Synthesis and Structure of Some Binuclear Carbonyl Complexes of Platinum(I)

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The complex $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dppm})_2]$ [2; dppm = bis(diphenylphosphino)methane] has been prepared by the reversible reaction of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with carbon monoxide and also by the reaction of $[NPr_4]_2[Pt_2Cl_4(CO)_2]$ with dppm. In polar solvents (2) isomerises to give the ion $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$, isolated as the $[PF_6]^-$ salt (3b). The i.r., Raman, and ^1H and ^{31}P n.m.r. spectra of these complexes are discussed. On the basis of its exceptionally low i.r. frequency, it is proposed that the carbonyl group in complex (2) is acting as an unsymmetrical four-electron bridging ligand. An arsine complex $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dpam})_2]$ [dpam = bis(diphenylarsino)methane] analogous to (2) has been prepared from $[Pt_2Cl_4(CO)_2]^{2-}$.

THE ligand bis(diphenylphosphino)methane, dppm, has a strong tendency to bridge between two platinum centres, thus keeping these atoms in close proximity. Probably as a result of this, dppm forms the stable platinum(I) complex $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (I) and also stable platinum(II) complexes, *e.g.* $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, with bridging hydride ligands.[1-3] The Pt–Pt bond of (1) can be protonated to give the $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ ion.[2] In this paper we report some carbonyl derivatives of (1), including a complex $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dppm})_2]$ having a bridging carbonyl group with an unusually low i.r. stretching frequency. A preliminary report of this work has been published.[3]

RESULTS AND DISCUSSION

Synthesis and Properties of the Carbonyl Complexes.—The preparative routes to the carbonyl complexes are summarised in the Scheme. Bubbling carbon monoxide through a solution of (1) in dichloromethane rapidly gave yellow needles of the adduct $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dppm})_2]$ (2), which could also be prepared by reaction of dppm with the anion $[Pt_2Cl_4(CO)_2]^{2-}$, initially reported by Goggin and Goodfellow.[4] In methanol solvent (2) isomerised to the ionic terminal carbonyl complex $[Pt_2Cl(CO)(\mu\text{-dppm})_2]Cl$ (3a), and the complex cation could readily be isolated as the hexafluorophosphate salt $[Pt_2Cl(CO)(\mu\text{-dppm})_2][PF_6]$ (3b) on addition of ammonium hexafluorophosphate. Attempts to isolate (3a) by evaporation of the solvent always led to partial isomerisation back to (2), although by rapid evaporation of the solvent this was minimised. Solutions of (3a) in methanol could be prepared directly by reaction of a suspension of (1) in methanol with carbon monoxide. The isomerisation of (2) $\rightleftharpoons$ (3a) could be studied more readily in 1,1,2,2-tetrachloroethane as solvent. Here an equilibrium mixture of (2) and (3a) in proportion *ca.* 1 : 3 was obtained. From (2) the equilibrium was reached in *ca.* 5 h at room temperature. As expected, the ratio of (3a) : (2) increases with solvent polarity in the order MeOH > $C_2H_2Cl_4$ > CH_2Cl_2.

As well as undergoing this isomerisation reaction, (2) slowly decomposed at room temperature both in the solid

TABLE 1

Infrared and Raman data (cm^{-1}) for the carbonyl complexes

Complex	ν(CO) I.r.	ν(CO) Raman	ν(PtCl) I.r.	ν(PtCl) Raman	ν(Pt–Pt) (Raman)
(2) $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dppm})_2]$	1 638	1 638	229 [a]	254 [b]	
(4) $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dpam})_2]$	1 639	1 637	228 [a]	253 [b]	
(3) $[Pt_2Cl(CO)(\mu\text{-dppm})_2][PF_6]$	2 072	2 071	279	283	157

[a] ν_{asym}(PtCl). [b] ν_{sym}(PtCl).

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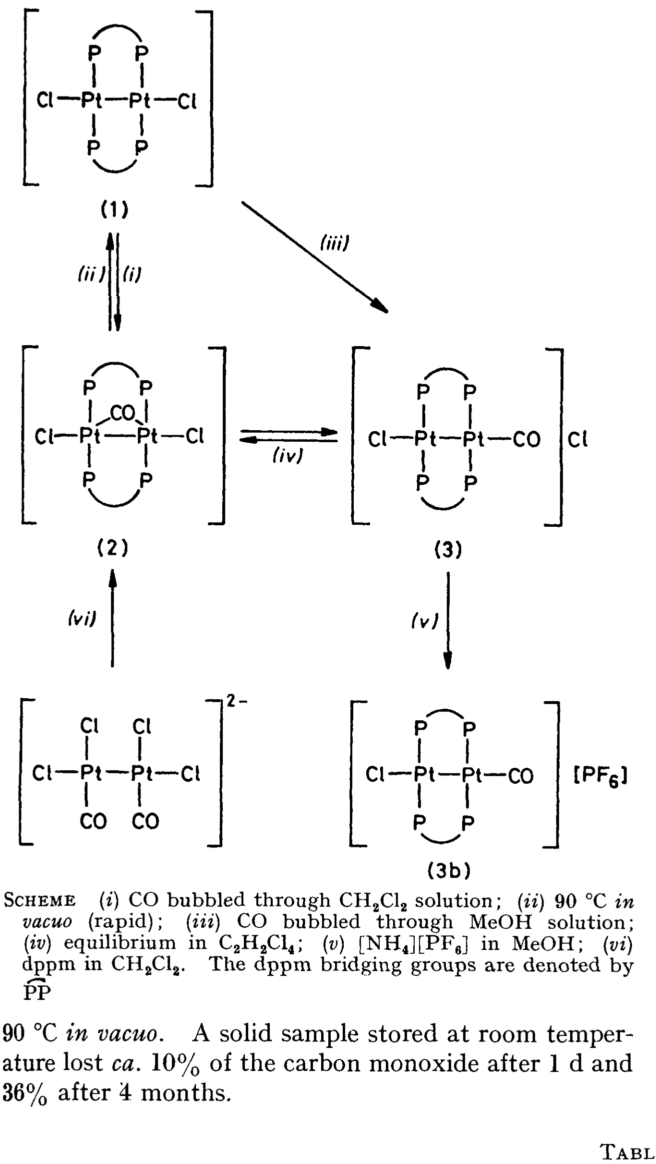
[1] M. P. Brown, R. J. Puddephatt, and M. Rashidi, *Inorg. Chim. Acta*, 1976, **19**, L33; M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J.C.S. Dalton*, 1977, 951.

[2] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *Inorg. Chim. Acta*, 1977, **23**, L27; *J.C.S. Dalton*, 1978, 516.

[3] M. P. Brown, R. J. Puddephatt, M. Rashidi, Lj. Manojlovic-Muir, K. W. Muir, T. Solomun, and K. R. Seddon, *Inorg. Chim. Acta*, 1977, **23**, L33.

[4] P. L. Goggin and R. J. Goodfellow, *J.C.S. Dalton*, 1973, 2355; A. Modinos and P. Woodward, *ibid.*, 1975, 1516.

state and in solution back to (1) and carbon monoxide, this decomposition being rapid and quantitative at 90 °C *in vacuo*. A solid sample stored at room temperature lost *ca*. 10% of the carbon monoxide after 1 d and 36% after 4 months.



SCHEME (*i*) CO bubbled through CH_2Cl_2 solution; (*ii*) 90 °C *in vacuo* (rapid); (*iii*) CO bubbled through MeOH solution; (*iv*) equilibrium in $C_2H_2Cl_4$; (*v*) $[NH_4][PF_6]$ in MeOH; (*vi*) dppm in CH_2Cl_2. The dppm bridging groups are denoted by $\overset{\frown}{PP}$

The bis(diphenylarsino)methane, dpam, complex $[Pt_2Cl_2(\mu\text{-}CO)(\mu\text{-}dpam)_2]$ (4) was prepared by reaction of dpam with $[Pt_2Cl_4(CO)_2]^{2-}$. In contrast to (2), (4) did not readily lose carbon monoxide on heating and did not isomerise to a cationic terminal carbonyl species on dissolution in 1,1,2,2-tetrachloroethane.

Characterisation of the Carbonyl Complexes.—Data from the i.r., Raman, and ^1H and ^{31}P n.m.r. spectra are given in Tables 1—3.

The bonding mode of the carbonyl ligand was deduced from the vibrational spectra. The terminal carbonyl complex (3b) gave ν(CO) at 2 072 cm^{-1} in the i.r. spectrum. This is slightly lower than in monomeric carbonyl complexes of Pt^{II} such as *trans*-$[PtCl(CO)(PPh_3)_2]^+$ which has ν(CO) at 2 100 cm^{-1} and indicates that back bonding is stronger in the dimeric platinum(I) carbonyl as would be expected.[5] Complex (3a), which could not be isolated in pure form, was similarly characterised in $C_2H_2Cl_4$ or MeOH solutions by the strong ν(CO) frequency at 2 070 cm^{-1} due to the terminal carbonyl ligand.

TABLE 2

Hydrogen-1 n.m.r. data for the carbonyl complexes

Complex	δ(CH_2) p.p.m.	^3J(PtH) Hz	Solvent
(3a) $[Pt_2Cl(CO)(\mu\text{-}dppm)_2]Cl$	4.90 [a]	64.2	CD_3OD
(3b)	4.65 [a]	60.6	$CDCl_3$
(4)	2.60 1.67	*b*	$C_2D_2Cl_4$

[a] Observed as the three central peaks of a 1 : 8 : 18 : 8 : 1 quintet. [b] Not observed.

Complexes (2) and (4), which contain a bridging carbonyl ligand, are characterised by a strong band at 1 638 ± 1 cm^{-1} in the vibrational spectra due to ν(CO). This frequency is considerably lower than expected for a normal bridging carbonyl ligand and is commented on below. These complexes also each give one band due to ν(PtCl) in the i.r. and one band in the Raman spectra, and in each case the i.r. and Raman bands are noncoincident. This suggests the presence of an essentially linear ClPtPtCl unit in the complexes. The values of ν(PtCl) for (2) are slightly lower than for (1),[1] indicating that the presence of the bridging carbonyl ligand weakens the PtCl bonds to some extent. In contrast, addition of H^+ to the Pt–Pt bond of (1) causes an increase in ν(PtCl).[2]

Complex (3b) gave a strong band in the Raman spectrum at 157 cm^{-1} due to ν(PtPt), similar to the value of ν(PtPt) at 150 cm^{-1} for the parent (1).[1] However, we were unable to identify a band due to ν(PtPt) in the Raman spectra of (2) or (4).

TABLE 3

$^{31}P\text{-}\{^1H\}$ n.m.r. data (Hz) for the carbonyl complexes

Complex *	Solvent	^1J(AX)	^2J(BX)	^1J(BY)	^2J(AY)	*N*	ν_A	ν_B	*J*(AB)	*J*(AB′)	*L*
(3a)	MeOD	2 706	62	2 573	92	89	2 417	2 468	46	43	3
	$C_2H_2Cl_4$	2 700		2 590		89					
(3b)	$CDCl_3$	2 711	71	2 591	90	88	3 407	3 467	45	43	2

* The complex $[Pt_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ in $C_2D_2Cl_4$ gives δ(P) 8.9 p.p.m. from trimethyl phosphate as reference: ^1J(PtP) 3 973, ^2J(PtP) 367, $N = J(AA'') + J(AA''')$ 65 Hz, $N' = {}^1J(PtP) + {}^2J(PtP)$ 4 360 Hz (calc. 4 340 Hz). For an explanation of the symbols see the text.

As discussed previously,[1] the bridging unit $Pt_2(\mu\text{-}dppm)_2$ can readily be characterised by the ^{31}P and ^1H n.m.r. spectra of the complexes. The ^{31}P n.m.r. spectrum of (3a) in MeOD is shown in Figure 1, and is of

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[5] W. J. Cherwinski and H. C. Clark, *Canad. J. Chem.*, 1969, **47**, 2665.

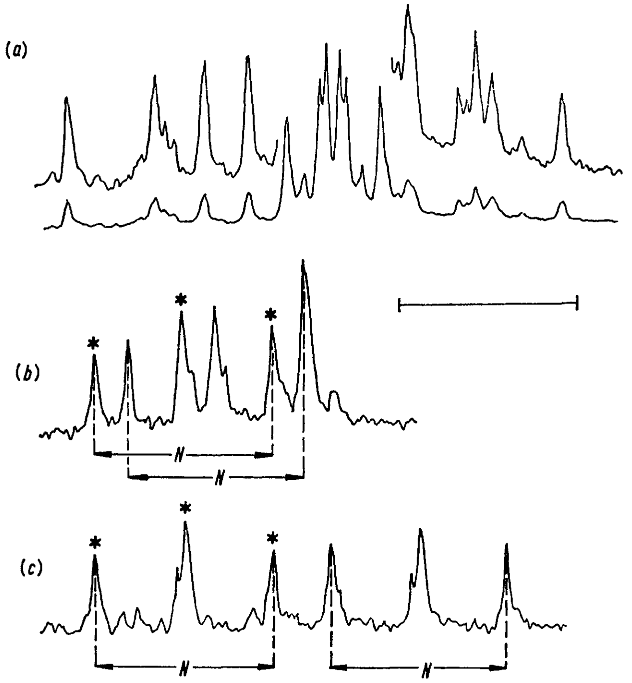
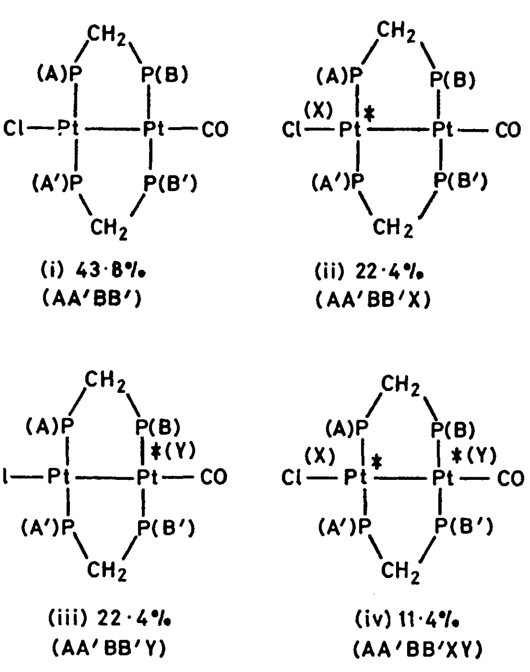


FIGURE 1 The central portion (*a*) and the low-field (*b*) and high-field ^{195}Pt satellites (*c*) of the ^{31}P n.m.r. spectrum (36.4 MHz) of [Pt$_2$Cl(CO)(μ-dppm)$_2$]Cl (3a) in MeOD. The bar indicates 100 Hz; (*b*) and (*c*) were recorded at approximately the same sensitivity as the top trace in (*a*). The unmarked peaks in (*b*) and (*c*) are due to species (ii) (Figure 2) and the asterisked peaks are due to species (iii). For the significance of *N* and for chemical shifts and coupling constants refer to the text and Table 3

particular interest. The spectrum has components due to the species (i)—(iv) shown in Figure 2, which are present due to the natural abundance of ^{195}Pt ($I = \frac{1}{2}$), and the non-equivalence of the ^{31}P atoms adjacent to chloride and carbonyl ligands respectively. For the AA'BB'X spin system the AA'BB' part can be analysed in terms of the parameters $N = J(\mathrm{AB}) + J(\mathrm{AB'})$, $L = J(\mathrm{AB}) - J(\mathrm{AB'})$, $K = J(\mathrm{AA'}) + J(\mathrm{BB'})$, and $M = J(\mathrm{AA'}) - J(\mathrm{BB'})$.[6] In the present case $M = 0$, and the triplet appearance of the ^{195}Pt satellites indicates that $L \sim 0$. The separation between outer peaks of a given triplet gives *N*. Overall the AA'BB'X spin system gives rise to four triplets in the ^{31}P n.m.r. spectrum, two of which are centred about ν(A) and separated by ^1J(AX) and the other two centred about ν(B) and separated by ^2J(BX). Similarly, the AA'BB'Y spin system gives four triplets, two of which are centred about ν(B) and separated by ^1J(BY) and the other two centred about ν(A) and separated by ^2J(AY). The inner triplets overlap with each other and with peaks due to species (i) but, knowing the above relations, the peaks can be fairly readily identified and the values of ^1J(AX), ^1J(BY), ^2J(BX), ^2J(BY), *N*, ν_A, and ν_B can be determined. The assignments of ν_A and ν_B to particular phosphorus atoms is arbitrary and the opposite assignment is equally likely. Having identified the peaks in the central multiplet which are due to the AA'BB'X and AA'BB'Y spin systems, the remaining peaks in the complex central part of the spectrum due to the AA'BB' spin system of species (i), Figure 2, can be identified and this spectrum analysed to give J(AB).[6] From this value and *N*, J(AB') can be calculated. Peaks due to species (iv), Figure 2, could not be identified.

The ^{31}P n.m.r. spectra of (3a) in MeOD and (3b) in CDCl$_3$ were very similar, and clearly the analysis of the spectra lends strong support for the proposed formulation, with both being ionic.

During the time required to accumulate the ^{31}P n.m.r. spectrum of (2) in C$_2$D$_2$Cl$_4$, considerable isomerisation to (3a) and dissociation of carbon monoxide to give (1) occurred. Since peaks due to these species are readily recognised, however, the spectrum due to (2) was identified. It gives a typical pattern for a symmetrical Pt$_2$(μ-dppm)$_2$-containing complex with peaks due to A$_4$, AA'A''A'''X, and AA'A''A'''XX' spin systems arising from complexes containing zero, one or two ^{195}Pt atoms respectively.[1,2] The analysis of the spectrum is the same as previously reported for (1), except that in (1) the coupling constants ^1J(PtP) and ^2J(PtP) are of opposite sign, whereas in (2) they have the same sign (both positive).



(i) 43·8% (AA'BB')
(ii) 22·4% (AA'BB'X)
(iii) 22·4% (AA'BB'Y)
(iv) 11·4% (AA'BB'XY)

FIGURE 2 Natural abundance of ^{195}Pt-containing species (Pt* = ^{195}Pt) and the resulting spin systems for ^{31}P and ^{195}Pt atoms for [Pt$_2$Cl(CO)(μ-dppm)$_2$]$^+$

The resonances of the CH$_2$ protons of the dppm ligands in the ^{1}H n.m.r. spectra of (3a) and (3b) were observed as the three central lines of a 1 : 8 : 18 : 8 : 1 quintet due to coupling to ^{195}Pt. This shows that the dppm ligands are bridging between platinum atoms [1,2] and that the two non-equivalent ^3J(PtPCH$_2$) coupling

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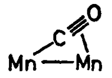
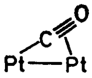
[6] R. J. Abraham, 'Analysis of High Resolution NMR Spectra,' Elsevier, Amsterdam, 1971.

constants are effectively equal. It was not possible to obtain a ^{1}H n.m.r. spectrum for (2) because partial isomerisation to (3a) occurs in suitable solvents. The ^{1}H n.m.r. spectrum of the bridging carbonyl complex (4) contained two peaks due to the CH_2 groups of the dpam ligands. This is expected for the proposed formulation, since the presence of the bridging carbonyl renders the two hydrogen atoms of each CH_2 group non-equivalent.

Bonding in the Complexes.—An interesting spectral feature is the low carbonyl-stretching frequency (1 638 cm^{-1}) of complexes (2) and (4). The complex $[Mn_2(CO)_5(\mu\text{-dppm})_2]$,[7] the only other known binuclear complex with a similarly low value (1 648 cm^{-1}), has been shown by *X*-ray structure determination to contain a bridging CO group which is σ bonded to one manganese atom and π bonded to the second, giving the structural unit (I)



(I)



(II)

in which the carbonyl acts as a four-electron ligand. The iron cluster complex $[Fe_4(CO)_{13}H]^-$ also contains a somewhat similar bridging carbonyl,[8] again with an exceptionally low i.r. frequency,[9] although in this case bonding to more than two metal centres appears to occur. We previously suggested,[1] by analogy, that (2) and (4) contain the structural unit (II) and we still adhere to this view despite the fact that the analogous palladium complex $[Pd_2Cl_2(\mu\text{-CO})(dpam)_2]$ has subsequently been reported and shown to contain a symmetrically bridging CO group.[10] The comparison between this palladium complex and the platinum complexes (2) and (4) is compounded by the bridging CO group in the palladium complex possessing a normal stretching frequency (1 720 cm^{-1}) but having apparently a unique large bridging Pd–C–Pd angle.

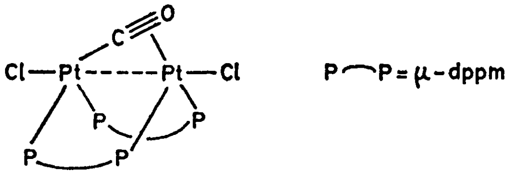


FIGURE 3 Proposed structure for $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dppm})_2]$ (2)

The other vibrational data throw no further light on the structure of the CO group in (2) and (4) since the apparent absence of an assignable Raman Pt–Pt band does not imply absence of a Pt–Pt bond. Such a bond would presumably be required by the four-electron unsymmetrical bridging mode if the platinum atoms are not each to be left with an odd electron count. The ^{31}P n.m.r. data on (2) are consistent with either bridging mode since fluxionality of an unsymmetrical CO bridge would be probable and would make the platinum and phosphorus atoms effectively equivalent. Attempts to prepare crystals of (2) and (4) suitable for *X*-ray study, although so far unsuccessful, are continuing.

Formation of the platinum(I) terminal carbonyl complex (3a) by isomerisation of (2) involves the unusual displacement of Cl$^-$ by CO at a platinum centre. This is probably accounted for by the Pt–Cl bond in (1) [3] (*trans* to platinum) being relatively weak and the Pt–CO bond in (3), as a consequence of platinum being in oxidation state I rather than II, being relatively strong.

The relative stabilities of the bridging CO complexes (2) and (4) is worthy of note. Unlike the dppm complex (2), the dpam complex (4) neither loses CO, to give the dpam analogue of (1), nor isomerises to the dpam analogue of (3). This provides additional evidence for dpam preferring a larger separation between the metal centres than dppm.[10] This has been postulated as a result of *X*-ray structural studies of $[Pd_2Br_2(dppm)_2]$,[11] which has a Pd–Pd bond distance of 2.699 Å, and of $[Pd_2Cl_2(\mu\text{-CO})(dpam)_2]$,[10] which has a Pd–Pd distance of 3.274 Å. Both products (1) and (3) have strong Pt–Pt bonds as shown by their Raman spectra and the known Pt–Pt bond distance [3] in (1) of 2.652 Å. The presence of the CO group in (2) and (4), irrespective of possible Pt–Pt bonding, can be expected to lengthen the Pt–Pt separation. Thus with dpam as a ligand the bridging CO structure is favoured with respect to the structure in (1) and (3). Attempts to prepare a complex $[Pt_2Cl_2(dpam)_2]$ by methods similar to those used for (1) have failed.

EXPERIMENTAL

General methods and spectroscopic techniques have been described previously.[1,2]

Bis-μ-bis(diphenylphosphino)methane-μ-carbonyl-bis-[chloroplatinum(I)](Pt–Pt), (2).—(*i*) A solution of dppm (0.5 g) in CH_2Cl_2 (5 cm^3) was added to a solution of $[NPr_4]_2[Pt_2Cl_4(CO)_2]$ [4] (0.5 g) in CH_2Cl_2 (15 cm^3). Vigorous effervescence occurred, the solution became brown in colour, and yellow crystals precipitated. After 2 h the *product* was filtered off, washed with CH_2Cl_2 (1 cm^3), and dried in air, yield 0.23 g (25%). On heating CO was evolved and the product (1) melted at 288—289 °C (Found: C, 49.0; H, 4.0; Cl, 5.9. Calc. for $C_{51}H_{44}Cl_2OP_4Pt_2$: C, 48.7; H, 3.5; Cl, 5.6%).

(*ii*) A stream of carbon monoxide was bubbled through a solution of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ [1] (0.5 g) in CH_2Cl_2 (10 cm^3) for 5 min. The orange-yellow crystals of the *product* which formed were filtered off, washed with CH_2Cl_2 (3 cm^3), and dried in air, yield 0.45 g (88%). It was identical (i.r. spectrum and m.p.) with the product described above.

Bis-μ-bis(diphenylphosphino)methane-carbonylplatinum(I)-*chloroplatinum*(I)(Pt–Pt) *Hexafluorophosphate*, (3b).—Carbon monoxide was bubbled through a suspension of (1) (0.4 g) in methanol (4 cm^3). A yellow solution was obtained. After 25 min the solution was filtered and $[NH_4][PF_6]$ (0.3 cm^3 of a 12% solution in methanol) was added. The yellow crystals which precipitated were filtered off, washed

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[7] C. J. Commons and R. Hoskins, *Austral. J. Chem.*, 1975, **28**, 1663; R. Colton and C. J. Commons, *ibid.*, p. 16.

[8] M. Manassero, M. Sansoni, and G. Longoni, *J.C.S. Chem. Comm.*, 1976, 919.

[9] P. Chini, personal communication.

[10] R. Colton, M. J. McCormick, and C. D. Pannan, *J.C.S. Chem. Comm.*, 1977, 823.

[11] R. G. Holloway, B. R. Penfold, R. Colton, and M. J. McCormick, *J.C.S. Chem. Comm.*, 1976, 485.

with methanol (5 cm^3), and dried *in vacuo*, yield 0.34 g (77%), m.p. 231—235 °C (decomp.) (Found: C, 44.9; H, 3.2; Cl, 2.6; F, 8.2. Calc. for $C_{51}H_{44}ClF_6OP_5Pt_2$: C, 44.8; H, 3.2; Cl, 2.6; F, 8.3%).

Bis-μ-bis(diphenylarsino)methane-μ-carbonyl-bis[chloroplatinum(I)].*-Dichloromethane* (1/1), (4).—A solution of bis(diphenylarsino)methane (1 g) in CH_2Cl_2 (10 cm^3) was added slowly to a solution of $[NPr_4]_2[Pt_2Cl_4(CO)_2]$ (1 g) in CH_2Cl_2 (25 cm^3). Effervescence occurred, the solution became orange in colour, and orange needles of the *product* precipitated as a 1 : 1 solvate with CH_2Cl_2. The product was filtered off, washed with CH_2Cl_2 (3 cm^3), and dried in air, yield 1.5 g (76%), m.p. 172—175 °C (decomp.) (Found: C, 41.4; H, 3.4; Cl, 8.8. Calc. for $C_{51}H_{44}As_4Cl_2OPt_2 \cdot CH_2Cl_2$: C, 41.0; H, 3.0; Cl, 9.3%).

Thermal Elimination of CO *from* $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dppm})_2]$.—A sample of $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dppm})_2]$ (*ca.* 0.1 g) was heated *in vacuo* at 180—190 °C for 45 min. The carbon monoxide evolved was collected using a Töpler pump and the volume was measured using a gas burette. A freshly prepared sample gave 98% of the expected volume of CO, a sample stored for 1 d gave 90%, and a sample stored for 4 months gave 64% of the expected CO based on the empirical formula.

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