A Comparison of the Ligand Behaviour of $Ph_2AsCH_2AsPh_2$ (dpam) with that of $Ph_2PCH_2PPh_2$ (dppm) in Mono- and Bi-metallic Platinum Complexes

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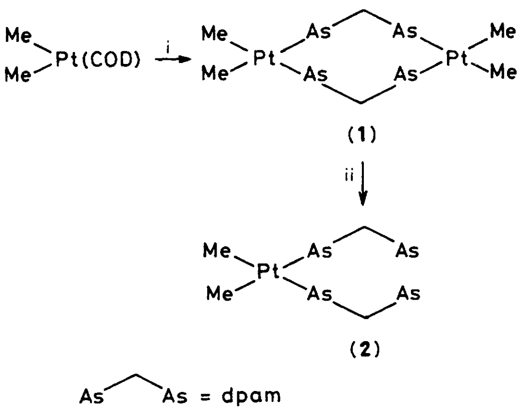
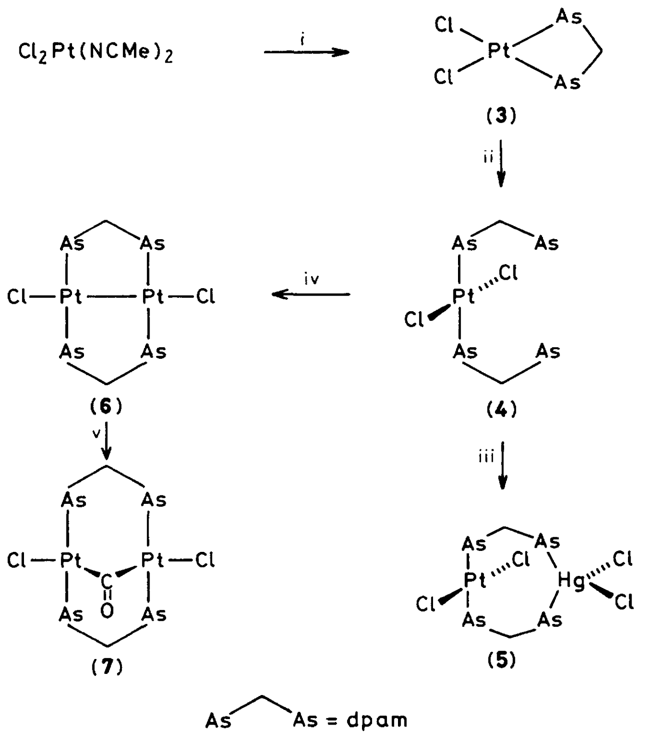
cis,cis-[$Me_2Pt(\mu$-dpam$)_2PtMe_2$] is more stable than [Me_2Pt(dpam-*AsAs'*)], the reverse is the case for dppm, and *trans*-[$PtCl_2$(dpam-*As*$)_2$] is formed from [$PtCl_2$(dpam-*AsAs'*)] + dpam whereas [$PtCl_2$(dppm-*PP'*)] gives [Pt(dppm-*PP'*$)_2]^{2+}$.

There is much interest in mono- and bi-metallic complexes of bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$, dppm)[1—3] but its arsenic analogue, $Ph_2AsCH_2AsPh_2$, dpam, has been relatively little studied. We anticipated that dpam would be a less good donor than dppm and with its greater 'bite angle' would be a less good chelating ligand, but to what extent these differences would influence the chemistry was difficult to predict. We now report that dpam frequently shows quite different behaviour and reactions from those which are well-established for dppm.

These new reactions of dpam are summarized in Schemes 1 and 2 and are discussed and compared with reactions of dppm below. Dppm displaces cyclo-octa-1,5-diene (COD) from [$PtMe_2$(COD)] to give exclusively [$PtMe_2$(dppm-*PP'*)][4] and indeed the binuclear isomer, [$Me_2Pt(\mu$-dppm$)_2PtMe_2$], made from [$Me_2Pt(\mu$-$SMe_2)_2PtMe_2$],[5] disproportionates in solution to give [$PtMe_2$(dppm-*PP'*)]. In contrast we find that [$PtMe_2$(COD)] reacts with dpam in C_6H_6 solution to give the



Scheme 1. *Reagents:* i, dpam in benzene at 80 °C; ii, dpam in benzene at 20 °C. COD = cyclo-octa-1,5-diene.



Scheme 2. *Reagents:* i, dpam in MeCN at 80 °C; ii, dpam in CH_2Cl_2 at 40 °C; iii, $HgCl_2$ in benzene at 80 °C; iv, ½[$Pt_2(\mu\text{-}OMe)_2(C_8H_{12}OMe)_2$] in benzene at 20 °C; v, CO in CH_2Cl_2 at 20 °C.

binuclear complex [$Me_2Pt(\mu\text{-dpam})_2PtMe_2$] (**1**), characterized by elemental analysis, molecular weight determination, and ^1H n.m.r. spectroscopy [in C_6D_6, $\delta(CH_2)$ 3.05, $\delta(Me)$ 1.16, $^2J(PtCH_3)$ 80 Hz]: we could not detect any resonance attributable to [$PtMe_2(dpam)$] in the ^1H n.m.r. spectrum (in C_6D_6). We also find that (**1**) reacts with dpam in C_6D_6 to give an equilibrium mixture containing the bis-monodentate complex [$Me_2Pt(dpam\text{-}As)_2$] (**2**), which was not isolated but characterized by ^1H n.m.r. data [$\delta(CH_2)$ 2.75, $^3J(PtCH_2)$ 9 Hz; $\delta(Me)$ 1.42, $^2J(PtCH_3)$ 82 Hz].

Treatment of an acetonitrile solution of [$PtCl_2(NCMe)_2$] with one equivalent of dpam gave the chelate [$PtCl_2(dpam\text{-}AsAs')$] (**3**) (82% yield) [$^1H$ n.m.r. (in $CDCl_3$) $\delta(CH_2)$ 4.72, $^3J(PtCH_2)$ 50 Hz; ν(Pt–Cl) 299 and 286 cm^{-1}]. Further treatment of the chelate (**3**) with another mole of dpam readily gave the neutral complex *trans*-[$Cl_2Pt(dpam\text{-}As)_2$] (**4**) (95% yield) [^1H n.m.r. (in $CDCl_3$) $\delta(CH_2)$ 2.97, $^3J(PtCH_2)$ 15 Hz]. The *trans*-configuration follows from the presence of a single intense band due to ν(Pt–Cl) at 340 cm^{-1}, absent from the spectrum of the corresponding dibromide, *trans*-[$PtBr_2(dpam\text{-}As)_2$], for which ν(Pt–Br) = 252 cm^{-1}. In contrast [$PtCl_2(dppm\text{-}PP')$] reacts with dppm to give the salt [$Pt(dppm\text{-}PP')_2]Cl_2$,[6] exclusively. The bis-monodentate complex (**4**) reacts with mercury(II) chloride to give the heterobimetallic complex *trans*-[$Cl_2Pt(\mu\text{-dpam})_2HgCl_2$] (**5**).

It has been shown that the methoxycyclo-octenyl complex [$Pt_2(\mu\text{-}OMe)_2(C_8H_{12}OMe)_2$] when treated with tertiary phosphine (L), readily gives platinum(0) complexes PtL_x.[7] We therefore attempted a redox synthesis of a binuclear platinum(I) complex. Treatment of (**4**) with an equivalent amount of [$Pt_2(\mu\text{-}OMe)_2(C_8H_{12}OMe)_2$] in benzene gave what we believe to be the diplatinum(I) complex [$Pt_2Cl_2(\mu\text{-dpam})_2$] (**6**) although we have not yet obtained this pure. This diplatinum complex (**6**) reacts rapidly with CO to give the bright yellow [$Pt_2Cl_2(\mu\text{-}CO)(\mu\text{-dpam})_2$] (**7**) [$^1H$ n.m.r. (in $CDCl_3$) $\delta(CH_2)$ 2.59 (broad); ν(CO) 1635 cm^{-1}]. This complex, characterized by its extremely low frequency i.r. absorption for ν(CO) was previously prepared by treating [$NPr^n{}_4]_2[Pt_2Cl_4(CO)_2$] with dpam.[8] [$Pt_2Cl_2(\mu\text{-dpam})_2$] (**6**) has not been described previously.

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