

## Synthesis of Homo and Hetero Palladium–Platinum Bimetallic Complexes; X-Ray Crystal Structure of $\text{Pt}_2\text{Cl}_2(\mu\text{-CO})(\text{PPh}_3)_3$

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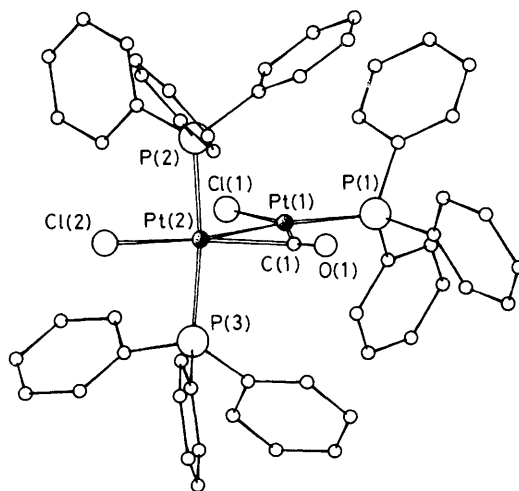
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The compounds  $\text{M}^1(\text{CO})(\text{PPh}_3)_3$  ( $\text{M}^1 = \text{Pt}, \text{Pd}$ ) react with  $\text{M}^2\text{Cl}_2(\text{PhCN})_2$  ( $\text{M}^2 = \text{Pt}, \text{Pd}$ ) in tetrahydrofuran at room temperature to afford the new homo [ $\text{M}^1 = \text{M}^2 = \text{Pt}$  (**1**);  $\text{M}^1 = \text{M}^2 = \text{Pd}$  (**2**)] or hetero [ $\text{M}^1 = \text{Pt}, \text{M}^2 = \text{Pd}$  (**3**);  $\text{M}^1 = \text{Pd}, \text{M}^2 = \text{Pt}$  (**4**)] bimetallic complexes  $\text{M}^1\text{M}^2\text{Cl}_2(\mu\text{-CO})(\text{PPh}_3)_3$  via formal oxidative-addition of the  $\text{M}^2(\text{II})\text{-Cl}$  bond at the  $\text{M}^1(0)$  centre; complex (**1**) has been structurally characterized by X-ray diffraction.

In the course of our studies on the synthesis of mixed transition metal clusters, we had found that the reaction of *cis*- or *trans*- $\text{PtCl}_2(\text{PPh}_3)_2$  with two equiv.  $\text{NaCo}(\text{CO})_4$  afforded *inter alia* the butterfly cluster  $\text{Pt}_2\text{Co}_2(\text{CO})_8(\text{PPh}_3)_2$ .<sup>1</sup> We have now discovered that the reaction with only one equiv.  $\text{NaCo}(\text{CO})_4$  [tetrahydrofuran (THF), 2 h, 55 °C] surprisingly affords *inter alia* the new bimetallic complex (**1**) (16% yield). This yellow complex<sup>†</sup> was recognized to be identical with a by-product obtained earlier in trace amounts in the reaction of  $\text{PtCl}_2(\text{PPh}_3)_2$  with  $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  and which had been erroneously formulated as  $\text{Pt}_3(\mu\text{-CO})_2(\text{PPh}_3)_4$ .<sup>1</sup>

After numerous attempts, we obtained crystals of (**1**) as the chlorobenzene solvate, suitable for X-ray diffraction<sup>‡</sup> from  $\text{PhCl}$ -hexane at room temperature (slow diffusion technique). The structure of this bimetallic complex is shown in Figure 1. The  $\text{Pt}(1)\text{-Pt}(2)$  bond of 2.643(3) Å is asymmetrically bridged by the carbonyl  $\mu_2\text{-}[\text{C}(1)\text{O}(1)]$ . The two metals are in different environments. Thus, the planar geometry about  $\text{Pt}(1)$  [including  $\text{Pt}(2)$ ,  $\text{Cl}(1)$ ,  $\text{C}(1)$ , and  $\text{P}(1)$ ] contrasts with the distorted trigonal bipyramidal arrangement about  $\text{Pt}(2)$  [including  $\text{Pt}(1)$ ,  $\text{C}(1)$ ,  $\text{Cl}(2)$ ,  $\text{P}(2)$ , and  $\text{P}(3)$ ]. The  $\text{Pt}(1)$ ,  $\text{Pt}(2)$ ,  $\text{Cl}(1)$ ,  $\text{Cl}(2)$ ,  $\text{P}(1)$ , and  $\text{C}(1)$  atoms are nearly coplanar, as they deviate from the mean plane passing through them by  $-0.01$ ,  $0.01$ ,  $0.03$ ,  $-0.10$ ,  $-0.02$ , and  $0.13$  Å, respectively. The geometry about  $\text{Pt}(2)$  can also be viewed as distorted square planar when considering  $\text{Cl}(2)$ ,  $\text{P}(2)$ ,  $\text{P}(3)$ , and the midpoint of



**Figure 1.** Molecular structure of  $\text{Pt}_2\text{Cl}_2(\mu\text{-CO})(\text{PPh}_3)_3$  (**1**). Important bond distances (Å) and angles (°):  $\text{Pt}(1)\text{-Pt}(2)$ , 2.643(3);  $\text{Pt}(1)\text{-Pt}(1)$ , 2.238(8);  $\text{Pt}(1)\text{-Cl}(1)$ , 2.368(8);  $\text{Pt}(1)\text{-C}(1)$ , 1.88(3),  $\text{Pt}(2)\text{-Pt}(2)$ , 2.299(8);  $\text{Pt}(2)\text{-P}(3)$ , 2.307(8);  $\text{Pt}(2)\text{-Cl}(2)$ , 2.373(8);  $\text{Pt}(2)\text{-C}(1)$ , 2.10(3);  $\text{C}(1)\text{-O}(1)$ , 1.19(4);  $\text{Cl}(1)\text{-Pt}(1)\text{-Pt}(2)$ , 100.8(2);  $\text{Pt}(2)\text{-Pt}(1)\text{-C}(1)$ , 52.2(9);  $\text{C}(1)\text{-Pt}(1)\text{-P}(1)$ , 108.2(9);  $\text{Cl}(1)\text{-Pt}(1)\text{-P}(1)$ , 98.8(3);  $\text{Pt}(2)\text{-C}(1)\text{-Pt}(1)$ , 83(1);  $\text{C}(1)\text{-Pt}(2)\text{-Pt}(1)$ , 44.8(8);  $\text{Pt}(1)\text{-Pt}(2)\text{-Cl}(2)$ , 161.0(2);  $\text{Cl}(2)\text{-Pt}(2)\text{-C}(1)$ , 154.1(8);  $\text{P}(2)\text{-Pt}(2)\text{-P}(3)$ , 172.4(3);  $\text{Pt}(1)\text{-Pt}(2)\text{-P}(3)$ , 93.8(2);  $\text{Pt}(1)\text{-Pt}(2)\text{-P}(2)$ , 89.1(2);  $\text{Cl}(2)\text{-Pt}(2)\text{-P}(3)$ , 88.7(3);  $\text{Cl}(2)\text{-Pt}(2)\text{-P}(2)$ , 86.3(3);  $\text{P}(3)\text{-Pt}(2)\text{-C}(1)$ , 91.3(8);  $\text{P}(2)\text{-Pt}(2)\text{-C}(1)$ , 95.7(8).

<sup>†</sup> The new complexes (**1**)–(**4**) were characterized by elemental analysis, i.r. spectroscopy, and particularly by  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectroscopy. Selected data: i.r. ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$  (**1**) 1822, (**2**) 1861, (**3**) 1822, (**4**) 1823  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. ( $\text{CD}_2\text{Cl}_2$ , positive downfield from  $\text{H}_3\text{PO}_4$ ) (**1**)  $\delta$  30.20 ( $\text{P}_A$ ) and 21.74 ( $\text{P}_B$ ) p.p.m.,  $^1J[\text{Pt}(1)\text{-P}_A]$  5440,  $^2J[\text{Pt}(2)\text{-P}_A]$  804,  $^2J[\text{Pt}(1)\text{-P}_B]$  59,  $^1J[\text{Pt}(2)\text{-P}_B]$  2680,  $J(\text{P}_A\text{P}_B) < 2$  Hz; (**4**)  $\delta$  28.48 ( $\text{P}_A$ ) and 19.29 ( $\text{P}_B$ ) p.p.m.,  $^2J(\text{Pt}\text{-P}_A)$  922,  $^1J(\text{Pt}\text{-P}_B)$  2562,  $J(\text{P}_A\text{-P}_B)$  9 Hz.

<sup>‡</sup> *Crystal data:*  $\text{C}_{55}\text{H}_{45}\text{Cl}_2\text{OP}_3\text{Pt}_2\cdot 2\text{C}_6\text{H}_5\text{Cl}$ ,  $M = 1501.09$ , monoclinic, space group  $P2_1/n$ ,  $a = 27.774(15)$ ,  $b = 12.400(8)$ ,  $c = 17.508(6)$  Å,  $\beta = 91.86(4)^\circ$ ,  $U = 6027(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.65$  g  $\text{cm}^{-3}$ ,  $F(000) = 2936$ ,  $\mu(\text{Mo-K}\alpha) = 49.84$   $\text{cm}^{-1}$ . The intensities of 8414 independent reflections were collected on a Siemens AED diffractometer (with  $\theta$  in the range  $3\text{--}23^\circ$ ); Nb-filtered  $\text{Mo-K}\alpha$  radiation and the  $\theta\text{-}2\theta$  scan technique were used. The structure was solved *via* conventional Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 4596 observed reflections [having  $I \geq 2\sigma(I)$ ] to an  $R$  value of 6.7%.

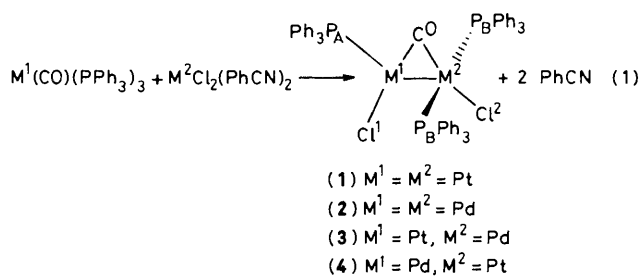
The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23799 (29 pp.) from the British Library Lending Division. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, issue 3, p. xvii.

the  $\text{Pt}(1)\text{-C}(1)$  bond. This plane, which intersects  $\text{Pt}(1)\text{-C}(1)$  nearly centrally, makes a dihedral angle of  $89.5(2)^\circ$  with the  $\text{Pt}(1)$  co-ordination plane.

Assigning formally the carbonyl ligand to  $\text{Pt}(1)$  confers a 16 electron environment to each metal. The asymmetric CO helps to balance the excess of electron density at  $\text{Pt}(2)$  originating from the two  $\text{PPh}_3$  ligands.

The experimental observations mentioned above concerning the preparation of (**1**), together with its crystal structure led us to consider that this complex may arise from the oxidative-addition of the  $\text{Pt}\text{-Cl}$  bond of  $\text{PtCl}_2(\text{PPh}_3)_2$  at a  $\text{Pt}(\text{CO})(\text{PPh}_3)_n$  ( $1 \leq n \leq 3$ ) centre. Thus, the platinum(0) fragment could result from the reductive carbonylation of  $\text{PtCl}_2(\text{PPh}_3)_2$  by the carbonylmetallate,<sup>2</sup> while excess of  $\text{PtCl}_2(\text{PPh}_3)_2$  would still be present because of the stoichiometry used ( $\text{Co}:\text{Pt} = 1:1$ ). We therefore treated a THF solution of  $\text{Pt}(\text{CO})(\text{PPh}_3)_3$ <sup>3</sup> with one equiv. of the labile platinum(II) complex  $\text{PtCl}_2(\text{PhCN})_2$ . Complex (**1**) formed (3 h, room temp.) and precipitated (61% yield).<sup>†</sup>

In order to evaluate the generality of the procedure represented in equation (1), we treated  $\text{Pd}(\text{CO})(\text{PPh}_3)_4$  with



$PdCl_2(PhCN)_2$  under the same conditions. This afforded the new palladium(I) bimetallic complex (2) (60% yield).

The cross-reactions  $Pt(CO)(PPh_3)_3 + PdCl_2(PhCN)_2$  and  $Pd(CO)(PPh_3)_3 + PtCl_2(PhCN)_2$  [equation (1)] afforded smoothly the mixed palladium(I)–platinum(I) complexes (3) (51% yield) and (4) (62% yield), respectively.† A related conproportionation reaction has been recently reported.<sup>5</sup>

Extending the results obtained with bimetallic Pd(I)–Pd(I) complexes<sup>6</sup> mixed Pd(I)–Pt(I) systems can be useful precursors for the synthesis of new heteropolymetallic clusters containing three or four different metals.<sup>7</sup> This should apply to (3) and (4). We have found that (2) reacts with two equiv.  $NaW(CO)_3(\eta-C_5H_5)$  (THF, 4 h, room temp.) to afford the heterotetrametallic cluster  $[PdW(\eta-C_5H_5)(\mu_3-CO)(\mu-CO)_2-$

$PPh_3]_2$  (58% yield) in which the palladium centres have been formally described as Pd(I).<sup>8</sup> This cluster has previously been obtained by partial reduction of Pd(II) precursors.<sup>8</sup>

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