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Heterobimetallic Complexes *via* η¹-Ph₂PCH₂PPh₂ Complexes of Platinum or Palladium Dicyanides

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The cyanide ion is shown to be an excellent ligand for stabilising the fluxional η^1 -dppm complexes, trans- $[M(CN)_2(\eta^1-dppm)_2]$ (M = Pt or Pd, dppm = Ph₂PCH₂PPh₂), which can be used as key intermediates in the systematic synthesis of heterobimetallic (μ -dppm) complexes with silver, mercury, or rhodium.

We have shown that monodentate Ph₂PCH₂PPh₂ (dppm) complexes of platinum(II) acetylides, *viz.* of the type *trans*-[Pt-(C=CR)₂(η^1 -dppm)₂], can be used as intermediates in very highyielding and systematic syntheses of homo- or heterobimetallic complexes of the type [Pt(C=CR)₂ (μ -dppm)₂MX_n]^{y+} (R = alkyl or aryl, M = Pt, Rh, Ir, W, Ag, Au, Cd, or Hg, X = ligand or radical, and y = 0 or 1).^{1,2} Once the heterobimetallic system has been formed, selective transformations at each metal centre could then be used to generate a whole new range of systems. It is therefore of interest to try to synthesise other complexes of type [MX₂(η^1 -dppm)₂], M = Pt (or Pd), the main problem being to find ligands, 'X', which would prevent chelation of the dppm. The cyanide ion seemed a good prospect since it is strongly bonding towards Pt or Pd and also has a marked preference to bond mutually *trans* in complexes of type $[M(CN)_2(PR_3)_2]$, *i.e.* we hoped that *trans*- $[M(CN)_2(\eta^1-dppm)_2]$ would be more stable than $[M(CN)_2(\eta^2-dppm)_2]^{2+}$ $2CN^-$ etc.

We have therefore treated the readily prepared bis-chelate salts (1a) and (1b)^{3,4} with NaCN and obtained the required η^1 -dppm complexes (2a) and (2b) (see Scheme 1). Both complexes are fluxional, *e.g.* the palladium complex shows a broad single ³¹P-{¹H} n.m.r. peak at +20 °C which broadens further on cooling and then separates into two peaks; at or below -80 °C the ³¹P-{¹H} spectrum corresponds to the static structure (2b), *i.e.* an AA'BB' pattern with δ (P_A) 16.9

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Scheme 1. Some transformations of η^{1} -, η^{2} -, and μ -dppm complexes of platinum or palladium dicyanides. i, M = Pt or Pd, NaCN (2 equiv.) in EtOH, 30 min, 20 °C; yield 98% (2a), 85% (2b). ii, M = Pt, NaCN (2 equiv.) in EtOH, 8 h, 80 °C; yield 90% (4a): M = Pd, NaCN (2 equiv.) in MeOH, 3 h, 80 °C; yield 90% (4b). iii, M = Pt or Pd, dppm (1 equiv.) in CDCl₃, 20 °C; yield >90%. iv, dppm (1 equiv.) in CH₂Cl₂; yield >90%. v, (2a) in CH₂Cl₂, AgNO₃ (1 equiv.) in aquous acetone at 20 °C; then add an excess of NaI in acetone; yield 65%. vi, (2a) in CH₂Cl₂, HgCl₂ (1 equiv.) in tetrahydrofuran at 20 °C; yield 85%. vii, (2a) or (2b) in CH₂Cl₂, [Rh₂Cl₂(CO)₄] in CH₂Cl₂ at 20 °C; yields (7a) 90%, (7b) 75%.

p.p.m., δ (P_B) – 26.9 p.p.m., and $|{}^{2}J(P_{A}P_{B}) + {}^{4}J(P_{A}P_{B'})|$ 93 Hz. The platinum complex (2a) is fluxional down to -30 °C; at -50 °C the n.m.r. parameters (in CDCl₃) are δ (P_A) 6.9 p.p.m., ${}^{1}J(PtP_{A})$ 2274 Hz, δ (P_B) –26.7 p.p.m., ${}^{3}J(PtP_{B}) < 10$, ${}^{2}J(P_{A}P_{B}) + {}^{4}J(P_{A}P_{B'})$ 23 Hz. The fluxionality corresponds to 'end over end' exchange, *viz*. MPh₂P*CH₂PPh₂ \rightleftharpoons MPh₂PCH₂-P*Ph₂. When heated with NaCN in EtOH, the chelate complexes (3a) or (3b) are converted into the binuclear 'face to face' complexes (4a) or (4b), respectively. [Pt₂(CN)₄(μ -dppm)₂] (4a) has the following ${}^{31}P$ - { $}^{1}H$ } n.m.r. parameters: δ (P_A) -1.0 p.p.m., ${}^{1}J(PtP_{A})$ 2498, ${}^{3}J(PtP_{B})$ 47, ${}^{2}J(P_{A}P_{B})$ + ${}^{4}J(P_{A}P_{B'})$ 22 Hz. When treated with dppm (4a) or (4b) is readily converted into the η^{1} -dppm complex (2a) or (2b), respectively.

We also show that these complexes $trans-[M(CN)_2(\eta^{1}-dppm)_2]$ give good yields of heterobimetallic complexes with Ag, Hg, and Rh (for M = Pt) and Rh (for M = Pd) (see Scheme 1). These complexes have been characterised by elemental analyses (C, H, and N), i.r., and particularly by ³¹P-{¹H} n.m.r. spectroscopy. These spectra show patterns characteristic of AA'BB' or AA'XX' spin systems together with satellites due to coupling with ¹⁹⁵Pt, ¹⁰⁹Ag, ¹⁰⁷Ag, ¹⁹⁹Hg, or ¹⁰³Rh. Thus the data for the platinum-mercury complex (6) are $\delta(P_A)$ +7.0 p.p.m., ${}^{1}J(\text{PtP}_{A})$ 2400, ${}^{3}J(\text{HgP}_{A})$ ca. 0 Hz, $\delta(\text{P}_{B})$ +18.3 p.p.m., ${}^{1}J(\text{HgP}_{B})$ 5258, ${}^{3}J(\text{PtP}_{B})$ 185, ${}^{2}J(\text{P}_{A}\text{P}_{B})$ + ${}^{4}J(\text{P}_{A}\text{P}_{B})$ 53 Hz, and for the palladium-rhodium complex (7b) $\delta(\text{P}_{A})$ -3.6, $\delta(\text{P}_{B})$ +7.2 p.p.m., ${}^{1}J(\text{RhP})$ 95, ${}^{2}J(\text{P}_{A}\text{P}_{B})$ + ${}^{4}J(\text{P}_{A}\text{P}_{B})$ 90 Hz, similarly for the other complexes. The structures shown, viz. (5), (6), (7a), and (7b) are analogous to the heterobinuclear acetylide complexes we have reported, except that the rhodium complexes are not salts.

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References

- 1 D. M. McEwan, P. G. Pringle, and B. L. Shaw, J. Chem. Soc., Chem. Commun., 1982, 859.
- 2 W. S. McDonald, P. G. Pringle, and B. L. Shaw, J. Chem. Soc., Chem. Commun., 1982, 861.
- 3 J. Chatt, F. A. Hart, and H. R. Watson, J. Chem. Soc., 1962, 2537.
- 4 M. P. Brown, J. R. Fisher, R. H. Hill, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chem.*, 1981, **20**, 3516.