

excellent yield (96%). Further studies in tetraene carbocyclizations are in progress.

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## Reductive-Elimination Reactions from Platinum Dimers Bridged by (Diphenylphosphino)cyclopentadienyl Ligands

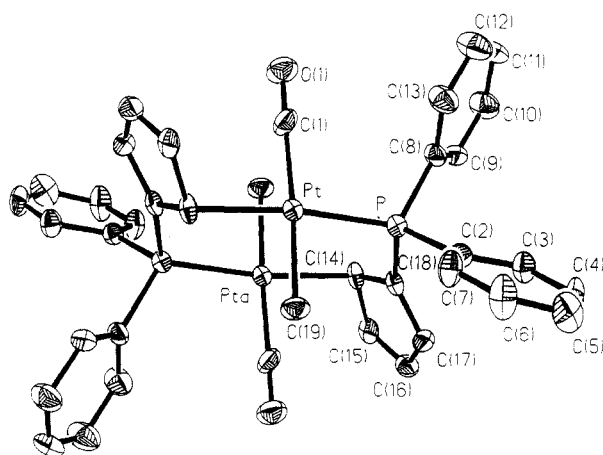
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**Summary:**  $[\text{Pt}_2\text{Me}_2(\text{CO})_2(\mu\text{-}\eta^1\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  (**2**), obtained by reaction of  $[\text{Pt}_2\text{Me}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  (**1**) with CO, has been characterized by X-ray crystallography as a face-to-face dimer, in which the cyclopentadienyl ring is 1,2-substituted. Thermolysis of **2** at 55 °C yields acetone and the platinum(I) dimer  $[\text{Pt}_2(\text{CO})_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  (**3**), and the crystal structure of the latter reveals that the platinum atoms have migrated to the ipso carbons of the cyclopentadienyl rings. The analogous  $[\text{Pt}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  is produced, along with ethane, when **1** is treated with  $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ .

Ligands that display variable hapticity are useful in the design of catalyst precursors, since changes in hapticity provide low-energy pathways between coordinatively saturated and unsaturated species.<sup>1</sup> The cyclopentadienyl group is one such ligand, and we have made an extensive study of the factors that affect its mode of binding to palladium and platinum.<sup>2</sup> The (diphenylphosphino)cyclopentadienyl (dppc) group has been used to construct homo- and heterobimetallic complexes,<sup>3-7</sup> and it also has the potential to adopt differing bonding modes. We have shown recently that platinum dimers bridged by  $\eta^5$ -dppc ligands may be converted to 16-electron  $\eta^1$  species under suitable conditions.<sup>8</sup> We report here the structures of two



**Figure 1.** Projection drawing of  $[\text{Pt}_2\text{Me}_2(\text{CO})_2(\mu\text{-}\eta^1\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ , showing the atom-labeling scheme. The molecule contains a crystallographic  $\bar{1}$  symmetry element. Selected bond distances (Å) and angles (deg) include the following: Pt–P = 2.298 (3), Pt–C1 = 1.897 (12), Pt–C19 = 2.088 (11), Pt–C14A = 2.160 (11), Pt···PtA = 3.157 (1), P–C2 = 1.835 (11), P–C8 = 1.834 (11), P–C18 = 1.796 (12), C18–C14 = 1.508 (14), C14–C15 = 1.479 (18), C15–C16 = 1.358 (16), C16–C17 = 1.400 (20), C17–C18 = 1.378 (16); P–Pt–C1 = 97.2 (4), P–Pt–C19 = 87.8 (4), P–Pt–C14A = 171.6 (3), C1–Pt–C19 = 173.6 (6).

different  $\eta^1$ -bonded dppc complexes and the reductive elimination of acetone or ethane from methylplatinum species bridged by dppc ligands.

Treatment of  $[\text{Pt}_2\text{Me}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  (**1**)<sup>8</sup> with carbon monoxide (1 atm) in dichloromethane or benzene solution affords, within a few minutes,  $[\text{Pt}_2\text{Me}_2(\text{CO})_2(\mu\text{-}\eta^1\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  (**2**) as a yellow solid in 90% yield. The structure of **2** has been determined by single-crystal X-ray crystallography (Figure 1).<sup>9</sup> The dimer has a face-to-face, square-planar structure, with a nonbonded Pt···Pt distance of 3.157 Å. The cyclopentadienyl groups of the bridging

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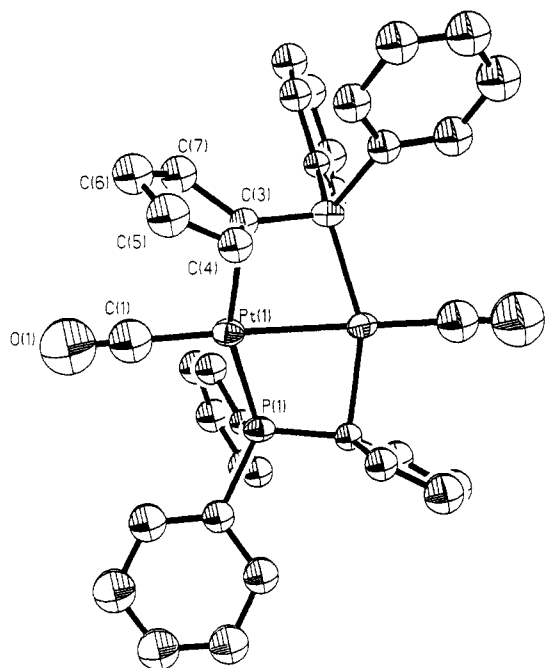
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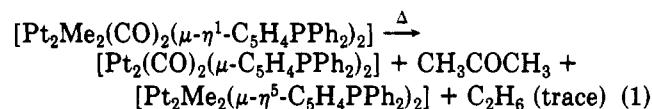
(9) Crystal data for  $[\text{Pt}_2\text{Me}_2(\text{CO})_2(\mu\text{-}\eta^1\text{-C}_5\text{H}_4\text{PPh}_2)_2]\cdot\text{Et}_2\text{O}$ :  $\text{C}_{42}\text{H}_{44}\text{O}_9$ ,  $\text{P}_2\text{Pt}_2$ ; space group  $C2/c$  (selected over  $Cc$  on the basis of behavior toward refinement); cell dimensions  $a = 14.989$  (3) Å,  $b = 16.031$  (4) Å,  $c = 16.469$  (4) Å,  $\beta = 104.31$  (2)°;  $Z = 4$ ;  $V = 3834.5$  (15) Å<sup>3</sup>;  $d(\text{calcd}) = 1.817$  Mg/m<sup>3</sup>. The 3534 measured reflections were collected with use of the  $2\theta$ - $\theta$  scanning technique and graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Siemens R3 diffractometer. The structure was solved by Patterson methods with use of the SHELXTL PLUS program. Hydrogen atoms were included in their calculated positions and were held fixed. Refinement of the 1764 unique observed reflections with  $F > 6.0\sigma(F)$  converged at  $R = 0.0288$  and  $R_w = 0.0348$ .



**Figure 2.** Projection drawing of one molecule of  $[\text{Pt}_2(\text{CO})_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ , showing the atom-labeling scheme. The molecule contains a crystallographic  $\bar{1}$  symmetry element. Selected bond distances (Å) and angles (deg) include the following (molecule 1): Pt1–Pt1A = 2.593 (1), Pt1–P1 = 2.244 (3), Pt1–C1 = 1.855 (15), Pt1–C3 = 2.200 (10), P1–C13 = 1.826 (11), P1–C19 = 1.866 (12), P1–C3A = 1.762 (11), C3–C4 = 1.486 (16), C4–C5 = 1.353 (16), C5–C6 = 1.402 (19), C6–C7 = 1.388 (18), C7–C3 = 1.514 (15); P1–Pt1–Pt1A = 73.5 (1), C3–Pt1–Pt1A = 82.8 (3), C1–Pt1–Pt1A = 176.5 (5), Pt1–P1–C3A = 104.6 (3), Pt1–C3–P1A = 93.8 (4).

$\eta^1$ -dppc ligands are 1,2-substituted.

When a benzene solution of **2** is heated at 50–55 °C in vacuo for 12 h, acetone is eliminated and a new platinum(I) dimer,  $[\text{Pt}_2(\text{CO})_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  (**3**), is generated, along with **1** and a trace amount of ethane (eq 1). Repeated



treatment of this mixture by addition of CO, followed by evacuation and thermolysis, leads to **3** in nearly quantitative yield.<sup>10</sup> The structure of the latter has been determined by single-crystal X-ray crystallography (Figure 2)<sup>11</sup> and reveals the following features. The complex contains the expected Pt–Pt bond (2.593 Å)<sup>12</sup> and a nearly

(10) Thermolysis in the presence of CO results in the formation of several unidentified products.

(11) Crystal data for  $[\text{Pt}_2(\text{CO})_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ :  $\text{C}_{36}\text{H}_{28}\text{O}_2\text{P}_2\text{Pt}_2$ ; space group  $C2/c$  (selected over  $Cc$  on the basis of behavior toward refinement); cell dimensions  $a = 21.229$  (3) Å,  $b = 14.243$  (3) Å,  $c = 21.065$  (3) Å,  $\beta = 90.17$  (1)°;  $Z = 8$ ;  $V = 6369$  (2) Å<sup>3</sup>;  $d(\text{calcd}) = 1.970$  Mg/m<sup>3</sup>. The 5980 measured reflections were collected, and the structure was solved and refined as in ref 9. Refinement of 2730 unique observed reflections with  $F > 6.0\sigma(F)$  converged at  $R = 0.0288$  and  $R_w = 0.0339$ . The structure contains two molecules per asymmetric unit. The carbonyl groups are disordered in one of the molecules. The O atoms were located in two positions, O(21) and O(22), each of 50% occupancy, and were refined to convergence as half-occupancy atoms.

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linear OC–Pt–Pt–CO arrangement. The bonding of the dppc unit is unexpected, however. The cyclopentadienyl group is 1,1-disubstituted, giving rise to two strained  $\text{Pt}_2\text{PC}$  rings. The P–Pt–Pt' and C–Pt–Pt' angles are 73.5 and 82.8°, respectively.

This geometry appears to be quite stable, however, and the terminal carbonyl ligands may be replaced by a range of neutral ligands without rupture of the four-membered ring. Thus, reaction of **3** with 2 mol equiv of CNBu<sup>t</sup>, PPh<sub>3</sub>, PMe<sub>2</sub>Ph, PEt<sub>3</sub>, or P(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>3</sub> leads to compounds of the type  $[\text{Pt}_2\text{L}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  in high yield.<sup>13</sup> The complex  $[\text{Pt}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  is formed directly when a chloroform solution of **1** is treated with tris(2-cyanoethyl)phosphine (2 mol equiv). This reaction is accompanied by ethane elimination.

Deuterium labeling studies have been performed in order to determine whether these elimination reactions are intra- or intermolecular. A 1:1 mixture of  $[\text{Pt}_2(\text{CH}_3)_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  and  $[\text{Pt}_2(\text{CD}_3)_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  in benzene solution was allowed to react with CO; then the reaction vessel was evacuated and maintained at 55 °C overnight. GC–MS analysis of the resulting gas phase revealed that acetone-*d*<sub>0</sub>, -*d*<sub>3</sub>, and -*d*<sub>6</sub> were formed in a 1:2:1 ratio, indicating that methyl group scrambling takes place either prior to or during the elimination process. In contrast, treatment of a 1:1 mixture of  $[\text{Pt}_2(\text{CH}_3)_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  and  $[\text{Pt}_2(\text{CD}_3)_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  with P(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>3</sub> produced ethane-*d*<sub>0</sub> and -*d*<sub>6</sub> exclusively, demonstrating that this reaction occurs by a strictly intramolecular mechanism in which the dimeric unit is maintained.

We believe that the structure of the platinum(I) dimer provides a clue regarding the mechanism of these elimination processes. We have seen previously that the C<sub>5</sub>H<sub>4</sub> group of the dppc ligand may dissociate,<sup>8</sup> and the fact that the platinum migrates to the phosphorus-bearing carbon during the reactions suggests that cleavage of the Pt–C<sub>5</sub>H<sub>4</sub> interaction takes place. Such a process would create a vacant site on the metal, allowing isomerization prior to CO insertion in the former case and transfer of an organic fragment from one metal to the other in both cases. Mechanistic studies of these elimination reactions are continuing.

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**Supplementary Material Available:** Tables of analytical and spectroscopic data and of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates for **2** and **3** (17 pages); tables of observed and calculated structure factors for **2** and **3** (32 pages). Ordering information is given on any current masthead page.

(13) Analytical and spectroscopic data for  $[\text{Pt}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$  are as follows. Anal. Calcd for  $\text{C}_{52}\text{H}_{52}\text{N}_6\text{P}_4\text{Pt}_2$ : C, 48.98; H, 4.08; N, 6.59. Found: C, 48.80; H, 4.13; N, 6.56. <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta(\text{P}_A) -5.2$ ,  $^1J(\text{PtP}_A) = 3480$ ,  $^2J(\text{PtP}_A) = 315$ ,  $^3J(\text{P}_A\text{P}_A) = 29$  Hz;  $\delta(\text{P}_B) 12.4$ ,  $^1J(\text{PtP}_B) = 3035$ ,  $^2J(\text{PtP}_B) = 326$ ,  $^3J(\text{P}_B\text{P}_B) = 195$  Hz. Analytical and spectroscopic data for the other compounds are given in the supplementary material.