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# Approaches to bi- and trimetallic platinum and palladium complexes using the DPPEPM ligand

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#### Abstract

Bis{(diphenylphosphinoethyl)phenylphosphino}methane (DPPEPM) reacts with [PtR<sub>2</sub>(cod)] in 1:1 ratio to give [PtR<sub>2</sub> (DPPEPM-*PP*)] (**2a**, R = Me; **2b**, R = Ph), whereas with [PtCl<sub>2</sub>(cod)] or [PdCl<sub>2</sub>(cod)] it yields the ionic species [M(DPPEPM-*PP*)<sub>2</sub>]<sup>2+</sup> (**3** and **4**). With [MClMe(cod)], the product is [MMe(DPPEPM-*PPP*)]<sup>+</sup> (**5**, M = Pt; **6**, M = Pd), in which one of the internal P atoms of the ligand is uncoordinated. These complexes undergo oxidation of the free P atom to give 7 and **8** on standing in solution. Complexes **2–4** may be used to construct bimetallic and trimetallic mixed metal complexes. The molecular structures of **7** and [PtMe<sub>2</sub>( $\mu$ -DPPEPM)PdCl<sub>2</sub>] (**11**) are reported.

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A number of phosphorus-containing ligands have been employed in the synthesis of homobimetallic complexes. Preparation of heterobimetallic complexes is less straightforward, however, because of the tendency for formation of symmetrical species. One method that can favor heterometallic species is the use of heterodifunctional ligands, such as Ph<sub>2</sub>Ppy [1], Ph<sub>2</sub>PCH<sub>2</sub>AsPh<sub>2</sub> [2], or  $R_2PC_5H_4$  [3]. Alternatively, unsymmetrical complexes can be prepared using simple bridging ligands, such as Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (dppm), but they must be constructed in a stepwise manner. Thus, reaction of  $[MoCl(\eta^5-C_5H_5)]$  $(CO)_2(dppm-P)$ ] with  $[Pt(C_2H_4)(PPh_3)_2]$  gives the mixed metal complex  $[Mo(\eta^5-C_5H_5)(CO)_2(\mu-dppm)Pt(PPh_3)]$ [4]. We have shown that the  $\eta^1$ -dppm cations [PtR (dppm-PP)(dppm-P)]<sup>+</sup> can serve as precursors to platinum-rhodium complexes [5], and to mixed metal complexes of platinum with silver, gold or mercury [6]. Similarly, the  $\eta^1$ -dppm derivatives [PtR<sub>2</sub>(dppm-P)<sub>2</sub>] have been used to prepare diplatinum complexes of the type  $[PtR_2(\mu-dppm)_2PtR'_2]$  [7]. Stanley's tetra- and

hexaphosphine ligands have been used primarily in the synthesis of homobimetallic compounds, but mixed metal complexes of these ligands have been prepared also [8]. We have shown previously that platinum and palladium precursors react with the tetraphosphine bis[(diphenylphosphinoethyl)phenylphosphino]methane (DPPEPM) in 2:1 ratio to generate symmetrical homobimetallic complexes of the form  $[MX_2(\mu\text{-DPPEPM})]$   $MX_2$ ] (M = Pt, X = Cl, methyl, benzyl, phenyl, 4-tolyl; M = Pd, X = Cl) [9]. Here we describe reactions of platinum and palladium precursors with DPPEPM in 1:1 ratio, and subsequent reactions to produce heterobimetallic derivatives.

Treatment of *meso*-DPPEPM (1) with 1 mol equiv of  $[PtR_2(cod)]$  (R = Me, Ph) in dilute acetone solution produces the monometallic complex  $[PtMe_2(DPPEPM-PP)]$ (2a) and  $[PtPh_2(DPPEPM-PP)]$  (2b) in good yield (Scheme 1). Each complex is characterized by four resonances in its <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. Complex 2a exhibits a doublet at -12.4 ppm (<sup>3</sup>J<sub>PP</sub> = 31 Hz) and a doublet of doublets at -28.7 ppm (<sup>2</sup>J<sub>PP</sub> = 68, <sup>3</sup>J<sub>PP</sub> = 31 Hz), due to the uncoordinated P atoms, and a doublet of doublet at 49.4 ppm (<sup>2</sup>J<sub>PP</sub> = 4 Hz, <sup>1</sup>J<sub>PtP</sub> = 1829 Hz),

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Scheme 1. Reactions of DPPEPM with [PtR<sub>2</sub>(cod)] (R = Me, Ph), [MCl<sub>2</sub>(cod)] and [MClMe(cod)] (M = Pd, Pt).

due to the two coordinated P atoms. The magnitudes of the couplings to <sup>195</sup>Pt are consistent with a phosphine ligand lying *trans* to an alkyl group. The NMR spectrum of **2b** is similar [10]. When dilute solutions are employed the monometallic complex is formed almost quantitatively, but with more concentrated samples the diplatinum complexes [Pt<sub>2</sub>R<sub>4</sub>( $\mu$ -DPPEPM)] [9] and some free ligand are observed also.

One might expect that the analogous reaction of DPPEPM with  $[PtCl_2(cod)]$ would produce [PtCl<sub>2</sub>(DPPEPM-PP)], but this is not the case. When dilute solutions of the two reagents are mixed in equimolar amounts, the major product is indeed a complex with four nonequivalent (two coordinated and two uncoordinated) P atoms. The magnitudes of the  ${}^{1}J_{PtP}$ coupling constants (2370 and 2665 Hz) indicate that each phosphine lies trans to another phosphine, however, instead of a chloride. The product is formulated as the  $[Pt(DPPEPM-PP)_2]^{2+}$  cation (3) [11], and the nature of the cation has been confirmed by high-resolution mass spectrometry. The <sup>1</sup>H NMR spectrum of **3** exhibits eight resonances due to the PCH2CH2P hydrogens, which can be separated into two sets of four on the basis of COSY experiments. The central CH<sub>2</sub> hydrogens give rise to broad peaks at 4.55 and 0.87 ppm, each of which simplifies to a doublet upon <sup>31</sup>P decoupling. The reaction with  $[PdCl_2(cod)]$  proceeds similarly. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of  $[Pd(DPPEPM-PP)_2]^{2+}$  (4) also exhibits signals due to two uncoordinated and two coordinated P atoms [11]. Again, the central CH<sub>2</sub> group of the DPPEPM ligand gives rise to two widely separated <sup>1</sup>H resonances at 4.35 and 0.91 ppm.

Reactions of DPPEPM with [PtClMe(cod)] and [PdClMe(cod)] follow yet a different path. The products are formulated as the cations **5** and **6** (Scheme 1) [12], in which the chloride has been displaced from the metal. DPPEPM acts a tridentate ligand, with one of the internal P atoms remaining uncoordinated. In each case, the  ${}^{31}P{}^{1}H{}$  NMR spectrum exhibits four resonances, one at low frequency due to the uncoordinated P atom, two that exhibit large  ${}^{2}J_{PP}$  couplings indicative of their mutually *trans* disposition, and a fourth that shows coupling to each of the other three P atoms. In **5**, this fourth signal also shows the smallest  ${}^{1}J_{PtP}$  value, indicating that it lies *trans* to the methyl group. If allowed to stand in acetone solution the uncoordinated P atom becomes oxidized, as evidenced by the disappearance of the low frequency signal and the appearance of a new signal at ca. 35 ppm, to give [MMe{DPPEPM(O)-*PPP*]Cl, 7 (M = Pt) and **8** (M = Pd). The structure of 7 has been determined by X-ray crystallography [13], and its molecular structure is shown in Fig. 1.



Fig. 1. Molecular structure of  $[PtMe{DPPEPM(O)-PPP}]^+$  (7). Selected bond distances (Å) and angles (deg): Pt(1)-P(1) 2.2953(8), Pt(1)-P(2) 2.3276(8), Pt(1)-P(4) 2.2859(8), Pt(1)-C(42) 2.131(3); P(1)-Pt(1)-P(2) 84.48(3), P(1)-Pt(1)-P(4) 174.92(3), P(2)-Pt(1)-P(4) 98.76(3), P(1)-Pt(1)-C(42) 88.38(11), P(2)-Pt(1)-C(42) 172.84(10), P(4)-Pt(1)-C(42) 88.33(10), P(2)-C(21)-P(3) 118.87(17).



Scheme 2. Preparation of mixed metal complexes.

The monometallic complexes 2-4 may be employed to prepare mixed metal derivatives. Addition of 1 mol equiv of [PtPh<sub>2</sub>(cod)] to an acetone solution of 2a produces the mixed diplatinum complex [PtMe2(µ-DPPEPM)PtPh<sub>2</sub>] (9) quite cleanly (Scheme 2) [14], although traces of  $[Pt_2R_4(\mu-DPPEPM)]$  (R = Me, Ph) are also formed. Reaction of 2a with [PtCl<sub>2</sub>(cod)] yields a mixture of [PtMe<sub>2</sub>(µ-DPPEPM)PtCl<sub>2</sub>] (10) and the trimetallic complex [{ $PtMe_2(\mu-DPPEPM)$ }<sub>2</sub>Pt]<sup>2+</sup> (12). The  ${}^{31}P{}^{1}H$  NMR spectrum of 10 consists of four resonances, the  ${}^{1}J_{PtP}$  couplings being typical of two P atoms lying trans to methyl groups, and two lying trans to chlorides. The structure of 10 has been determined by X-ray crystallography, and its molecular structure is shown in Fig. 2 [15]. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 12 contains two signals with small <sup>195</sup>Pt couplings, due to the two P atoms lying trans to methyls, and two signals that are very similar to those found for the central P atoms in 3. Complex 10 would be formed by displacement of cod from [PtCl<sub>2</sub>(cod)] by the free phosphine groups in 2a, whereas further reaction of 10 with a second equivalent of 2a would generate 12. When the reaction is performed in reverse order, namely, by addition of DPPEPM to [PtCl<sub>2</sub>(cod)] to give 3, followed by addition of [PtMe<sub>2</sub>(cod)], the trimetallic complex 12 is formed quantitatively. Here the two uncoordinated diphosphine units in 3 would displace cod from two molecules of [PtMe<sub>2</sub>(cod)] (Scheme 2).

We have shown that it is possible, by careful addition of 1 equiv of a suitable platinum or palladium precursor to DPPEPM, to produce complexes containing two coordinated and two uncoordinated phosphine moieties, i.e., it is possible to add one metal center to one "half" of the tetradentate ligand. The remaining free diphosphine



Fig. 2. Molecular structure of  $[PtMe_2(\mu-DPPEPM)PtCl_2]$  (10). Selected bond distances (Å) and angles (deg): Pt(1)-P(1) 2.240(1), Pt(1)-P(2) 2.243(1), Pt(1)-C(6) 2.259(2), Pt(1)-C(7) 2.271(2), Pt(2)-P(3) 2.252(1), Pt(2)-P(4) 2.227(1), Pt(2)-Cl(3) 2.319(2), Pt(2)-Cl(4) 2.287(2); P(1)-Pt(1)-P(2) 86.33(5), P(1)-Pt(1)-C(6) 91.22(8), P(1)-Pt(1)-C(7) 179.01(7), P(2)-Pt(1)-C(6) 177.29(8), P(2)-Pt(1)-C(7) 92.68(7), C(6)-Pt(1)-C(7) 89.77(10), P(3)-Pt(2)-P(4) 85.83(4), P(3)-Pt(2)-Cl(3) 94.33(5), P(3)-Pt(2)-Cl(4) 176.46(6), P(4)-Pt(2)-Cl(3) 174.04(5), P(4)-Pt(2)-Cl(4) 92.01(6), Cl(3)-Pt(2)-Cl(4) 88.11(7), P(2)-C(5)-P(3) 121.1(2).

unit may be employed subsequently to generate unsymmetrical diplatinum, or mixed platinum-palladium, derivatives. These include the expected bimetallic species **9–11**, and the unexpected trimetallic complexes **12** and **13**. Studies of the chemistry of the bi- and trimetallic complexes are continuing.

## Supporting information available

Complete spectroscopic characterization for all compounds, and full X-ray structural details for [PtMe (DPPEPM(O)-*PPP*)]Cl (7) and [PtMe<sub>2</sub>(µ-DPPEPM) PtCl<sub>2</sub>] (10).

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- [10] For **2a**, <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-d<sub>6</sub>):  $\delta P$  –28.7 (dd, <sup>2</sup>J<sub>PP</sub> = 68 Hz, <sup>3</sup>J<sub>PP</sub> = 31 Hz, <sup>3</sup>J<sub>PtP</sub> = 17 Hz), -12.4 (d, <sup>3</sup>J<sub>PP</sub> = 31 Hz), 42.0 (dd,

 ${}^{2}J_{PP} = 68 \text{ Hz}, {}^{3}J_{PP} = 4 \text{ Hz}, {}^{1}J_{PtP} = 1814 \text{ Hz}), 49.4 \text{ (d}, {}^{3}J_{PP} = 4 \text{ Hz}, {}^{1}J_{PtP} = 1829 \text{ Hz}).$  For **2b**,  ${}^{3}P\{{}^{1}\text{H}\}$  NMR:  $\delta P - 28.0 \text{ (dd}, {}^{2}J_{PP} = 78 \text{ Hz}, {}^{3}J_{PtP} = 30 \text{ Hz}, {}^{3}J_{PtP} = 15 \text{ Hz}), -12.8 \text{ (d}, {}^{3}J_{PP} = 30 \text{ Hz}), 37.9 \text{ (d}, {}^{2}J_{PP} = 78 \text{ Hz}, {}^{1}J_{PtP} = 1723 \text{ Hz}), 41.6 \text{ (s}, {}^{1}J_{PtP} = 1733 \text{ Hz}).$ 

- [11] For **3**, <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-d<sub>6</sub>):  $\delta P$  –27.7 (dt, <sup>3</sup>J<sub>PP</sub> = 32 Hz, <sup>2</sup>J<sub>PP</sub> = <sup>4</sup>J<sub>PP</sub> = 18 Hz), -12.7 (d, <sup>3</sup>J<sub>PP</sub> = 32 Hz), 34.3 (ddd, <sup>2</sup>J<sub>PP</sub> = 18 Hz, <sup>1</sup>J<sub>PtP</sub> = 2370 Hz), 44.7 (dd, <sup>2</sup>J<sub>PP</sub> = 18 Hz, <sup>1</sup>J<sub>PtP</sub> = 2665 Hz). HRMS: observed, 1508.3933; calcd. for <sup>12</sup>C<sub>82</sub>H<sub>81</sub>P<sub>8</sub><sup>195</sup>Pt<sup>+</sup>, 1508.3887. For **4**, <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta P$  –26.9 (dt, <sup>3</sup>J<sub>PP</sub> = 32 Hz, <sup>2</sup>J<sub>PP</sub> = 16 Hz), -12.6 (d, <sup>3</sup>J<sub>PP</sub> = 32 Hz), 47.4 (ddd, <sup>2</sup>J<sub>PP</sub> = 16 Hz), 57.3 (dd, <sup>2</sup>J<sub>PP</sub> = 16 Hz).
- [12] For **5**, <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-d<sub>6</sub>):  $\delta P$  -19.5 (dd, <sup>2</sup>J<sub>PP</sub> = 24 Hz, <sup>3</sup>J<sub>PP</sub> = 9 Hz), 28.9 (ddd, <sup>2</sup>J<sub>PP</sub> = 384, 19, 9 Hz, <sup>1</sup>J<sub>PtP</sub> = 2833 Hz), 43.7 (ddd, <sup>2</sup>J<sub>PP</sub> = 24, 19, 5 Hz, <sup>1</sup>J<sub>PtP</sub> = 1785 Hz), 54.8 (dd, <sup>2</sup>J<sub>PP</sub> = 384, 5 Hz, <sup>1</sup>J<sub>PtP</sub> = 2718 Hz). For **6**, <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta P$ -17.0 (dd, <sup>2</sup>J<sub>PP</sub> = 26 Hz, <sup>3</sup>J<sub>PP</sub> = 11 Hz), 31.3 (ddd, <sup>3</sup>J<sub>PP</sub> = 374, 23 Hz, <sup>3</sup>J<sub>PP</sub> = 11 Hz), 39.3 (dt, <sup>2</sup>J<sub>PP</sub> = 37, 26, 26 Hz), 56.0 (dd, <sup>2</sup>J<sub>PP</sub> = 374, 26 Hz).
- [13] Crystals of 7 are triclinic, space group P(-1), with a = 10.7382(11) Å, b = 10.8073(11) Å, c = 18.6111(19) Å,  $\alpha = 99.493(8)^{\circ}$ ,  $\beta = 99.685(8)^{\circ}$ ,  $\gamma = 112.983(7)^{\circ}$ , V = 1895.7(3) Å<sup>3</sup>, Z = 2, and  $\rho_{\text{caled.}} = 1.609$  g cm<sup>-3</sup> for fw = 918.18. A total of 9725 independent reflections were collected at 120(2) K in the  $\theta$  range 2.12–29.00°,  $wR_2 = 0.0546$  and  $R_1 = 0.0301$ .
- [14] For 9,  ${}^{31}P{}^{1}H$  NMR (acetone-d<sub>6</sub>):  $\delta P$  32.3 (dd,  ${}^{2}J_{PP} = 19, 6$  Hz,  ${}^{1}J_{PtP} = 1654$  Hz), 40.5 (dd,  ${}^{2}J_{PP} = 19$ , 7 Hz,  ${}^{1}J_{PtP} = 1785$  Hz), 40.5 (d,  ${}^{2}J_{PP} = 6$  Hz,  ${}^{1}J_{PtP} = 1820$  Hz), 48.8 (d,  ${}^{2}J_{PP} = 7$  Hz,  ${}^{1}J_{PtP} = 1811$  Hz). HRMS: observed, 1061.1636; calcd. for  $^{12}C_{42}H_{43}P_4^{195}Pt_2^+$  (M–CH\_3,2C\_6H\_5^+), 1061.1611. For  $10,\ ^{31}P\{^1H\}$ NMR:  $\delta P$  36.4 (br s,  ${}^{1}J_{PtP} = 3535$  Hz), 39.2 (br s,  ${}^{1}J_{PtP} = 1743$  Hz), 41.5 (br s,  ${}^{1}J_{PtP} = 3648$  Hz), 48.5 (br s,  ${}^{1}J_{PtP} = 1786$  Hz). For **11**, <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta P$  40.3 (br s, <sup>1</sup> $J_{PtP} = 1740$  Hz), 48.9 (br s,  ${}^{1}J_{\text{PtP}} = 1795 \text{ Hz}$ , 61.0 (br s), 64.8 (br s). For 12,  ${}^{31}P{}^{1}H$  NMR:  $\delta P$  30.3 (t,  ${}^{2}J_{PP} = 16$  Hz,  ${}^{1}J_{PtP} = 2375$  Hz), 40.2 (d,  ${}^{2}J_{PP} = 9$  Hz,  ${}^{1}J_{\text{PtP}} = 1790$  Hz), 43.1 (t,  ${}^{2}J_{\text{PP}} = 16$  Hz,  ${}^{1}J_{\text{PtP}} = 2693$  Hz), 49.7 (d,  ${}^{2}J_{PP} = 9$  Hz,  ${}^{1}J_{PtP} = 1791$  Hz). HRMS: observed, 1958.3901; calcd. for  ${}^{12}C_{86}H_{93}P_8^{195}Pt_3^+$ , 1958.4122. For 13,  ${}^{31}P{}^{1}H$  NMR: *P* 41.1 (br t,  ${}^{2}J_{PP} = 8$  Hz,  ${}^{1}J_{PtP} = 1756$  Hz), 43.5 (br), 49.4 (d,  ${}^{2}J_{PP} = 8$  Hz,  ${}^{1}J_{PtP} = 1789$  Hz), 56.0 (t,  ${}^{2}J_{PP} = 15$  Hz). HRMS: observed, 1869.3434; calcd. for  $^{12}C_{86}H_{93}P_8^{106}Pd^{195}Pt_2^+,$  1869.3509.
- [15] Crystals of 10 are triclinic, space group P(-1), with a = 12.3043(2) Å, b = 13.7558(2) Å, c = 13.9551(2) Å,  $\alpha = 104.6490(10)^\circ$ ,  $\beta = 101.7410(10)^\circ$ ,  $\gamma = 100.1730(10)^\circ$ , V = 2171.56(6) Å<sup>3</sup>, Z = 2, and  $\rho_{calcd.} = 1.800$  g cm<sup>-3</sup> for fw = 1176.80. A total of 11,046 independent reflections were collected at 170(2) K in the  $\theta$  range 1.86–29.93°,  $wR_2 = 0.0641$  and  $R_1 = 0.0323$ . Due to the small sizes of the methyl and chloride ligands attached to platinum, the ligands show positional disorder. The disorder was resolved using partial occupancies of 50% for the ligands on both metals.