The Synthesis of Mono- and Bi-metallic Complexes containing the Ligand Bis(diphenylarsino)methane

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Treatment of [$PtMe_2$(cod)] (cod = cyclo-octa-1,5-diene) with bis(diphenylarsino)methane (dpam) gives the binuclear complex [$Me_2Pt(\mu$-dpam$)_2PtMe_2$] and none of the mononuclear complex [$PtMe_2$(dpam-*AsAs'*)]. Treatment of [$Me_2Pt(\mu$-dpam$)_2PtMe_2$] with dpam results in an equilibrium mixture containing the bis-monodentate complex *cis*-[$PtMe_2$(dpam-*As*$)_2$]. The chelate complexes [PtX_2(dpam-*AsAs'*)] (X = Cl, Br, or I) have been prepared, which on further treatment with one equivalent of dpam gave the neutral complexes *trans*-[PtX_2(dpam-*As*$)_2$] (X = Cl or Br). The complex *trans*-[$PtCl_2$(dpam-*As*$)_2$] gives the heterobimetallic complex *trans*-[$Cl_2Pt(\mu$-dpam$)_2HgCl_2$] on treatment with $HgCl_2$. Treatment of *trans*-[$PtCl_2$(dpam-*As*$)_2$] with the methoxycyclo-octenyl complex [$Pt_2(\mu$-$OMe)_2(C_8H_{12}OMe)_2$] gives the Pt^I dimer [$ClPt(\mu$-dpam$)_2PtCl$], which on further treatment with CO yields [$ClPt(\mu$-CO$)(\mu$-dpam$)_2PtCl$].

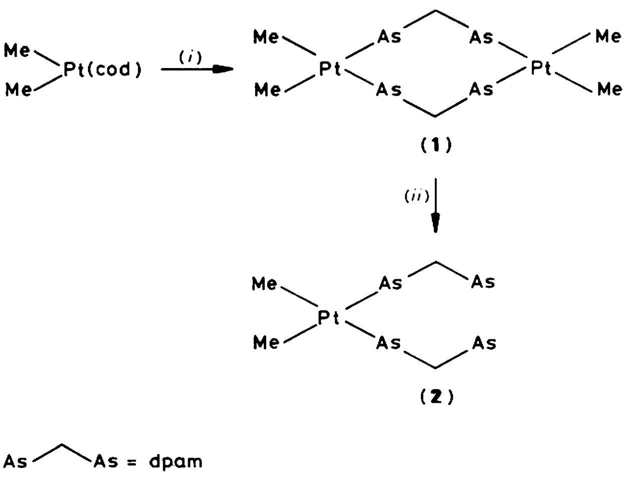
There is much interest in mono- and bi-metallic complexes of bis(diphenylphosphino)methane (dppm)[1–3] but, in contrast, its arsenic analogue, bis(diphenylarsino)methane (dpam), has been relatively little studied. We anticipated that dpam would be a poorer donor than dppm and with its greater 'bite angle' would be a less good chelating ligand, but to what extent these differences would influence the chemistry of its platinum complexes was difficult to predict.

Results obtained in the preparation of a range of phosphine- and arsine-substituted halogenocarbonyls of molybdenum(II) and tungsten(II) indicated that dpam complexes frequently showed different behaviour to their dppm analogues.[4] The four-membered ring formed by the chelating dpam molecule was invariably weak and could be readily cleaved by carbon monoxide or excess of ligand, reactions that were not paralleled by dppm. Therefore, the preference for dpam to display monodentate behaviour rather than chelation in these systems was illustrated. We now report that dpam frequently shows quite different behaviour and reactions from those which are well established for dppm in platinum complexes. A preliminary account of some of this work had been published.[5]

Table 1. Microanalytical data[a] (%) for platinum–dpam complexes

Complex	C	H	Halogen
(**1**)·$0.75CHCl_3$[b]	44.45 (44.3)	3.85 (3.85)	5.35 (5.35)
(**3a**)	40.75 (40.7)	3.0 (3.0)	9.8 (9.6)
(**3b**)	36.1 (36.3)	2.6 (2.7)	19.45 (19.3)
(**3c**)	33.0 (32.6)	2.45 (2.4)	27.15 (27.55)
(**4a**)[c]	49.35 (49.6)	3.5 (3.7)	6.05 (5.8)
(**4b**)·$0.2CH_2Cl_2$	46.1 (45.8)	3.6 (3.4)	13.2 (13.2)
(**5**)	40.75 (40.15)	3.0 (3.0)	9.3 (9.6)
(**6**)·$0.5C_6H_6$	43.4 (44.1)	3.5 (3.3)	4.8 (4.9)
(**7**)	43.0 (42.7)	3.1 (3.1)	5.15 (4.95)

[a] Calculated values (%) in parentheses. [b] *M* ($CHCl_3$ solution), 1 310 (calc. 1 395). [c] Λ (acetone solution, 20 °C) = 2.34 ohm^{-1} cm^2 mol^{-1}.

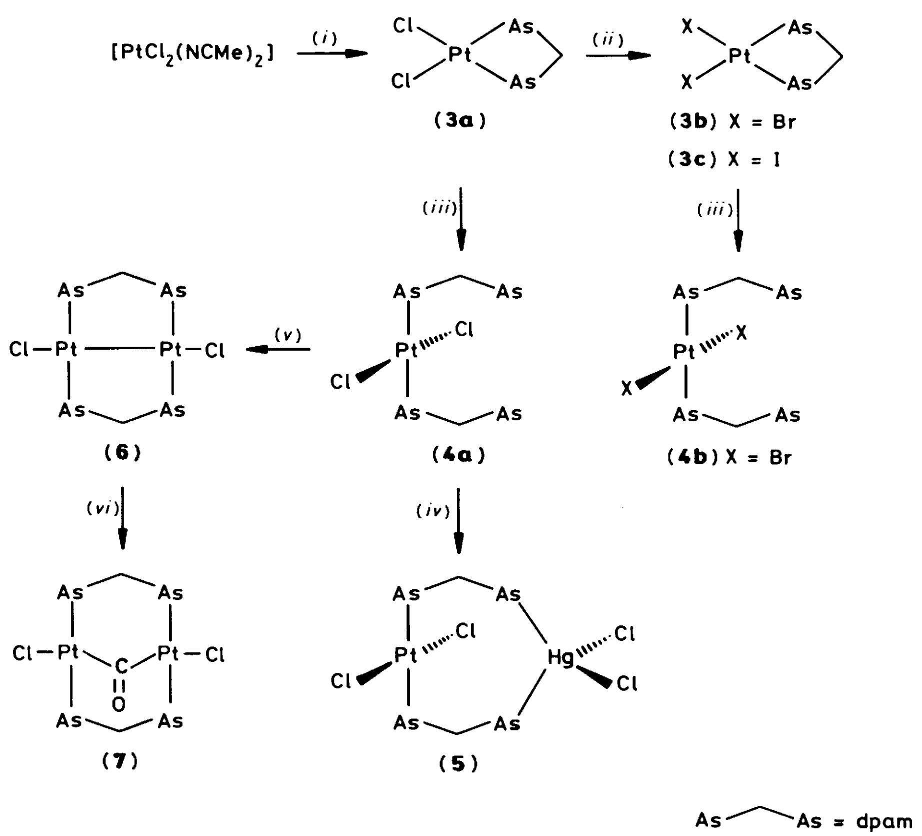


Scheme 1. (*i*) 1 equiv. dpam; (*ii*) 2 equiv. dpam

Results and Discussion

The new reactions of dpam are summarised in Schemes 1 and 2 and are discussed and compared with reactions of dppm below. Dppm has been shown to displace cyclo-octa-1,5-diene (cod) from [$PtMe_2$(cod)] to give exclusively [$PtMe_2$(dppm-*PP'*)][6] and indeed the binuclear isomer [$Me_2Pt(\mu$-dppm$)_2PtMe_2$], prepared from [$Me_2Pt(\mu$-$SMe_2)_2PtMe_2$],[7] breaks down in a hot (*ca.* 60 °C) solution, with a catalytic amount of SMe_2 or dppm, to give [$PtMe_2$(dppm-*PP'*)]. Thus the monomer is the thermodynamically more stable form. In contrast, we find that [$PtMe_2$(cod)] reacts with dpam in refluxing benzene solution to give the binuclear complex [$Me_2Pt(\mu$-dpam$)_2PtMe_2$] (**1**). It was characterised on the basis of (*i*) elemental analysis (see Table 1 for analytical data), (*ii*) molecular-weight determination, and (*iii*) ^1H n.m.r. spectroscopy, which showed a broad resonance at δ 3.05 assigned to the methylene protons of the dpam ligands and a singlet at δ 1.16, with associated ^{195}Pt satellites, assigned to the methyl protons (see Table 2 for ^1H n.m.r. spectral data). We could not detect any resonances attributable to the monomer [$PtMe_2$(dpam-*AsAs'*)] in the ^1H n.m.r. spectrum. These results show that the binuclear complex (**1**) is the thermodynamically more stable form, the reverse of the preference found for dppm. Presumably the C–As–Pt bond angles (larger than C–P–Pt bond angles) produce enough steric strain to make chelation unfavourable and this strain is somewhat relieved by bridging two platinum centres.

We also find that the dimer (**1**) reacts with two equivalents of dpam in benzene to give an equilibrium mixture containing the bis-monodentate complex *cis*-[$PtMe_2$(dpam-*As*$)_2$] (**2**) which was not isolated but characterised on the basis of its ^1H n.m.r. spectrum at 400 MHz (Figure). This clearly shows a mixture of



Scheme 2. (*i*) 1 equiv. dpam; (*ii*) LiBr or NaI; (*iii*) 1 equiv. dpam; (*iv*) $HgCl_2$; (*v*) ½ $[Pt_2(\mu\text{-}OMe)_2(C_8H_{12}OMe)_2]$; (*vi*) CO

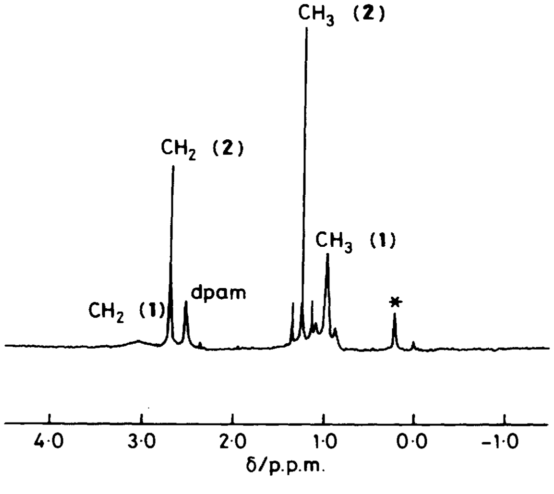


Figure. Methyl and methylene region of the 400-MHz ^1H n.m.r. spectrum of a mixture of (**1**), (**2**), and uncomplexed dpam in C_6D_6 (peak marked * is due to an impurity)

Table 2. Proton n.m.r.[a] and i.r. data[b]

Complex	$\delta(CH_2)$	$^3J(PtCH_2)$	$\delta(CH_3)$	$^2J(PtCH_3)$	ν(Pt–X)
(**1**)[c]	3.05	n.r.	1.16	80	
(**2**)[c,d]	2.75	9	1.42	82	
(**3a**)	4.72	50			299, 286
(**3b**)	4.82	51			227, 216
(**3c**)	5.06	50			
(**4a**)	2.97	15			340
(**4b**)	3.26	n.r.			252
(**5**)	3.40	n.r.			
(**7**)[e]	2.59	n.r.			

[a] Spectra measured in $CDCl_3$ at 100 MHz at 20 °C; δ values in p.p.m. to high frequency of $SiMe_4$; *J* values in Hz (± 1 Hz); n.r. = not resolved. [b] Nujol mulls. [c] Measured in C_6D_6. [d] Also measured at 400 MHz. [e] ν(CO) = 1 635 cm^{-1}.

(**1**), (**2**), and uncomplexed dpam. The reaction was slow at room temperature (several days) but in refluxing benzene it proceeded quickly.

Treatment of an acetonitrile solution of $[PtCl_2(NCMe)_2]$ with one equivalent of dpam gave the chelate [$PtCl_2$(dpam-*AsAs′*)] (**3a**), characterised on the basis of (*i*) elemental analysis, (*ii*) ^1H n.m.r. spectroscopy, which showed a singlet resonance at δ 4.72, with associated ^{195}Pt satellites, assigned to the methylene protons of the dpam ligand, and (*iii*) i.r. spectroscopy, which showed two bands attributable to ν(Pt–Cl) indicating a *cis* configuration of chlorines. Metathesis in acetone afforded the bromo- or iodo-analogues of (**3**). Further treatment of [$PtCl_2$(dpam-*AsAs′*)] with another equivalent of dpam readily gave the neutral complex *trans*-[$PtCl_2$(dpam-*As*)$_2$] (**4a**), characterised on the basis of (*i*) elemental analysis, (*ii*) ^1H n.m.r. spectroscopy, (*iii*) i.r. spectroscopy, which showed the presence of a single intense band due to ν(Pt–Cl) at 340 cm^{-1}, indicating a *trans* configuration {this band was absent from the spectrum of the corresponding dibromide, *trans*-[$PtBr_2$(dpam-*As*)$_2$], for which ν(Pt–Br) = 252 cm^{-1}}, and (*iv*) a conductance measurement in acetone solution which indicated a non-electrolyte. These results differ from the behaviour of dppm in similar systems. In contrast, [$PtCl_2$(dppm-*PP′*)] reacts with dppm to give the salt [Pt(dppm-*PP′*)$_2$]Cl_2[8] exclusively.

Therefore the poorer ability of dpam to chelate, with respect to dppm, and its preference to be monodentate or to bridge two metal centres, as discussed above, is again illustrated.

In recent papers we have described how complexes of the type $[MX_2(dppm\text{-}P)_2]^{n+}$ (M = Pt or Pd; $n = 0$, X = C≡CR or R; $n = 2$, X = CNR; R = alkyl or aryl) could be used in the systematic synthesis of hetero- and homo-bimetallic complexes.[9–11] We therefore anticipated that *trans*-$[PtCl_2(dpam\text{-}As)_2]$, containing two monodentate dpam ligands, would be a suitable starting material for the synthesis of bimetallic complexes containing bridging dpam ligands. Thus, treatment of *trans*-$[PtCl_2(dpam\text{-}As)_2]$ with mercury(II) chloride gave the heterobimetallic complex *trans*-$[Cl_2Pt(\mu\text{-}dpam)_2HgCl_2]$ (**5**), which was characterised by ^1H n.m.r. spectroscopy and elemental analysis. This approach could be extended to include a wide range of metal fragments.

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, $[PtL_x]$ (x = 3 or 4).[12] We therefore attempted a redox synthesis of a binuclear platinum(I) complex. Treatment of *trans*-$[PtCl_2(dpam\text{-}As)_2]$ with one equivalent of $[Pt_2(\mu\text{-}OMe)_2(C_8H_{12}OMe)_2]$ in benzene gave what we believe to be the diplatinum(I) complex $[ClPt(\mu\text{-}dpam)_2PtCl]$ (**6**). This was characterised only by elemental analysis, as the ^1H n.m.r. spectrum was continually complicated by resonances arising from solvent and/or impurities. However, good evidence for the correct formulation of (**6**) as $[ClPt(\mu\text{-}dpam)_2PtCl]$ came from its reaction with carbon monoxide to give the bright yellow 'A-frame' complex $[ClPt(\mu\text{-}CO)(\mu\text{-}dpam)_2PtCl]$ (**7**). This complex, characterised by its extremely low-frequency i.r. absorption for ν(CO) at 1 635 cm^{-1}, was previously prepared by treating $[NPr^n{}_4]_2[Pt_2Cl_4(CO)_2]$ with dpam.[13] Complex (**6**) has not been reported previously.

Experimental

General methods were as previously described in recent papers from this laboratory.[14]

$[Me_2Pt(\mu\text{-}dpam)_2PtMe_2]$.—The complex $[PtMe_2(cod)]$ (0.270 g, 0.81 mmol) and dpam (0.383 g, 0.81 mmol) were heated together in refluxing benzene (30 cm^3) for 3 h. The solution was cooled to room temperature and the solvent removed under reduced pressure. The residue was triturated with benzene (20 cm^3) and the product isolated by filtration. Recrystallisation from chloroform–hexane yielded a white solid. Yield: 0.30 g, 53%.

cis-$[PtMe_2(dpam\text{-}As)_2]$.—(*a*) $[Me_2Pt(\mu\text{-}dpam)_2PtMe_2]$ (0.060 g, 0.043 mmol) and dpam (0.040 g, 0.086 mmol) were dissolved in C_6D_6 (1 cm^3). Examination of the reaction solution by ^1H n.m.r. spectroscopy showed that no reaction had occurred after *ca.* 20 min. After *ca.* 5 d the ^1H n.m.r. spectrum was re-recorded and indicated the presence of starting materials and new resonances assigned to *cis*-$[PtMe_2(dpam\text{-}As)_2]$.

(*b*) $[Me_2Pt(\mu\text{-}dpam)_2PtMe_2]$ (0.030 g, 0.0215 mmol) and dpam (0.020 g, 0.043 mmol) were refluxed together in benzene (3 cm^3) for 3 h. The solution was cooled to room temperature and the solvent removed under reduced pressure. The white solid residue was dissolved in $CDCl_3$ (1 cm^3) and examined by ^1H n.m.r. spectroscopy, which indicated the presence of starting materials and *cis*-$[PtMe_2(dpam\text{-}As)_2]$.

$[PtCl_2(dpam\text{-}AsAs')]$.—Platinum(II) chloride (1.30 g, 4.89 mmol) was boiled in acetonitrile (25 cm^3) for 2 h to produce a pale yellow solid and a yellow solution. Dpam (2.79 g, 5.90 mmol) was added and the mixture heated under reflux for 1 h and then cooled to *ca.* 20 °C. The pale yellow solid was filtered off, washed with MeOH, and dried *in vacuo*. Yield: 2.95 g, 82%.

$[PtBr_2(dpam\text{-}AsAs')]$.—The complex $[PtCl_2(dpam\text{-}AsAs')]$ (0.1 g, 0.135 mmol) was suspended in acetone (10 cm^3). To this was added LiBr (0.3 g, 3.45 mmol) and the mixture boiled for 15 min. The solvent was removed under reduced pressure and the residue triturated with methanol (15 cm^3). The yellow solid was filtered off and dried *in vacuo*. Yield: 0.085 g, 76%.

The complex $[PtI_2(dpam\text{-}AsAs')]$ was prepared similarly in 81% yield using NaI.

trans-$[PtCl_2(dpam\text{-}As)_2]$.—A suspension of $[PtCl_2(dpam\text{-}AsAs')]$ (0.470 g, 0.636 mmol) in CH_2Cl_2 (15 cm^3) was treated wiith dpam (0.312 g, 0.660 mmol) and the mixture boiled for 5 min to produce a yellow solution. The solvent was removed under reduced pressure and the residue triturated with Et_2O (30 cm^3). The pale yellow solid was filtered off, washed with Et_2O and dried *in vacuo*. Yield: 0.75 g, 97%.

The complex *trans*-$[PtBr_2(dpam\text{-}As)_2]$ was prepared similarly in 89% yield from $[PtBr_2(dpam\text{-}AsAs')]$.

trans-$[Cl_2Pt(\mu\text{-}dpam)_2HgCl_2]$.—The complex *trans*-$[PtCl_2(dpam\text{-}As)_2]$ (0.206 g, 0.170 mmol) was dissolved in benzene (25 cm^3) with gentle heating. A solution of $HgCl_2$ (0.045 g, 0.170 mmol) in thf (3 cm^3) was added and a fine precipitate separated. The mixture was boiled for 10 min, cooled to room temperature, and the yellow solid filtered off, washed with benzene and dried *in vacuo*. Yield: 0.18 g, 72%.

$[ClPt(\mu\text{-}dpam)_2PtCl]$.—The complex *trans*-$[PtCl_2(dpam\text{-}As)_2]$ (0.726 g, 0.6 mmol) was suspended in benzene (25 cm^3). Solid $[Pt_2(\mu\text{-}OMe)_2(C_8H_{12}OMe)_2]$ (0.219 g, 0.3 mmol) was added and the mixture stirred for 1 h. The solution was filtered and the filtrate reduced in volume to *ca.* 2 cm^3. n-Hexane (30 cm^3) was added to precipitate the yellow solid product which was filtered off, washed with n-hexane and dried *in vacuo*. Yield: 0.595 g, 70%.

$[ClPt(\mu\text{-}CO)(\mu\text{-}dpam)_2PtCl]$.—The complex $[ClPt(\mu\text{-}dpam)_2PtCl]$ (0.15 g, 0.107 mmol) was dissolved in CH_2Cl_2 (2 cm^3). Carbon monoxide was bubbled through the solution for 30 min, after which time the orange solid product was filtered off, washed with CH_2Cl_2 (1 cm^3) and dried *in vacuo*. Yield: 0.1 g, 65%.

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