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Binuclear Analogues of Bis(triphenylphosphine) Complexes: Synthesis of Palladium(II) and Platinum(II) Complexes of *m*-Bis(diphenylphosphino)benzene. X-ray Crystal Structure of $[Pt_2Cl_4\{\mu\text{-}1,3\text{-}(PPh_2)_2C_6H_4\}_2]$

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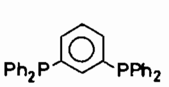
Triphenylphosphine complexes are widely used in organometallic synthesis and as catalysts for hydroformylation, hydrogenation, carbonylation, decarbonylation, hydrosilylation, oxidation and carbon–carbon bond formation [1]. We reasoned that the phosphorus donor atoms in *m*-bis(diphenylphosphino)benzene (**1**) would be sterically and electronically similar to the phosphorus in triphenylphosphine and, in addition, would form binuclear complexes since it cannot chelate without imposing great strain. We therefore hoped to generate complexes from ligand **1** possessing similar properties to mononuclear triphenylphosphine complexes but modified by the presence of an adjacent metal centre.

Surprisingly **1** has not been studied as a ligand before despite the popularity of its isomers: **2**, which forms very stable chelates, and **3** which forms polymeric species [2]. We report here our successful attempts to make binuclear complexes of **1** with the d^8-metal centres palladium(II) and platinum(II).



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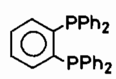

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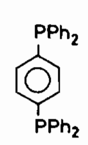

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Results and Discussion

The ligand **1** was made by literature methods [3, 4] and characterised by elemental analysis and by comparison of its IR spectrum with that reported [4]. At 36.4 MHz the ^{31}P chemical shift for **1** was indistinguishable from that of triphenylphosphine. Only at 162 MHz, using resolution enhancement, was it possible to distinguish **1** from added triphenylphosphine: the chemical shift difference was of the order of 0.02 ppm which is much less than the variation in shift due to concentration or temperature effects (see Table I).

TABLE I. Phosphorus-31 NMR Data[a]

	$\delta(P)$	$^1J(PtP)$
$m\text{-}C_6H_4(PPh_2)_2$	-4.51 ± 0.18[b]	
PPh_3	-4.53 ± 0.18[b]	
4a[c]	+22.8	2664
6a[c]	+20.1	2638
4b	+19.6	2574
6b	+19.7	2465
4c	+12.6	2500
6c	+12.6	2477
4d[c]	+23.5	–
6d[c]	+22.6	–
4e	+24.3	–
6e	+22.6	–
4f	+13.4	–
6f	+13.4	–

[a] In $CDCl_3$; chemical shifts in ppm (±0.1) to high frequency of 85% H_3PO_4; coupling constants in Hz (±3). Spectra measured at 298 K and 162 MHz unless otherwise stated. [b] Exact shift depends on concentration and temperature. $\delta(PPh_3)$ was always slightly to high frequency of $\delta(C_6H_4(PPh_2)_2)$. [c] Spectrum at 308 K and 36.4 MHz.

The labile platinum(II) complex $[PtCl_2(NCBu^t)_2]$ was treated with the diphosphine (**1**) in dichloromethane and the resulting yellow solution cooled to −78 °C to give yellow crystals of the binuclear complex **4a** in over 90% yield. The formulation of **4a** follows from elemental analysis (C, H, Cl) and molecular weight determination in chloroform (calc: 1424; found: 1306); the assignment of a *trans* configuration follows from both infrared ($\nu_{Pt-Cl} = 351\ cm^{-1}$) and ^{31}P NMR ($^1J_{Pt-P} = 2664$ Hz) spectroscopy.

The structure of **4a** has been determined by X-ray crystallography*. The conformation of the 12-membered ring is shown in Fig. 1. Both platinum atoms are square planar with the coordination planes parallel to each other. The metal centres are well separated: the Pt···Pt distance is 4.740(8) Å.

The chloride ligands in complex **4a** are readily exchanged by treatment with LiBr or LiI to give the bromide (**4b**) or iodide (**4c**) derivatives respectively. Both have been fully characterised (see Table I for ^{31}P NMR data).

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*Crystal data: $C_{60}H_{48}Cl_4P_4Pt_2$, $M = 1424$, triclinic, space group $P\bar{1}$; $a = 10.610(2)$, $b = 10.821(2)$, $c = 15.076(2)$ Å, $\alpha = 93.54(1)$, $\beta = 90.71(2)$, $\gamma = 112.92(1)°$, $U = 1589(5)$, $Z = 1$. The final $R = 0.052$ is for 4558 unique observed ($I/\sigma(I) \geq 3.0$) reflections (diffractometer data, corrected for absorption).

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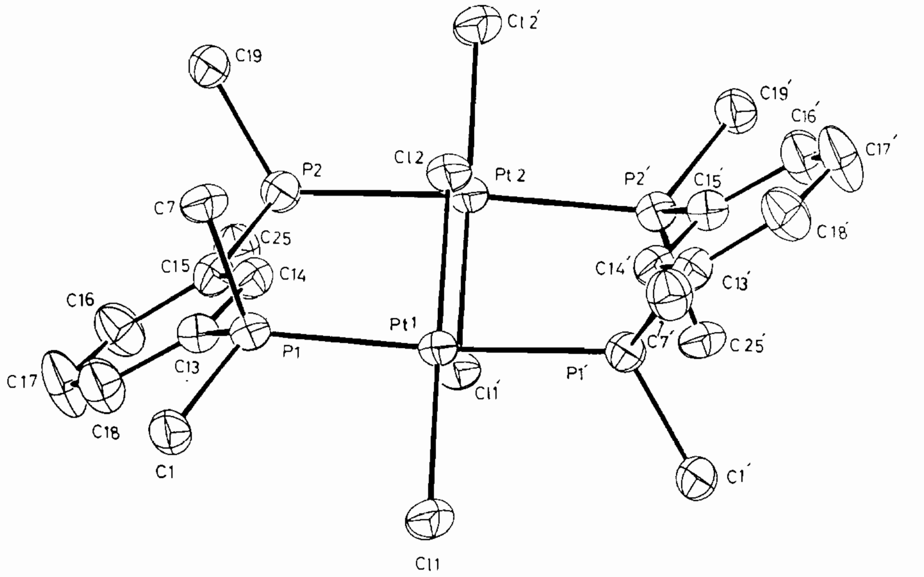
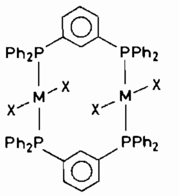
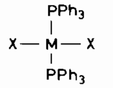


Fig. 1. Molecular structure of $[Pt_2Cl_4(\mu\text{-}1,3\text{-}(PPh_2)_2C_6H_4)_2]$ (**4a**). Selected bond distances: Pt(1)–Pt(2), 4.740(8); Pt(1)–Cl(1), 2.301(2); Pt(1)–P(1), 2.322(2) Å; selected bond angles P(1)–Pt–P(1′) 176.0(1); Cl(1)–Pt(1)–P(1) 88.5(1)°.

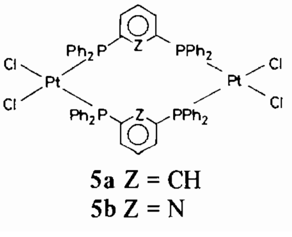
The dipalladium complex (**4d**) was made from $[PdCl_2(NCPh)_2]$ and diphosphine (**1**) in acetone and was characterised by elemental analysis (C, H and Cl) and a molecular weight determination in chloroform (calc.: 1246; found: 1257). The *trans* structure follows from the IR spectrum (ν_{Pd-Cl} 362 cm^{-1}) and the ^{31}P NMR spectrum (see Table I). Metathesis of the chloride ligands in **4d** using LiBr or LiI gave the bromide (**4e**) and iodide (**4f**) in good yields.





4a M = Pt, X = Cl
4b M = Pt, X = Br
4c M = Pt, X = I
4d M = Pd, X = Cl
4e M = Pd, X = Br
4f M = Pd, X = I

6a M = Pt, X = Cl
6b M = Pt, X = Br
6c M = Pt, X = I
6d M = Pd, X = Cl
6e M = Pd, X = Br
6f M = Pd, X = I



5a Z = CH
5b Z = N

Treatment of a dichloromethane or benzene solution of $[PtCl_2(COD)]$ (COD = 1,5-cyclo-octadiene) with diphosphine (**1**) gave a white crystalline solid. Elemental analysis (C, H and Cl) are in agreement with the empirical formula $[PtCl_2(Ph_2PC_6H_4PPh_2)]_n$ and the well resolved IR spectrum shows that the chloride ligands are *cis*: ν_{Pt-Cl} 295, 315 cm^{-1} *cf.* ν_{Pt-Cl} 295, 319 cm^{-1} in *cis*-$[PtCl_2(PPh_3)_2]$. Unfortunately lack of solubility precluded NMR studies or molecular weight determination. We tentatively assign the structure **5a** to this white compound by analogy with the recently reported [5] closely related complex **5b**.

Very small differences in the chemical environment of phosphorus nuclei are readily detected by ^{31}P NMR spectroscopy; in particular ^{31}P chemical shifts are very sensitive to small changes. The similarity in chemical shift between the ligand **1** and triphenylphosphine (see Table I) indicates that the phosphorus donors in each are very similar. Table I shows a comparison of the ^{31}P NMR data for our new binuclear complexes (**4a**–**f**) and the corresponding bis(triphenylphosphine) complexes (**6a**–**f**). The similarity in the two sets of data clearly support the idea that the metal centres in the binuclear complexes (**4a**–**f**) are in a similar environment to the metal centres in the mononuclear complexes (**6a**–**f**). We are investigating the chemistry of complexes (**4a**–**f**) to see how closely it resembles that of the analogous triphenylphosphine complexes (**6a**–**f**) and to what extent the chemistry is modified by the presence of the adjacent metal centre. In addition we are extending our studies to other d^8-metal centres and, in particular, to complexes of catalytic interest.

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