals of six carbon atoms chain length and shorter are often postulated as reactive intermediates in organic reaction mechanisms.[1] The structural and electronic properties of such species have long been difficult to quantify, with transient optical spectroscopy and product analyses being the predominant characterization tools.[2] The recent advance of time-resolved magnetic resonance techniques[3] in the study of biradicals has, to date, been applicable only to longer chains (1,7- and longer) where the singlet–triplet splitting ($2J$) is small enough to allow substantial mixing of the EPR active triplet sublevels with the highly reactive singlet level.[4] As the biradicals become shorter, large J values lead to a small degree of singlet–triplet mixing, which in turn leads to weak polarization of the EPR active populations. This situation is depicted graphically in Figure 1. The resulting EPR signals are then below the sensitivity limit of a typical X-band (9.5 GHz) spectrometer operating without field modulation.[5] Two strategies exist for overcoming this problem. The first is to alter the structure of the biradical so that the value of $|2J|$ is decreased, moving the singlet state closer to at least one of the triplet levels (usually T^-, the lowest level). This can be accomplished by restricting the number of conformations with large overlap between the unpaired electrons or by delocalization of the electrons into aromatic rings. The second strategy is to move the time-resolved EPR experiment (TREPR) to a higher frequency (Q-band, 35 GHz), pushing the T^- level closer to the singlet via a larger Zeeman interaction. In this communication we report the successful combination of both strategies to obtain the solution EPR spectra of 1,5- and 1,6-bis(benzyl) biradicals, using the photochemistry shown in Scheme I. These are the first solution EPR spectra of transient biradicals with a chain length of less than seven carbon atoms at either frequency.[6]

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[5] The minimum detectable number of spins in direct detection experiments is usually at least 1 order of magnitude greater than that in field-modulated experiments, i.e., approximately 10^{13} per sample for our X-band spectrometer.

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