Bis-μ-[bis(diphenylphosphino)methane]-bis(halogenoplatinum)(*Pt–Pt*); Dimeric Complexes of Platinum(I) containing a Platinum–Platinum Bond

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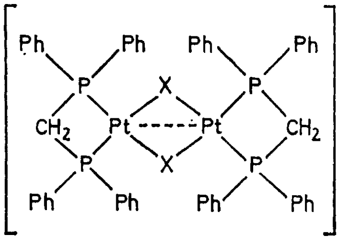
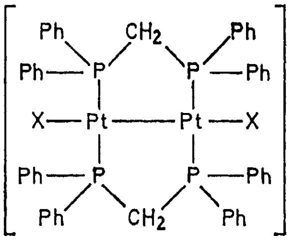
Bis-μ-[bis(diphenylphosphino)methane]-bis(chloroplatinum) (*Pt–Pt*), [{PtCl(dppm)}$_2$] (dppm = Ph$_2$PCH$_2$PPh$_2$), is obtained by treatment of the platinum(II) complex [PtCl$_2$(dppm)] with Na[BH$_4$]–MeOH followed by HCl–C$_6$H$_6$. The corresponding dimeric bromo- and iodo-complexes of Pt^I are obtained from the chloro-complex by halide exchange. The ^{1}H and ^{31}P n.m.r. and vibrational spectra of these complexes are analysed and strongly support the assigned structure rather than the halogenide-bridged structure proposed earlier. Bands assigned to ν(Pt–Pt) are present in the Raman spectra.

ALTHOUGH platinum(I) is an uncommon oxidation state of platinum, several well characterized complexes of it are known. These include [Pt$_2$(CO)(PPh$_3$)$_3$S],[1] [Pt$_2$(PPh$_2$)$_2$(PPh$_3$)$_2$],[2] [Pt$_2$(cod)$_2${OC(CF$_3$)$_2$}], and [Pt$_2$(cod)$_2${C(CF$_3$)$_2$}] [3] (cod = cyclo-octa-1,5-diene) which have bridging groups in addition to a Pt–Pt bond, and the complex ions [Pt$_2$(CO)$_2$X$_4$]$^{2-}$ (X = Cl or Br), [Pt$_2$(CNMe)$_6$]$^{2+}$ and [Pt$_2$(CNMe)$_4$(PPh$_3$)$_2$]$^{2+}$ in which there is a Pt–Pt bond but no bridging groups.[4,5] A further example of Pt^I is the complex [{PtCl(dppm)}$_2$] [dppm = bis(diphenylphosphino)methane] (1a) reported by Glockling and Pollock.[6] These workers obtained this complex in excellent yield (92%) from the reaction of equimolar concentrations of [PtCl$_2$(dppm)] and Hg(SiMe$_3$)$_2$ in boiling benzene, a reaction which under different conditions gave other products. Subsequent attempts by them to obtain this or similar complexes by other routes failed.

We recently discovered a less esoteric route to [{PtCl(dppm)}$_2$] and found that the complex did not possess the chloride-bridged structure (A) proposed by Glockling and Pollock but had instead a dppm-bridged structure (B). A preliminary account of this work has been published.[7] Since then a similar complex [8] of Pd^I, *viz.* [{PdBr(dppm)}$_2$], has been reported and shown by *X*-ray structure determination to have an identical dppm-bridged structure. We now report full details of the preparation and characterization of complexes (1).



(A)



(B)

(1a) X = Cl
(1b) X = Br
(1c) X = I

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[7] M. P. Brown, R. J. Puddephatt, and M. Rashidi, *Inorg. Chim. Acta*, 1976, **19**, L33.

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RESULTS AND DISCUSSION

The complex [{PtCl(dppm)}$_2$] (1a) was readily prepared from [PtCl$_2$(dppm)] by a two-stage reaction. Reduction with Na[BH$_4$] in MeOH afforded a platinum hydride complex which has not yet been fully characterized but which on treatment with HCl in boiling benzene gives (1a) in high overall yield (70%). The bromo- and iodo-complexes, (1b) and (1c) respectively, were readily obtained from (1a) by halide exchange.

These platinum(I) complexes are yellow air-stable solids. They are soluble in chlorinated hydrocarbons and crystallize with solvent of crystallization which is not completely removed *in vacuo* even by prolonged heating. The chloro-complex (1a) is the most stable in solution, appreciable reaction with CH$_2$Cl$_2$, for example, occurring only after several days to give [PtCl$_2$(dppm)] together with other unidentified products. Complexes (1b) and (1c) underwent halide exchange to give (1a) in addition to other products when dissolved in chlorinated solvents. For example, appreciable reaction between (1c) and CH$_2$Cl$_2$ occurred over a period of only a few hours. Although complex (1a) is obtained initially from benzene solution (as a solvate), it does not redissolve in this solvent in the absence of HCl.

During this work difficulty was experienced in obtaining pure [PtCl$_2$(dppm)] by the usual method of treating the phosphine, in this case dppm, with K$_2$[PtCl$_4$].[9] Displacement of the ligand from [Pt(cod)X$_2$] by dppm was however found to be an excellent route to [Pt(dppm)X$_2$] (X = Cl, Br, and I).

Characterization of Complexes (1).—Glockling and Pollock[6] reported that [{PtCl(dppm)}$_2$] gave a parent ion in the mass spectrum and took this as evidence for its dimeric structure. We found that the complexes [{Pt(dppm)X}$_2$], (1a)—(1c), gave peaks in the mass spectrum, with approximately correct isotope patterns, two mass units lower than expected for the dimeric structure. However, this cannot be taken as evidence for the dimeric structure since monomeric [PtCl$_2$(dppm)] gave an almost identical mass spectrum to that of (1a), presumably due to decomposition in the mass spectrometer. Molecular-weight determination in 1,2-dichloroethane solution, however, does confirm that (1a) is a dimer (Table 1), although (1b) and (1c) decomposed too rapidly in solution for similar measurements to be made on them. The platinum(II) complexes [Pt(dppm)X$_2$] (X = Cl, Br, or I) are all monomeric in solution (Table 1) and hence contain the chelated rather than the bridging dppm ligand.[9]

TABLE 1

Analytical data, molecular weights, and melting points

Complex	M.p. (θ_c/°C) [a]	Analysis (%) [b] C	H	Cl	Br	I	M [b]
[{PtCl(dppm)}$_2$]·C$_6$H$_6$	292	51.2 (51.4)	3.8 (3.9)	5.4 (5.4)			
[{PtCl(dppm)}$_2$]·0.5CH$_2$Cl$_2$ [c]	292	47.4 (47.7)	3.5 (3.6)	8.7 (8.4)			1 200 (1 230) [d]
[{PtBr(dppm)}$_2$]·0.5CH$_2$Cl$_2$ [c]	296—297	44.3 (44.6)	3.4 (3.3)	2.5 (2.6)	11.7 (11.7)		
[{PtI(dppm)}$_2$]·0.5CH$_2$Cl$_2$ [c]	292—294	41.8 (41.7)	3.2 (3.1)	2.5 (2.4)		17.2 (17.4)	
[PtCl$_2$(dppm)]	>360	46.0 (46.2)	3.4 (3.4)	10.8 (10.9)			637 (650) [e]
[PtBr$_2$(dppm)]	>360	40.8 (40.6)	3.1 (3.0)		21.9 (21.6)		717 (739) [e]
[PtI$_2$(dppm)]	333	36.2 (3610)	2.6 (2.7)			31.4 (30.5)	797 (833) [e]

[a] All the complexes decomposed on melting. [b] Calculated values are given in parentheses. [c] The presence of CH$_2$Cl$_2$ and the stoicheiometry of the solvate are in agreement with the integrated n.m.r. spectrum. [d] Determined osmometrically in 1,2-dichloroethane at 30 °C after replacement of CH$_2$Cl$_2$ by C$_2$H$_2$Cl$_4$ of crystallization. [e] Determined osmometrically in 1,1,2,2-tetrachloroethane at 50 °C.

The distinction between the chloride- and dppm-bridged structures (A) and (B) can be made on the basis of the ^{1}H and ^{31}P n.m.r. and vibrational spectra of the complexes. Particularly important in analysing the n.m.r. spectra is the occurrence of ^{195}Pt-containing molecules, since ^{195}Pt (natural abundance, 33.8%) has nuclear spin $I = \frac{1}{2}$. The ^{195}Pt distributions and resulting platinum–phosphorus nuclear-spin systems for structure (B) are given in Figure 1.

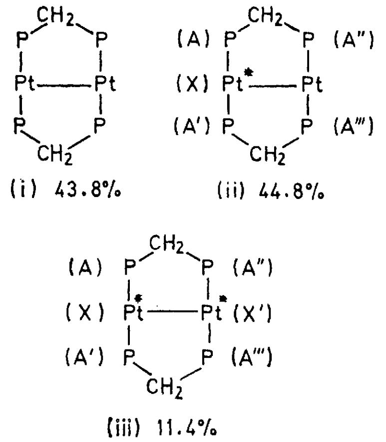

FIGURE 1 Natural abundance of ^{195}Pt-containing species (Pt* = ^{195}Pt)

In the ^{1}H n.m.r. spectrum of (1a) the signal due to the CH$_2$ protons of dppm is most useful in determining the structure. Thus for structure (B) this signal will contain superimposed components due to molecules (i)—(iii) in Figure 1. In (i) no coupling to ^{195}Pt is observed, in (ii) the signal due to the CH$_2$ protons will be a 1 : 1 doublet due to coupling to ^{195}Pt, while in (iii) it will give a 1 : 2 : 1 triplet due to coupling with two ^{195}Pt nuclei. Overall then five peaks of relative intensity 1 : 7.8 : 17.3 : 7.8 : 1 with peak separations equal to $\frac{1}{2}[^3J(\text{PtH})]$ are expected due to coupling with ^{195}Pt. In our spectra, coupling of the CH$_2$ protons to ^{31}P was

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[9] T. G. Appleton, M. A. Bennett, and I. B. Tomkins, *J.C.S. Dalton*, 1976, 439.

not resolved although Glocking and Pollock[6] reported ^{2}J(PH) 3.8 Hz for (1a), but the resonance has the appearance predicted above due to coupling only with ^{195}Pt. Details are given in Table 2 and a diagram of a typical spectrum has been published.[7] This shows that the dppm ligand is bridging the platinum atoms. If a chelated dppm ligand were present as in structure (A) the typical 1 : 3.9 : 1 pattern, with the outer peaks due to coupling of the CH_2 protons to a single ^{195}Pt nucleus, would be expected. This was the observed pattern in the ^{1}H n.m.r. spectrum of the CH_2 protons in monomeric [Pt(dppm)X_2] (Table 2). For these complexes the coupling of the CH_2 protons to ^{31}P was much greater than in (1) and was clearly resolved.

TABLE 2

Hydrogen-1 and ^{31}P n.m.r. data

Complex	δ(CH_2) p.p.m.	^{2}J(PH) Hz	^{3}J(PtH) Hz	δ(P) [a] p.p.m.	^{1}J(PtP) Hz	^{2}J(PtP) Hz	^{3}J(PP) [b] Hz	^{3}J(PP) [c] Hz	N′/Hz obs. (calc.) [d]
[PtCl_2(dppm)]	4.46 [e]	10.8	72.0	−69.70 [f]	3 088				
[PtBr_2(dppm)]	4.47 [e]	11.1	73.8						
[PtI_2(dppm)]	4.58 [e]	10.8	70.8						
(1a)	4.46 [e]		54.0	−0.02 [e,g]	2 936	−136	62.5	26.4	2 800 (2 800)
				−0.20 [e,h]	2 942	−134	63.0	25.9	2 808 (2 808)
(1b)	4.34 [e]		58.8	−3.92 [e]	2 331				
(1c)	4.44 [e]		57.6	−8.99 [e]	2 212				

[a] Trimethyl phosphate reference. [b] J(AA″) in Figure 1. [c] J(AA‴) in Figure 1. Assignments of J(AA″) and J(AA‴) are only probable and are made on the basis of the magnitudes of the coupling. [d] N′ is defined in Figure 2. [e] Solvent $C_2D_2Cl_4$. [f] Solvent $CDCl_3$. [g] At 27 °C. [h] At 60 °C.

The proton-decoupled ^{31}P n.m.r. spectrum of (1a) also contained superimposed components from structures (i)—(iii) as shown in Figure 2. For structure (i) the ^{31}P signal is a singlet, but for structures (ii) and (iii) more complex signals appear due to the presence of ^{195}Pt. For structure (ii) the ^{195}Pt and four ^{31}P atoms give rise to an AA′A″A‴X spin system, and the coupling constants other than J(AA′) can be calculated readily.[10] Thus the parameters K, L, M, and N (L and N are illustrated in Figure 2) are given by: $N = J(AA'') + J(AA''')$; $L = J(AA'') - J(AA''')$; $K = J(AA') + J(A''A''')$; $M = J(AA') - J(A''A''')$. It is to be noted that for this system $J(AA') = J(A''A''')$, so that $M = 0$, and that for the observed spectral form K must be much greater than L or N.[10] The derived coupling constants are given in Table 2.

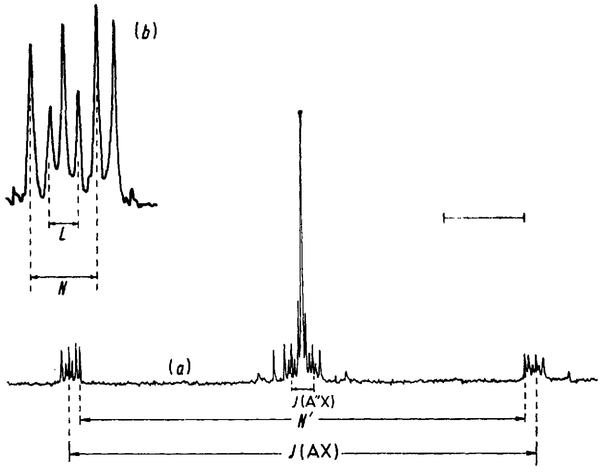

FIGURE 2 Phosphorus-31 n.m.r. spectrum (36.4 MHz) (a) of complex (1a) at 60 °C. Field strength increases from left to right and the bar represents 500 Hz. Chemical shifts and coupling constants are given in Table 2. Low-field satellites are shown on an expanded scale in (b)

For structure (iii) the four ^{31}P and two ^{195}Pt atoms give rise to an AA′A″A‴XX′ spin system.[11] The resulting doublet separation (see Figure 2) is given by $N' = J(AX) + J(A''X)$. Since the observed doublet separation is given accurately by $|^{1}J(PtP)| - |^{2}J(PtP)|$, as given in Table 2, these coupling constants are clearly of opposite sign. Thus taking ^{1}J(PtP) to be positive,[12] ^{2}J(PtP) is negative.

The ^{31}P n.m.r. spectrum of (1a) at 27 °C differed from that at 60 °C in that the high-field ^{195}Pt satellites observed at the former temperature were broad and unresolved although the low-field satellites were still well resolved. The reason for this difference is not understood.

Some changes occur in the ^{31}P n.m.r. spectra of (1) due to decomposition during the spectrum accumulation period. Thus the spectrum of (1a) in $C_2H_2Cl_4$ solvent gave a peak due to [PtCl_2(dppm)] and other minor decomposition products. The spectra of (1b) and (1c) in $C_2H_2Cl_4$ also gave peaks due to (1a) as well as [PtCl_2(dppm)], this decomposition being faster for the iodide complex (1c). Thus halide exchange and oxidation by the solvent both take place in chlorinated solvents. The ^{31}P n.m.r. spectra of (1b) and (1c) are similar to that of (1a) but the fine structure of the ^{195}Pt satellites was not clearly resolved.

Although the ^{31}P n.m.r. spectra are fully consistent with structure (B), it should be pointed out that the chloride-bridged structure (A) would give the same spin systems. The distinction between these structures on the basis of the ^{31}P n.m.r. spectra must therefore rest on the magnitudes of the spectral parameters. The magnitude of ^{1}J(PtP) is fully consistent with a square-planar platinum complex with mutually *trans* phosphine ligands[13] as in structure (B), but is not inconsistent

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[10] N. Sheppard and J. J. Turner, *Proc. Roy. Soc.*, 1959, **252**, 506.

[11] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[12] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 1922.

[13] J. D. Kennedy, W. McFarlane, R. J. Puddephatt, and P. J. Thompson, *J.C.S. Dalton*, 1976, 874.

with structure (A). Thus the magnitudes of ^1J(PtP) for (1a) and for [PtCl$_2$(dppm)] are similar. More useful is the magnitude of ^2J(PP), which is known to be large for mutually *trans* and small for mutually *cis* phosphine ligands.[13] Although we did not measure ^2J(PP), the form of the ^{31}P n.m.r. spectrum clearly shows that this coupling is large [10] and hence strongly favours the dppm-bridged structure (B). The relatively large values of ^3J(PP) are also easier to rationalize on the basis of structure (B).

The Raman spectrum (Table 3) of (1a) contains a very strong band at 150 cm^{-1} which is assigned to the Pt–Pt stretching vibration, ν(PtPt). There is also a much weaker band at 272 cm^{-1} (absent in the i.r.) and a strong band at 249 cm^{-1} in the i.r. (absent in the Raman). These bands are assigned to the symmetric and asymmetric Pt–Cl stretching vibrations. This behaviour may be compared with that for Hg$_2$Cl$_2$ which gives [14] ν(HgHg) at 169 cm^{-1}, ν_{sym}(HgCl) at 279 cm^{-1}, and ν_{asym}(HgCl) at 250 cm^{-1}, and for [Pt$_2$(CO)$_2$Cl$_4$]$^{2-}$ which gives [4a] ν(PtPt) at 170 cm^{-1}, ν_{sym} (PtCl) at 270 cm^{-1}, and ν_{asym}(PtCl) at 240 cm^{-1}. The similarity between the spectra again strongly suggests that (1a) contains the linear ClPtPtCl unit as required in structure (B).

TABLE 3

Infrared and Raman data (cm^{-1}) (X = halide)

Complex	$\bar{\nu}$(PtPt)	$\bar{\nu}_{sym}$(PtX)	$\bar{\nu}_{asym}$(PtX)
[PtCl$_2$(dppm)]		304 [a]	291 [a]
		305 [b]	292 [b]
(1a)	150 [a]	272 [a]	249 [b]
(1b)	118 [a]	199 [a]	*c*
(1c)	106 [a]	118 [a]	*c*

[a] Raman data. [b] Infrared data. [c] <200 cm^{-1}.

The value of ν(PtPt) decreases with the mass of the halogen in (1), being 150 cm^{-1} for (1a), 118 cm^{-1} for (1b), and 106 cm^{-1} for (1c). This trend also reflects the increasing *trans* influence of the halides, and has been observed previously for [Pt$_2$(CO)$_2$X$_4$]$^{2-}$ for which ν(PtPt) is at 170 cm^{-1} when X = Cl and at 135 cm^{-1} when X = Br.[4a]

In conclusion, the combined spectroscopic data show conclusively that the dimeric complexes (1) have the dppm-bridged structure (B). The preference for this over the alternative chloride-bridged structure (A) is probably in part due to the lower ring strain when dppm acts as a bridging ligand (giving a five-membered ring) than when it chelates (giving a four-membered ring). Thus some platinum(II) complexes are known which contain bridging rather than chelating dppm,[9] and bis(diphenylstibino)methane also acts as a bridging ligand in many of its complexes.[15]

EXPERIMENTAL

Hydrogen-1 and ^{31}P n.m.r. spectra were recorded using Perkin-Elmer R12B (60 MHz) and Bruker WH-90 spectrometers respectively. Infrared spectra were obtained using a Perkin-Elmer 577 spectrometer and Raman spectra using a Spex Ramalog 5 spectrometer. Elemental analyses are given in Table 1.

Molecular Weights.—These were determined on a Hewlett-Packard 302B vapour-pressure osmometer using at least four different concentrations for each complex. A solution of [{PtCl(dppm)}$_2$]·0.5CH$_2$Cl$_2$ in 1,2-dichloroethane (dried and distilled) was evaporated to dryness in a stream of N$_2$ to remove the CH$_2$Cl$_2$. The stoicheiometry of the [{PtCl(dppm)}$_2$]·1.0C$_2$H$_4$Cl$_2$ complex thus obtained and from which the solutions were made up was deduced from the weight of the residue and confirmed by integrating the ^{1}H n.m.r. spectrum (in CDCl$_3$). The molecular weight (Table 1) is given for the unsolvated complex. The complexes [PtX$_2$(dppm)] (X = Cl, Br, and I) are only sparingly soluble in C$_2$H$_4$Cl$_2$ and molecular weights were measured in 1,1,2,2-tetrachloroethane solutions (at 50 °C).

Complexes [PtX$_2$(dppm)] (X = Cl, Br, *and* I).—In a typical reaction, [Pt(cod)Cl$_2$] (5 g) was treated with dppm (5.2 g) in CH$_2$Cl$_2$ (200 cm^3) for 48 h. The product, which was solvated with CH$_2$Cl$_2$, was isolated by filtration and, when heated at 150 °C for 2 h *in vacuo* to remove CH$_2$Cl$_2$, gave pure [PtCl$_2$(dppm)] (6.0 g, 60% yield) as a white solid.

The complexes [PtBr$_2$(dppm)] and [PtI$_2$(dppm)] were obtained similarly from [PtBr$_2$(cod)] and [Pt(cod)I$_2$] respectively. These are solvated by CH$_2$Cl$_2$ but less strongly than is [PtCl$_2$(dppm)]. The dibromo-complex, a creamy white solid, loses CH$_2$Cl$_2$ at 100 °C *in vacuo* and the di-iodo-complex, a pale yellow solid, loses CH$_2$Cl$_2$ at room temperature *in vacuo*.

Complex (1a), [Pt$_2$Cl$_2$(dppm)$_2$].—In a typical reaction, [PtCl$_2$(dppm)] (2.35 g) was suspended in MeOH (40 cm^3) and a solution of Na[BH$_4$] (1 g) in MeOH (30 cm^3) was added over a period of 1 h. The yellow, impure, and uncharacterized Pt–H complex [ν(Pt–H) at 2 110 cm^{-1}] (2.0 g) was filtered off, washed with MeOH, and dried *in vacuo*. Concentrated HCl (3 cm^3) was added to a suspension of the Pt–H complex (2.0 g) in benzene (85 cm^3) and the mixture was heated under reflux for 5 min. The yellow solution thus formed was decanted from a small amount of brown residue and allowed to cool. On slow addition of iso-octane (30 cm^3), complex (1a) crystallized as a lemon-yellow benzene solvate, [{PtCl(dppm)}$_2$]·C$_6$H$_6$ (1.64 g, 70% overall yield). Attempts to remove the benzene of crystallization by pumping at 100 °C were unsuccessful and at higher temperatures decomposition of the complex occurred. The benzene solvate was pure provided the above reaction conditions were closely followed. Repeated crystallizations from CH$_2$Cl$_2$ gave samples of complex (1a) solvated with CH$_2$Cl$_2$ and all had identical i.r. spectra (and m.p.s) to the benzene solvate except for the presence of weak peaks attributed to solvent. Crystallizations were carried out at room temperature by the addition of iso-octane to nearly saturated (4—5%) solutions of the complex in CH$_2$Cl$_2$.

Complex (1b), [Pt$_2$Br$_2$(dppm)$_2$].—Complex (1a) (0.5 g) and [NEt$_4$]Br (1.0 g) in CH$_2$Cl$_2$ (24 cm^3) were allowed to react for 48 h. The [NEt$_4$]Cl formed, together with the excess of bromide, was removed by extraction with water. Following similar treatment with another sample of [NEt$_4$]Br (1.0 g), the bromo-complex (1b) was recrystallized rapidly from dichloromethane–iso-octane to give the CH$_2$Cl$_2$ solvate [{PtBr(dppm)}$_2$]·0.5CH$_2$Cl$_2$ (0.41 g, 76%) as yellow crystals.

Complex (1c), [Pt$_2$I$_2$(dppm)$_2$].—A suspension of complex (1a) (0.6 g) in a solution of NaI (1.0 g) in acetone (50 cm^3) was stirred for 48 h. The crude product (0.51 g), which was solvated with acetone (i.r. spectrum), was filtered off and washed with water, acetone, and diethyl ether. The

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[14] J. R. Durig, K. K. Lau, G. Nagarajan, M. Walker, and J. Bragin, *J. Chem. Phys.*, 1969, **50**, 2130.

[15] R. Okawara and Y. Matsumura, *Adv. Organometallic Chem.*, 1976, **14**, 187.

acetone of solvation was removed by dissolving the complex in CH_2Cl_2 (30 cm^3) and evaporating the solution to dryness in a stream of N_2. This was repeated twice and the crude product was finally recrystallized from dichloromethane–iso-octane and dried in *vacuo* to give the iodo-complex (1c), $[\{PtI(dppm)\}_2]\cdot 0.5CH_2Cl_2$, as orange-yellow crystals (0.44 g, 70%). Even though the complex (1c) was less stable in CH_2Cl_2 than (1b), recrystallization from this solvent was satisfactory provided contact with the solvent was brief (*ca.* 30 min or less).

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