Synthesis of Heterobimetallic and Unsymmetrical Diplatinum Complexes from *cis*-[$PtR_2(\eta^1$-dppm$)_2$], prepared from [$PtR_2(\eta^2$-dppm)], R = alkyl or aryl, (dppm = $Ph_2PCH_2PPh_2$)

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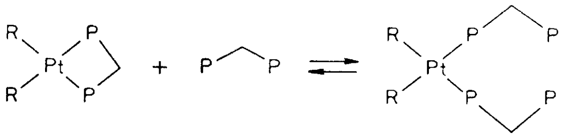
Complexes of type *cis*-[$PtR_2(\eta^1$-dppm$)_2$], R = Me, *o*-tolyl, or 1-naphthyl, can be readily made from *cis*-[$PtR_2(\eta^2$-dppm)] and then used in the systematic synthesis of diplatinum complexes and heterobimetallic complexes with silver, gold, or rhodium, all containing two bridging dppm groups.

We have shown that fluxional η^1-bisdiphenylphosphinomethane (dppm) complexes of the type *trans*-[$MX_2(\eta^1$-$Ph_2PCH_2PPh_2)_2$] {M = Pt, X = C≡CR; R = alkyl or aryl; M = Pt or Pd, X = CN} can be readily prepared[1] and used in the systematic synthesis of a whole range of heterobimetallic complexes containing μ-dppm moieties with metals such as Rh, Ir, W, Hg, Ag, Au, and Cd;[2–4] in these complexes the *trans*-arrangement around Pt or Pd is retained. It was of interest to try to synthesise complexes of type *cis*-[PtR_2-(η^1-dppm$)_2$] (**1**) which might then be used in heterobimetallic syntheses in which the two metals would be slightly further apart than some of those already described. We find that treatment of *cis*-[$PtCl_2(\eta^2$-dppm)] with a Grignard or lithio-reagent gives *cis*-[$PtR_2(\eta^2$-dppm)] (**2**) and subsequent treatment with dppm (1 mol) sets up equilibrium (1).

Equilibrium constants ($mol^{-1}\,dm^3$) as determined by ^{31}P-{^1H} n.m.r. spectroscopy in CD_2Cl_2 solution at 22 °C are, for R = Me, 39; Et, 4; CH_2Ph, *ca.* 0; CH_2CMe_3, *ca.* 0; Ph, 22; *p*-tolyl, 27; 1-naphthyl, 78; *o*-tolyl, 58; and for C_6F_5, 28. At −30 °C K_{equil} for R = Me is *ca.* 940 $mol^{-1}\,dm^3$. Estimated errors <10%. At 22 °C equilibration takes *ca.* <5 min (R = Me), *ca.* 30 min (R = Ph), and *ca.* 7 days (R = 1-naphthyl or *o*-tolyl). No *trans*-isomer corresponding to (**1**) was produced. Compounds of type (**1**), with R = 1-naphthyl or *o*-tolyl, exist as *syn*- and *anti*-isomers (see below). Several complexes of type (**1**) were readily isolated and fully characterized.

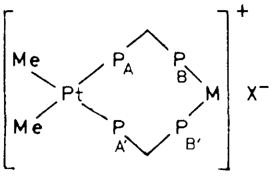
Since these dialkyl- or diaryl-complexes [$PtR_2(\eta^1$-dppm$)_2$] (**1**) dissociate into the chelates (**2**) and free dppm, as shown in equation (1), we usually attempted to make bimetallic



(1)

(**2**) (**1**)

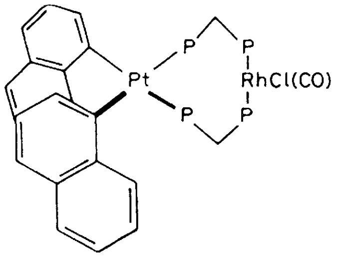
complexes from them at high concentration and, if possible, at low temperatures: both factors would favour the right-hand side of equation (1). A dichloromethane solution of equimolar amounts of [$PtMe_2(\eta^2$-dppm)] and dppm was allowed to equilibrate [equation (1)] for 10 min at −30 °C {platinum concentration 320 mM}. An equivalent amount of $AgI(PPh_3)$ was added at −30 °C and the required heterobimetallic compound (**3a**) was formed almost immediately [^{31}P-{^1H} n.m.r. evidence]. It was isolated, by adding diethyl ether, in 88% yield. The formulation follows from microanalytical (C, H, I) data, the electrical conductivity in nitrobenzene solution corresponding to a 1 : 1 electrolyte and particularly the n.m.r. data. At 20 °C the ^{31}P-{^1H} n.m.r. spectrum was broad but, on cooling, it sharpened up, and at −60 °C corresponded to the static structure (**3a**): $\delta(P_A)$ +21.9 p.p.m., $^1J(PtP_A)$ 1866 Hz, $\delta(P_B)$ −11.6 p.p.m., ^3J-(PtP_B) 196 Hz, $^1J(^{109}AgP_B)$ 403 Hz, $^1J(^{107}AgP_B)$ 349 Hz, $|^2J(P_AP_B) + {}^4J(P_AP_{B'})|$ 112 Hz. Similar treatment of a [$PtMe_2$-(η^2-dppm)]/dppm equilibrated mixture with [$AuCl(PPh_3)$] readily gave (**3b**) in 74% yield. This heterobinuclear complex (**3b**) could be recrystallized from CH_2Cl_2–MeOH without decomposition. The formulation follows from the microanalytical data, the electrical conductivity in nitrobenzene



(3)

a; M = Ag, X = I

b; M = Au, X = Cl



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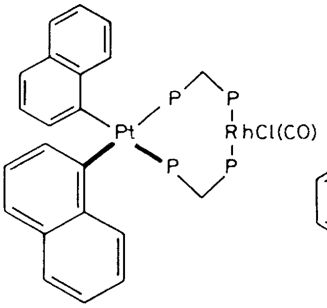

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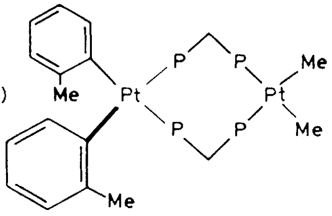

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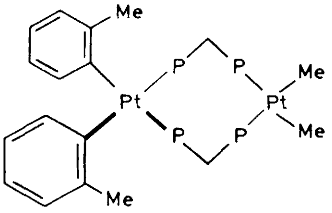

(7)

solution corresponding to a 1 : 1 electrolyte, and particularly the n.m.r. data (at 20 °C in $CDCl_3$) $^{31}P-\{^1H\}$, $\delta(P_A)$ 23.9 p.p.m., $^1J(PtP_A)$ 1843 Hz, $\delta(P_B)$ 32.9 p.p.m., $^3J(PtP_B)$ 166 Hz, $|^2J(P_AP_B) + {}^4J(P_AP_{B'})|$ 92 Hz; $^1H-\{^{31}P\}$, $\delta(CH_3)$ 0.79, $^2J(PtCH_3)$ 66.9 Hz, $\delta(CH_2)$ 3.88 and 4.06 (broad, coupling to ^{195}Pt not resolved at room temperature).

We have also studied the formation of heterobimetallic complexes from the 1-naphthyl and *o*-tolyl derivatives of type (**1**): the *ortho*-substituents greatly reduce the rate of dissociation of complexes of type (**2**), which are not labile, and also give *syn*- and *anti*-isomers owing to restricted rotation around the Pt–aryl bonds, see above and refs. 5 and 6. Addition of 1 mol. equiv. of $[Pt(1\text{-}C_{10}H_7)_2(\eta^1\text{-dppm})_2]$ (**2**) to $[Rh_2Cl_2(CO)_4]$ in CH_2Cl_2 solution at 20 °C gave, after addition of diethyl ether, the hoped-for platinum–rhodium product, *cis,trans*-$[(1\text{-}C_{10}H_7)_2Pt(\mu\text{-dppm})_2RhCl(CO)]$, (67% isolated yield) which probably exists in solution as a mixture of *syn*- and *anti*-isomers (**4**) and (**5**) with further possibilities of isomerism due to the Cl and CO groups and different conformations of the 8-membered ring. The formulation follows from elemental analysis (C, H, Cl) the non-electrical conductivity in nitrobenzene solution, the i.r. spectrum $\nu(C{\equiv}O)$ 1972vs cm^{-1} and the $^{31}P-\{^1H\}$ n.m.r. spectrum, which showed broad peaks ($w_{\frac{1}{2}}$ *ca.* 35 Hz) at 20 °C, $\delta(P_A)$ +6.3 p.p.m., $^1J(PtP_A)$ *ca.* 1840 Hz, $\delta(P_B)$ +19.2 p.p.m., $^1J(RhP)$ *ca.* 130 Hz. When cooled, each of the broad peaks of the spectrum separated into several closely-spaced sharp peaks. We interpret this behaviour as being due to the interconversion of various isomers and conformers of types (**4**) and (**5**). Fluxionality in 8-membered rings containing two bridging dppms is common.[1,7,8] We similarly find that $[Pt(o\text{-tolyl})_2(\eta^1\text{-dppm})_2]$ reacts with $[Rh_2Cl_2(CO)_4]$ to give *cis,trans*-$[(o\text{-tolyl})_2Pt(\mu\text{-dppm})_2RhCl(CO)]$ as a mixture of *syn*- and *anti*-isomers.

We have also studied the action of $[Pt(o\text{-tolyl})_2(\eta^1\text{-dppm})_2]$ on *cis*-$[PtMe_2(\text{cyclo-octa-1,5-diene})]$ in dichloromethane solution at 20 °C. This gave the hoped-for *cis*, *cis*-$[(o\text{-tolyl})_2Pt(\mu\text{-dppm})_2PtMe_2]$ (dichloromethane solvate) as a white precipitate. The $^{31}P-\{^1H\}$ n.m.r. spectrum showed that this product was mainly one species 'X' but *ca.* 15% of a closely related species 'Y' was present. Over a period of 2 h at 20 °C the proportion of 'Y' slowly increased to 30%. Moreover, the mother liquors of a dichloromethane solution from which the solid had crystallized initially showed more 'Y' than 'X' to be present, *i.e.* 'X' and 'Y' slowly interconvert at 20 °C and 'X' has the lower solubility. The n.m.r. data (*vide infra*) show that these two species are the expected *syn*-(**6**) and *anti*-(**7**) isomers although we do not yet know which is 'X' and which is 'Y'. The n.m.r. data are: 'X' $\delta(P_A)$ -0.6 p.p.m., $^1J(PtP_A)$ 1669 Hz, $^3J(PtP_A)$ *ca.* 25 Hz, $\delta(P_B)$ 7.1 p.p.m., $^1J(PtP_B)$ 1831 Hz, $^3J(PtP_A)$ <20 Hz, $|^2J(P_AP_B) + {}^4J(P_AP_{B'})|$ 24 Hz; $\delta(PtCH_3)$ -0.11, $^2J(PtCH_3)$ 60.4 Hz, $J(PPtCH_3)$ 'N-doublet' 15.5 Hz, $\delta(CH_3)$(tolyl) 1.39, $^4J(PtCH_3)$(tolyl) 5.9 Hz, the CH_2 hydrogens form an 'AB' quartet, $\delta(H_A)$ 3.19, $\delta(H_B)$ 3.96, $^2J(H_AH_B)$ 14.1 Hz, coupling to platinum not resolved. 'Y' $\delta(P_A)$ 1.1 p.p.m., $^1J(PtP_A)$ 1663 Hz, $^3J(PtP_A)$ *ca.* 18 Hz, $\delta(P_B)$ 6.4 p.p.m., $^1J(PtP_B)$ 1819 Hz, $^3J(PtP_A)$ <20 Hz, $\delta(PtCH_3)$ 0.10, $^2J(PtCH_3)$ 70.3 Hz, $J(PCH)$ 'N-doublet' *ca.* 14 Hz, $\delta(CH_2)$ unresolved multiplet 3.5—3.8. We have also treated *cis*-$[PtMe_2(\eta^1\text{-dppm})_2]$ (prepared *in situ*) with $[PtMe_2(\text{cyclo-octa-1,5-diene})]$ but this gave only *cis*-$[PtMe_2(\eta^2\text{-dppm})]$. It is known that $[Me_2Pt(\mu\text{-dppm})_2PtMe_2]$ is unstable with respect to disproportionation to $[PtMe_2(\eta^2\text{-dppm})]$.[7]

Although the previously described complexes of type *trans*-$[X_2Pt(\mu\text{-dppm})_2HgCl_2]$ (X = C≡CR or CN) are formed particularly easily and cleanly[3] we find that treatment of *cis*-$[PtR_2(\eta^1\text{-dppm})_2]$ complexes of type (**2**) with mercuric chloride gives more complicated reaction products than we expected and these we have not yet identified.

Thus the work described in this communication extends the range of di-μ-dppm-heterobimetallic complexes which are available. In particular it should now be possible to synthesize heterobimetallic complexes with a wide range of intermetallic distances and reactivities.

We thank the Science and Engineering Research Council for support and Johnson Matthey Ltd. for the generous loan of platinum salts.

Received, 23rd August 1982; Com. 1020

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