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A Route to Homonuclear Pt_3 and Heteronuclear Pt_2M Complexes

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The complex $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(\sigma\text{-}dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) prepared by reaction of $[Pt_2(\mu\text{-}dppm)_3]$ with COS, acts as a tridentate (P_2S donor) ligand for square planar metal atoms and hence gives homonuclear (Pt_3) or heteronuclear (Pt_2M, M = Pd, Rh, or Ir) complexes, which show unusual fluxional behaviour involving sulphur inversion.

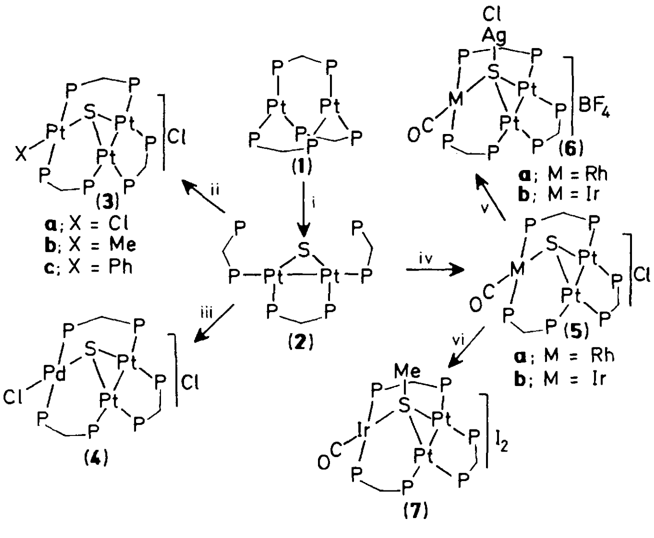
The ability of $Pt_2(\mu\text{-}S)$ and $Pt(\sigma\text{-}dppm)$ (dppm = $Ph_2PCH_2PPh_2$) groups to act as assembling ligands is known.[1,2] It is now shown that the combination of these groups can give a route to new homonuclear Pt_3 and heteronuclear Pt_2M complexes and that inversion of the resulting $Pt_2M(\mu_3\text{-}S)$ groups occurs readily.

The synthetic method is shown in Scheme 1 and is based on the formation of $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(\sigma\text{-}dppm)_2]$ (**2**) in high yield by reaction of $[Pt_2(\mu\text{-}dppm)_3]$ (**1**) with carbonyl sulphide (COS).† Complex (**2**) contains two σ dppm ligands and a μ_2-S group and acts as a powerful tridentate ligand towards square planar metal centres as shown in Scheme 1.

The homonuclear complexes (**3**) are isostructural with $[Pt_3H(\mu\text{-}S)(\mu\text{-}dppm)_3]^+$, prepared in a different way,[3] and were readily characterized by elemental analysis and by their spectroscopic properties.† The derivatives (**3b**) and (**3c**) are rare examples of stable clusters with σ-alkyl or aryl ligands.[4] The heteronuclear complexes (**4**) and (**5**), containing Pt_2Pd, Pt_2Rh, and Pt_2Ir units, were prepared in almost quantitative yields as shown in Scheme 1, and were characterized similarly.† These appear to be the first known Pt_2Pd and Pt_2Ir clusters.[1—4]

The only metal–metal bonding in complexes (**3**)—(**6**) is between the Pt_2 atoms as shown by the large values of $^1J(\mathrm{PtPt})$ 2485—3087 Hz, $^2J(\mathrm{Pt^bP^b})$ 150—190 Hz, and $^3J(\mathrm{P^bP^b})$ 160—180 Hz,[3] whereas, for example, no coupling $J(\mathrm{Pt^aPt^b})$ was observed in (**3**).

The Pt_2Rh cluster (**5a**) was readily converted into the hexafluorophosphate salt by treatment with $NH_4[PF_6]$, but an attempt to prepare the tetrafluoroborate salt by reaction of (**5a**) with $Ag[BF_4]$ gave (**6a**), in which the silver chloride formed remained co-ordinated to sulphide. Complex (**6a**) is therefore a tetranuclear complex containing three different metal atoms. The analogous Pt_2IrAg complex (**6b**) was prepared in a similar way. Methyl iodide also reacted at the sulphur atom of (**5b**) to give (**7**),† rather than undergoing oxidative addition at the Ir^I or Pt^I centres.



Scheme 1. PP = $Ph_2PCH_2PPh_2$; *reagents:* i, COS, −CO; ii, *trans*-$[PtXCl(SMe_2)_2]$, $-2SMe_2$; iii, $PdCl_2(PhCN)_2$, −2PhCN; iv, $[RhCl(CO)_2]_2$, (**5a**); $[IrCl(CO)_3]_n$, (**5b**); v, $AgBF_4$; vi, excess of MeI.

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† Selected n.m.r. [refs. $SiMe_4$, $(MeO)_3PO$, or K_2PtCl_4; *J* in Hz], mass spectroscopic [found (calc.)], and i.r. data: (**2**), δ(P) −29.6 [m, $^2J(\mathrm{P^aP^b})$ 41, P^a]; 16.0 [m, $^1J(\mathrm{PtP})$ 3200, $^2J(\mathrm{PtP})$ 190, $^3J(\mathrm{P^bP^b})$ 180, P^b]; −11.7 p.p.m. [m, $^1J(\mathrm{PtP})$ 3500, $^2J(\mathrm{PtP})$ −80, P^c]; $\delta(^{195}Pt)$ −3200 p.p.m. [m, $^1J(\mathrm{PtPt})$ 3100]; *m/z* 1575 (*M*, 1575). (**3b**), $\delta(^1H)$ −0.46 [t, $^2J(\mathrm{PtH})$ 66, $^3J(\mathrm{PH})$ 7, MePt]; δ(P) 25.4 [m, $^1J(\mathrm{PtP})$ 3060, $^2J(\mathrm{P^aP^b})$ 20, $^4J(\mathrm{P^aP^c})$ 7, P^a]; 1.7 [m, $^1J(\mathrm{PtP})$ 3080, $^2J(\mathrm{PtP})$ 210, $^3J(\mathrm{PP})$ 170, P^b]; −12.6 p.p.m. [m, $^1J(\mathrm{PtP})$ 3840, $^2J(\mathrm{PtP})$ −80, P^c]; $\delta(^{195}Pt)$ −2991 [m, Pt^a]; −3199 p.p.m. [m, $^1J(\mathrm{Pt^bPt^b})$ 2850, Pt^b]; *m/z* 1785 (*M* − Cl, 1785). (**4**), δ(P) 20.85 [m, $^2J(\mathrm{P^aP^b})$ 25, $^4J(\mathrm{P^aP^c})$ 5, P^a]; 4.9 [m, $^1J(\mathrm{PtP})$ 3042, $^2J(\mathrm{PtP})$ 150, $^3J(\mathrm{P^bP^b})$ 163, P^b]; −9.3 p.p.m. [m, $^1J(\mathrm{PtP})$ 3848, $^2J(\mathrm{PtP})$ −78, P^c]; $\delta(^{195}Pt)$ −3123 p.p.m. [m, $^1J(\mathrm{PtPt})$ 2750, Pt^b]; *m/z* 1717 (*M* − Cl, 1717). (**5a**), δ(P) 26.9 [m, $^1J(\mathrm{RhP})$ 130.5, $^2J(\mathrm{P^aP^b})$ 32, $^4J(\mathrm{P^aP^c})$ 8, P^a]; 4.2 [m, $^1J(\mathrm{PtP})$ 3080, $^2J(\mathrm{PtP})$ 170, $^3J(\mathrm{P^bP^b})$ 170, P^b]; −9.3 p.p.m. [m, $^1J(\mathrm{PtP})$ 3920, $^2J(\mathrm{PtP})$ −68, P^c]; $\delta(^{195}Pt)$ −3173 p.p.m. [m, $^1J(\mathrm{PtPt})$ 2490, $^2J(\mathrm{RhPt})$ 177, Pt^b]; *m/z* 1742, 1706 (*M*, 1742); i.r. ν(CO) 1973 cm^{-1}. (**6a**), δ(P) 31.8 [m, $^1J(\mathrm{RhP})$ 120, $^2J(\mathrm{P^aP^b})$ 32, $^4J(\mathrm{P^aP^c})$ 7, P^a]; 11.1 [m, $^1J(\mathrm{PtP})$ 3100, $^2J(\mathrm{PtP})$ 195, $^3J(\mathrm{P^bP^b})$ 145, P^b]; −9.3 p.p.m. [m, $^1J(\mathrm{PtP})$ 3700, $^2J(\mathrm{PtP})$ −80, P^c]; $\delta(^{195}Pt)$ −2896 p.p.m. (m); *m/z* 1814 (*M* − Cl, BF_4, 1814); i.r. ν(CO) 1998 cm^{-1}. (**7**), δ(H) 1.78 [t, *J*(PH) 6, MeS]; δ(P) −18.1 (m, P^a); −1.96 [m, $^1J(\mathrm{PtP})$ 3150, $^2J(\mathrm{PtP})$ 135, $^3J(\mathrm{PP})$ 165, P^b]; −10.4 p.p.m. [m, $^1J(\mathrm{PtP})$ 3925, P^c]; *m/z* 1937 (*M* − I); i.r. ν(CO) 2047 cm^{-1}. The couplings $^3J(\mathrm{P^bP^b})$ are observed in the ^{195}Pt satellite spectra.

The inversion of the $Pt_2M(\mu_3\text{-}S)$ unit in (**3**)—(**5**) was shown by the presence of non-equivalent $CH^aH^bP^aP^b$ and $CH^cH^dP^cP^c$ resonances in the ^1H n.m.r. spectra at low temperature, but which coalesced to single resonances in each case on warming. The activation energies ($\Delta G^\ddagger$/kJ mol^{-1}) for the inversion process were: (**3a**) 52; (**3b**), 51; (**3c**), 51; (**4**), 53; (**5a**), 42; (**5b**), 44.5. The $\Delta G^\ddagger$ values for (**3**) and (**4**) are almost independent of the *trans*-influence of X or the substitution of Pt for Pd, in contrast to other sulphur inversions,[5] but lower $\Delta G^\ddagger$ values are observed for (**5a**) and (**6a**) which contain the good π-acceptor ligand CO on Rh or Ir. Co-ordination of AgCl in (**6**) prevents the sulphur inversion process from occurring and these compounds are not fluxional.

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