Organoplatinum complexes containing bis(diphenylphosphino)amine as ligand: uncommon case of N–H · · · I–Pt hydrogen bonding

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Received 2nd January 2007, Accepted 20th February 2007
First published as an Advance Article on the web 15th March 2007
DOI: 10.1039/b700009j

The complex [$PtMe_2$(dppa)], **1a**, dppa = $Ph_2PNHPPh_2$, which has previously been prepared as a mixture with the dimeric form [Pt_2Me_4(μ-dppa)$_2$], was synthesized in pure form by the reaction of [$PtCl_2$(dppa)] with MeLi. The aryl analogue [Pt(*p*-MeC_6H_4)$_2$(dppa)], **1b**, was prepared by replacement of SMe_2 in *cis*-[Pt(*p*-MeC_6H_4)$_2$(SMe_2)$_2$] with dppa. The reaction of the chelate complexes **1** with one equiv. of dppa afforded the complexes [PtR_2(dppa-*P*)$_2$], R=Me, **2a** and R = *p*-MeC_6H_4 **2b**. The reaction of [PtR_2(dppa)], **1**, with neat MeI gave the organoplatinum(IV) complexes [PtR_2MeI(dppa)], R=Me, **5a** and R = *p*-MeC_6H_4, **5b**. The structure of **5a**, determined by X-ray crystallography, indicated that the complex undergoes self-assembly by intermolecular N–H · · · I–Pt hydrogen bonding. MeI was also double oxidatively added to organodiplatinum(II) complex *cis*,*cis*-[Me_2Pt(μ-SMe_2)(μ-dppa)$PtMe_2$], to give diorganoplatinum(IV) complex [Me_3Pt(μ-dppa)(μ-I)$_2PtMe_3$], **4**. The aryl analogue organodiplatinum(II) complex *cis*,*cis*-[(*p*-MeC_6H_4)$_2$Pt(μ-SMe_2)(μ-dppa)Pt(*p*-MeC_6H_4)$_2$], **3b**, was prepared by the reaction of *cis*-[Pt(*p*-MeC_6H_4)$_2$(SMe_2)$_2$] with half equiv. of dppa, but **3b** refused to react with MeI, probably because of the steric effects of the aryl ligands. The tetramethyl complex [$PtMe_4$(dppa)], **6**, was prepared either by reaction of **5a** with MeLi or by replacement of SMe_2 in [Pt_2Me_8(μ-SMe_2)$_2$] with dppa. All the complexes were fully characterized in solution by multinuclear NMR (^{1}H, ^{13}C, ^{31}P and ^{195}Pt) methods and their coordination compared with that of the corresponding known dppm complexes.

Introduction

In designing the molecular structures of coordination complexes suitable for special chemical and/or industrial studies, it is often necessary to use closely related ligands in order to finely tune the properties of the complexes. A popular ligand which has been widely used in making many organometallic and coordination complexes, is bis(diphenylphosphino)methane, dppm = $Ph_2PCH_2PPh_2$.[1] This versatile and robust ligand is normally known to act as a bridging ligand and as such many binuclear[2] and multinuclear[3] platinum complexes are reported, although there are cases in which it acts as a chelate or a monodentate ligand.[4] However, the closely related ligand bis(diphenylphosphino)amine, dppa = $Ph_2PNHPPh_2$, which might be used in conjunction with dppm for the above mentioned purpose, has not yet received the same scrutiny.[5] Although dppa and dppm seem to behave in a similar way in the formation of complexes, differences do also exist in their coordination behavior.[6,7] Besides, the NH proton of the coordinated dppa ligand has a greater acidity than the CH_2 protons of dppm and this would considerably affect, for example, N-functionalization reactions[8] and hydrogen bond formation in crystal engineering.[9]

In this study, several new organoplatinum complexes containing dppa are synthesized and characterized by multinuclear NMR studies and their structures and coordination behaviors are compared with those of the corresponding known dppm complexes. The structure of one of the platinum(IV) complexes, [$PtMe_3I$(dppa)], **5a**, has been determined by X-ray crystallography.

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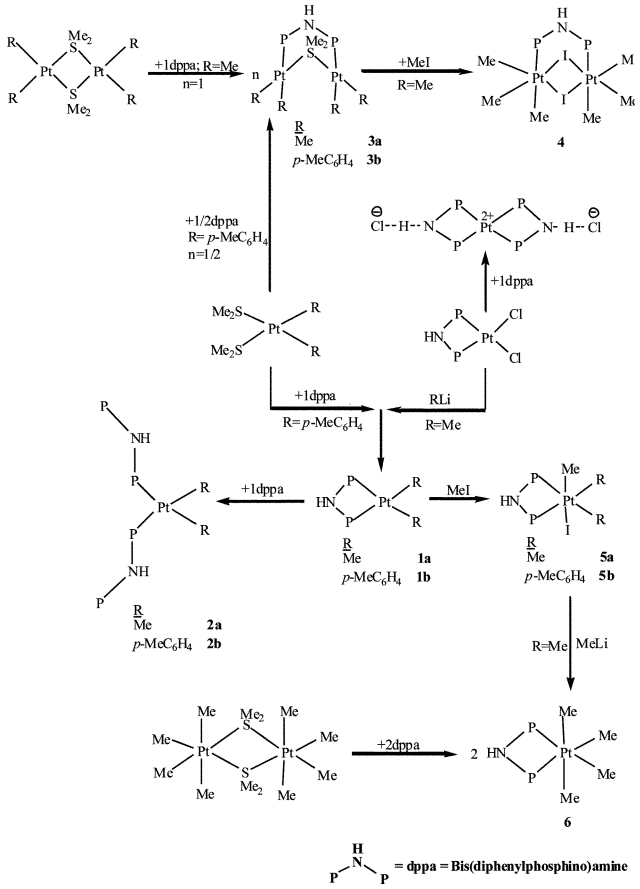
Results and discussion

The synthetic routes and the related chemistry studied in this work are described in Schemes 1 and 2. All the characterization data are collected in the Experimental.

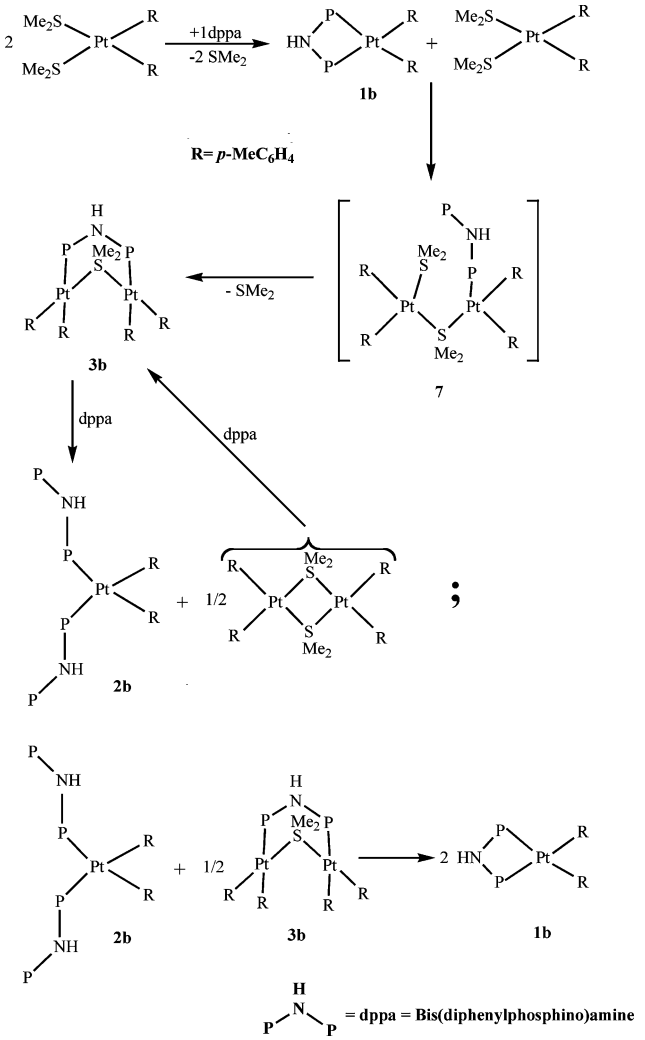
Synthesis and characterization of the organoplatinum(II) complexes

The starting complex [$PtCl_2$(dppa)] and the product of its reaction with one mole of dppa, *i.e.* [Pt(dppa)$_2$][Cl]$_2$, were prepared as reported elsewhere.[7,10] In the ^{1}H NMR spectrum of the latter cation in $CDCl_3$, we have observed a broad singlet at very low field (δ = 12.5) which as shown in Scheme 1, is suggested to be due to the formation of strong N · · · H · · · Cl^- hydrogen bonding.

The reaction of [$PtCl_2$(dppa)] with MeLi or the reaction of *cis*-[Pt(*p*-MeC_6H_4)$_2$(SMe_2)$_2$] with one equiv. of dppa was used to prepare the diorganoplatinum(II) complexes [$PtMe_2$(dppa)], **1a**, or [Pt(*p*-MeC_6H_4)$_2$(dppa)], **1b**, respectively. Note that complex **1a** has previously been prepared with difficulty by heating its mixture with the dimeric form [Pt_2Me_4(μ-dppa)$_2$].[6] The complex **1a** was characterized by its NMR data.[6] The observation of a singlet in the ^{31}P NMR spectrum of **1b** at δ = 30.6 accompanied by platinum satellites with ^1J(PtP) = 1463 Hz clearly confirms the dppa ligand being chelated with the coordinating phosphorus atoms being *trans* to aryl ligands having high *trans* influence. In the ^{1}H NMR



Scheme 1



Scheme 2

spectrum of **1b**, a rather broad singlet with platinum satellites at $\delta = 5.4$ with $^{3}J(\mathrm{PtH}) = 65$ Hz was assigned to the NH proton of dppa. The H^{m} resonance of the tolyl ligands appeared at 6.64 which coupled to H^{o} with $^{3}J(\mathrm{HH}) = 6.8$ Hz, while the H^{o} appeared at 7.18 as a multiplet (due to coupling to H^{m} as well as the phosphorus atom) which then coupled to platinum with $^{3}J(\mathrm{PtH}) = 53$ Hz.

The reaction of $[PtR_2(dppa)]$, **1**, with one equiv. of dppa gave the complexes $[PtR_2(dppa\text{-}P)_2]$, **2**, separated at room temperature in pure form and good yield. In the ^{31}P NMR spectrum of $[Pt(p\text{-}MeC_6H_4)_2(dppa\text{-}P)_2]$, **2b** (see Fig. 1A), the co-ordinated phosphorus atoms (indicated as P^b as compared to P^a which is the unco-ordinated phosphorus atom) appeared as a doublet at $\delta = 52.2$ with $^{1}J(\mathrm{PtP^b}) = 2062$ Hz and $^{2}J(\mathrm{P^bP^a}) = 17$ Hz. P^a atoms however appeared shifted to a higher field as a doublet at $\delta = 25.2$ with $^{2}J(\mathrm{PtP^a})$ approximately 74 Hz and $^{2}J(\mathrm{P^bP^a}) = 17$ Hz. In the ^{1}H NMR spectrum of **2b**, the NH protons appeared as a doublet of doublets at $\delta = 3.9$ with $^{2}J(\mathrm{PH}) = 7.5$ and 5.0 Hz. In the ^{31}P NMR spectrum of $[PtMe_2(dppa\text{-}P)_2]$, **2a**, a 2 : 1 mixture of two isomers was observed at $\delta = 64.2$ (P^b); 30.8 (P^a) and $\delta = 64$ (P^b); 31.3 (P^a) (see Experimental for details) each showing an AA′XX′ pattern.[4b] In accord with this, in the ^{1}H NMR spectrum of **2a**, two doublet of doublets at $\delta = 3.38$ and 4.86 were observed for the NH protons of the two isomers. The observation of two isomers in the case of complex **2a**, where R=Me, is probably due to the relative positions of the two dppa ligands, something that is not happening in the related aryl complex **2b**, most likely due to the steric restriction created by the aryl ligands. In contrast, for the analogous dppm complexes $[Pt(p\text{-}MeC_6H_4)_2(dppm\text{-}P)_2]$ and $[PtMe_2(dppm\text{-}P)_2]$, it has been reported that they dissociate extremely rapidly in solution and only the latter complex could be isolated and characterized at low temperatures; the related complexes with *ortho*-substituted aryl ligands, *e.g.* $o\text{-}MeC_6H_4$, however were readily isolated at room temperature.[4b] Also, the dppm complexes $[PtR_2(dppm\text{-}P)_2]$ have been widely used to systematically synthesize the homo-bimetallic complexes such as $[Me_2Pt(\mu\text{-}dppm)_2Pt(o\text{-}tolyl)_2]$[12a] and hetero-bimetallic complexes containing the $Pt(\mu\text{-}dppm)_2M$ moiety, M being different transition metals such as Ag, Au, Rh, Ir, Mo and W.[12] However, our similar attempts using the dppa analogues $[PtR_2(dppa\text{-}P)_2]$, **2**, have led to the formation of the chelate complexes $[PtR_2(dppa)]$, **1**.

The binuclear dimethylplatinum(II) complex **3a**, as described in Scheme 1, has been reported previously.[6] The new bis-tolyl analogue *cis*,*cis*-$[(p\text{-}MeC_6H_4)_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppa)Pt(p\text{-}MeC_6H_4)_2]$, **3b**, was prepared by the reaction of *cis*-$[Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2]$ with 1/2 equiv. of dppa in high yield. The course of the reaction was monitored by ^{1}H NMR spectroscopy and as described in Scheme 2, an equivalent mixture of the chelating complex $[Pt(p\text{-}MeC_6H_4)_2(dppa)]$, **1b**, and the starting complex *cis*-$[Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2]$ was first formed which then reacted

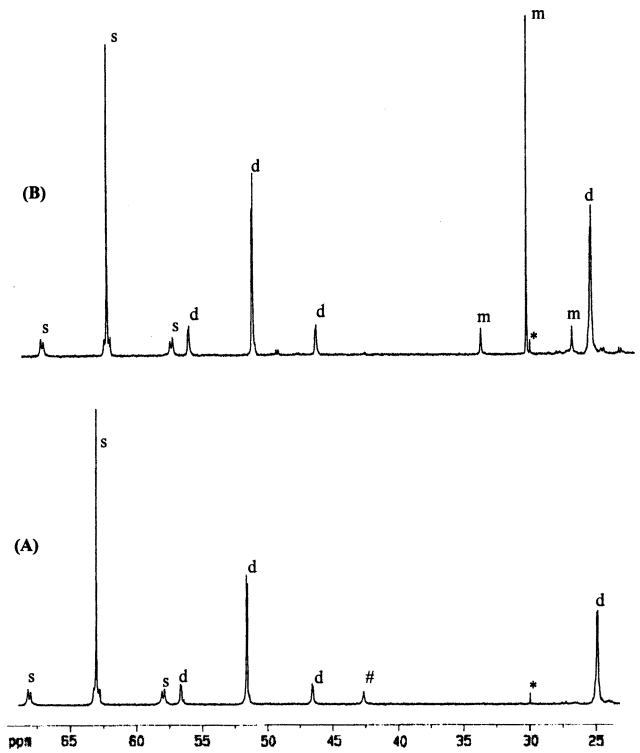


Fig. 1 The ^{31}P NMR spectra of the reaction of *cis*,*cis*-[(*p*-$MeC_6H_4)_2$-Pt(μ-SMe_2)(μ-dppa)Pt(*p*-$MeC_6H_4)_2$], **3b** (shown by s), with 1 equiv. of dppa after (A) 5 min and (B) 2 h. The complex [Pt(*p*-$MeC_6H_4)_2$(dppa-*P*)$_2$], **2b** (shown by d), is formed very fast, and the final monomeric complex [Pt(*p*-$MeC_6H_4)_2$(dppa)], **1b** (shown by m) is then gradually formed. The reaction was completed after 10 h. The small amount of free dppa in (A) is indicated by #. Trace impurity is shown by the asterisks.

to form the final dimeric product **3b**, probably *via* the presumed intermediate **7**. In the ^{31}P NMR spectrum of **3b**, the two equivalent phosphorus atoms resonated as a singlet at $\delta = 63.8$ and showed platinum satellites. When one platinum atom is ^{195}Pt, the two phosphorus atoms are no longer equivalent and appeared as two sets of satellites, one set is due to the short range coupling with ^1J(PtP) = 2067 Hz and the other set due to long range coupling with ^3J(PtP) = 33 Hz. The splitting in the satellites corresponds to a ^2J(PP) value of 47 Hz. Consistently, in the ^{195}Pt NMR spectrum of **3b**, a doublet of doublets was observed at $\delta = -4256$ with ^1J(PtP) = 2097 Hz and ^3J(PtP) = 33 Hz, very close to the coupling values obtained from the corresponding ^{31}P spectrum. In the ^{1}H NMR spectrum of **3b**, the Me groups of SMe_2 ligand appeared as a multiplet at $\delta = 1.5$ with ^3J(PtH) = 23.5 Hz, and two singlets at $\delta = 1.9$ and 2.0 were assigned to the two different Me groups on the tolyl ligands. A broad peak at $\delta = 2.6$ was observed for the NH proton of the dppa ligand.

The reaction of the latter complex **3b** with one equiv. of dppa is interesting and was monitored by ^{1}H and ^{31}P NMR spectroscopy. The ^{31}P NMR spectra of the reaction after 5 min and after 2 h are shown in Fig. 1. As described in Scheme 2, the complex [Pt(*p*-$MeC_6H_4)_2$(dppa-*P*)$_2$], **2b**, and the diplatinum(II) complex [(*p*-$MeC_6H_4)_2$Pt(μ-$SMe_2)_2$Pt(*p*-$MeC_6H_4)_2$] are first formed; the latter dimer has of course very rapidly reacted with dppa to give back the starting dimer **3b**. Subsequently, the complex **2b**, slowly reacted with **3b** to form the final chelate product [Pt(*p*-$MeC_6H_4)_2$(dppa)], **1b**. The conversion of **3b** to **1b** was completed after 10 h, while the conversion of the related dppm dimer *cis*,*cis*-[Ph_2Pt(μ-SMe_2)(μ-dppm)$PtPh_2$] to the monomeric product [$PtPh_2$(dppm)] was completed after more than 30 h.[2b] We believe that the dppm conversion takes place with a similar mechanism as described here for the dppa complex and the faster rate of the dppa reaction is probably due to the fact that the dppa intermediate **2b** is far more stable than the presumed dppm intermediate [Pt(*p*-$MeC_6H_4)_2$(dppm-*P*)$_2$], which is hard to form and is not observable at room temperature.[2b]

Synthesis and characterization of the organoplatinum(IV) complexes

The oxidative addition of MeI to the monomeric complexes [PtR_2(dppa)], **1**, gave the platinum(IV) complexes [PtR_2MeI-(dppa)], **5**, as described in Scheme 1.

In the ^{31}P NMR spectrum of [Pt(*p*-$MeC_6H_4)_2$MeI(dppa)], **5b**, a singlet at $\delta = 2.6$ with ^1J(PtP) = 964 Hz, typical of phosphorus ligands *trans* to aryl ligands in platinum(IV) complexes, was observed. The observation of only one singlet confirms the existence of only one isomer in which Me and I ligands are in *trans* positions with respect to each other. In line with this, in the ^{1}H NMR spectrum of **5b**, a signal at 1.39 was observed for the Me ligand *trans* to I which is a triplet due to coupling with two equivalent phosphorus atoms with ^3J(PH) = 7.8 Hz; the Pt satellites gave ^2J(PtH) = 67.7 Hz. A broad peak at 5.66 with ^3J(PtH) = 46.6 Hz, was assigned to the NH proton of dppa. The H^m of the tolyl ligands appeared at 6.65 which coupled to H^o with ^3J(HH) = 6.2 Hz, while the H^o appeared at 7.17 as a multiplet (due to coupling to H^m as well as the phosphorus atom) which then coupled to platinum with ^3J(PtH) = 42 Hz. Note that, as expected, the coupling constants of H^o protons or the NH proton of dppa with platinum atoms in the platinum(IV) complex **5b** have considerably reduced as compared to the values in the corresponding platinum(II) complex **1b**. Thus, ^3J(PtH) values for NH protons have reduced from 65 to 46.6 Hz and ^3J(PtH) values for H^o protons have reduced from 53 to 42 Hz.

For the methyl analogue [$PtMe_3$I(dppa)], **5a**, in the ^{31}P NMR spectrum, a singlet at $\delta = 10.5$ with ^1J(PtP) = 927 Hz, typical of the coupling values obtained for organoplatinum(IV) complexes with phosphorus atoms being *trans* to C, was observed. In the ^{1}H NMR spectrum of the complex, the Me ligand *trans* to I appeared at $\delta = 0.74$ as a triplet due to coupling with two equivalent *cis* phosphorus atoms with ^3J(PH) = 8.1 Hz, which further coupled to platinum with ^2J(PtH) = 70.0 Hz. The two Me ligands *trans* to P were observed as a multiplet at $\delta = 1.26$ with a considerably lower ^2J(PtH) = 63.0 Hz, and the triplet at $\delta = 5.67$ with ^2J(PH) = 3.7 Hz and ^3J(PtH) = 42.0 Hz was assigned to the NH proton of dppa.

It is interesting to note that the latter complex [$PtMe_3$I(dppa)], **5a**, was obtained in pure form when the reaction of [$PtMe_2$(dppa)], **1a**, with neat MeI was performed for at least 2 h. However, for shorter reaction times, a second species was formed as a mixture with **5a**. This new species has ^{31}P and ^{1}H NMR patterns very similar to those of **5a** with almost identical coupling values, but each peak appeared at a slightly lower chemical shift compared to the corresponding one obtained for **5a** (see Experimental for details). The ^{31}P NMR spectrum of the products of the reaction

of [$PtMe_2$(dppa)], **1a**, with neat MeI after 15 min and after work-up, is shown in Fig. 2. Thus, the new second species is formed along with the first one and then gradually converted to the final product which is the first species, called **5a**. We tentatively assign this observation to be due to some kind of change in the degree of aggregation of the molecules of [$PtMe_3I$(dppa)], **5a**, *via* the formation of intermolecular hydrogen bonding of type N–H · · · I–Pt; the crystal structure of **5a** (*vide infra*) indicated intermolecular hydrogen bonding of this type in crystal state. Complex **5a** can either exist in monomeric or oligomeric form in solution although the formation of two intermolecular hydrogen bonds to give a dimeric form of the type shown in Scheme 3 is also a possibility.[13]

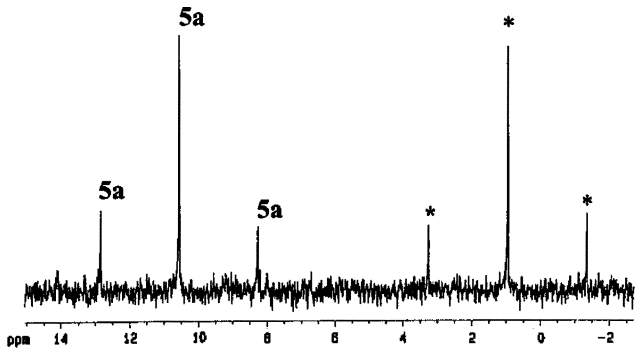
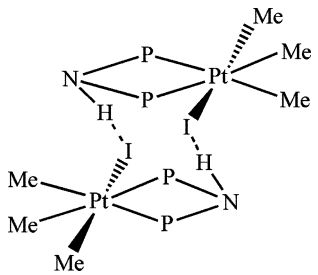


Fig. 2 ^{31}P NMR spectrum of the products of reaction of [$PtMe_2$(dppa)], **1a**, with neat MeI after 15 min and after work-up. The second species is shown by asterisks; it disappeared when the reaction time was at least 2 h.



Scheme 3

The structure of complex [$PtMe_3I$(dppa)], **5a**, was determined by X-ray crystallography and is shown in Fig. 3, with the selected bond distances and angles in Table 1. The complex contains an octahedral platinum(IV) centre with 3 methylplatinum groups, a chelating dppa ligand, and an iodide ligand. Due to the presence of the 4-membered PtPNP ring, considerable distortions are expected for the four angles involved in the dppa chelate unit. Thus, P(1)Pt(1)P(2) = 68.93(5)° is much less than the ideal angle of 90°, P(1)N(1)P(2) = 105.8(3)° is significantly less than in the free ligand [118.9(2)°], and the angles NPPt = 92.63(16)° or 92.51(16)° are less than the tetrahedral angle. The formation of intermolecular

Table 1 Selected bond distances (Å) and angles (°) for complex [$PtMe_3I$(dppa)], **5a**

Pt(1)–C(2)	2.091(5)	Pt(1)–P(2)	2.383(2)
Pt(1)–C(1)	2.094(5)	Pt(1)–I(1)	2.7813(4)
Pt(1)–C(3)	2.095(5)	P(1)–N(1)	1.689(5)
Pt(1)–P(1)	2.380(2)	P(2)–N(1)	1.690(4)
C(2)–Pt(1)–C(1)	85.5(2)	P(1)–Pt(1)–P(2)	68.93(5)
C(2)–Pt(1)–C(3)	86.6(2)	C(2)–Pt(1)–I(1)	174.6(2)
C(1)–Pt(1)–C(3)	87.1(2)	C(1)–Pt(1)–I(1)	91.4(2)
C(2)–Pt(1)–P(1)	91.2(2)	C(3)–Pt(1)–I(1)	88.9(2)
C(1)–Pt(1)–P(1)	169.6(2)	P(1)–Pt(1)–I(1)	92.65(3)
C(3)–Pt(1)–P(1)	102.5(2)	P(2)–Pt(1)–I(1)	95.25(3)
C(2)–Pt(1)–P(2)	89.7(2)	N(1)–P(1)–Pt(1)	92.6(2)
C(1)–Pt(1)–P(2)	101.2(2)	N(1)–P(2)–Pt(1)	92.5(2)
C(3)–Pt(1)–P(2)	170.6(2)	P(1)–N(1)–P(2)	105.8(3)

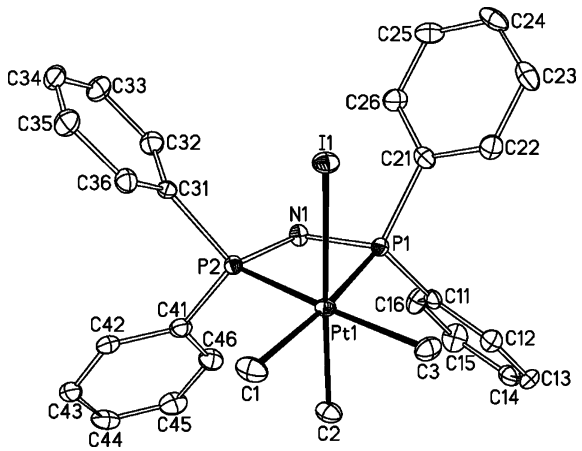


Fig. 3 Molecular structure of complex [$PtMe_3I$(dppa)], **5a** (50% probability ellipsoids, H atoms and solvent molecules omitted for clarity).

hydrogen bonding of type N–H · · · I–Pt [N(1) · · · I(1)#1 = 3.756(5) Å, N(1)H(1)I(1)#1 = 167.4°], as is described in Table 2, has caused the self-assembling of the molecules of complex **5a**. The normalized distance, R_{HI},[14–16] calculated for this hydrogen bond is 0.915 Å, which is in the hydrogen bonding viability range, established by Brammer *et al.* for the N–H · · · I–M donor–acceptor combination.[14] The observed H · · · I–M angle for complex **5a** is 119.9° which is in the preferred range of 90–130° established by Brammer *et al.* based on their analysis of N–H · · · I–M systems.[14] Note also that Rheingold *et al.*[18] in their study of angular preference in M–Cl · · · H–N hydrogen bonding, suggested that an H · · · Cl–M angle close to 90° is preferred and ascribed the observed angles of >90° to steric hindrance created by the group attached to Cl. These are explained as probably due to higher basicity of the p-type X lone pair relative to the sp lone pair.[14,18]

MeI performed double oxidative addition to the dimeric organoplatinum(II) complex *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-}$dppa)-$PtMe_2$], **3a**, to give the diplatinum(IV) complex [$Me_3Pt(\mu\text{-}$dppa)($\mu\text{-}I)_2PtMe_3$], **4**, as is described in Scheme 1. In the ^{31}P NMR spectrum

Table 2 Hydrogen bonds for complex [$PtMe_3I$(dppa)], **5a**

D–H · · · A	d(D–H)/Å	d(H · · · A)/Å	d(D · · · A)/Å	∠DHA/°
N(1)–H(1) · · · I(1)[a]	0.88	2.89	3.756(5)	167.4

[a] $-x + 3/2, y + 1/2, -z + 1/2$.

of **4**, the two equivalent phosphorus atoms resonated as a singlet at $\delta = 36.8$ with the short range platinum satellites with $^1J(PtP) = 1181$ Hz, while the long range coupling $^3J(PtP)$ was not resolved. The splitting in the satellites corresponds to a $^2J(PP)$ value of 4.6 Hz. Consistently, in the ^{195}Pt NMR spectrum of **4**, a doublet was observed at $\delta = -3744$ with $^1J(PtP) = 1209$ Hz, close to the value obtained from the corresponding ^{31}P spectrum. In the ^{1}H NMR spectrum of **4**, a doublet at $\delta = 0.72$ with $^3J(PH) = 7.7$ Hz and $^2J(PtH) = 74.4$ Hz was assigned to the two equivalent Me ligands *trans* to I, while the Me ligand *trans* to the phosphorus atom was located at $\delta = 1.83$ as a doublet with $^3J(PH) = 8.1$ Hz and $^2J(PtH) = 59.4$ Hz. A broad peak at $\delta = 4.0$ was observed for the NH proton of the dppa ligand. The ^{13}C NMR spectrum of **4** was also useful and gave a doublet at $\delta = 9.7$ for the Me groups *trans* to phosphorus with $^2J(CP) = 133$ Hz, with coupling to platinum with $^1J(CPt) = 507$ Hz. The two equivalent Me groups *trans* to I did not give resolvable phosphorus couplings and appeared as a singlet at $\delta = 12.3$ with a higher value of $^1J(CPt) = 652$ Hz.

The tetramethylplatinum(IV) complex [$PtMe_4$(dppa)], **6**, as is described in Scheme 1, was prepared either by the replacement of SMe_2 with dppa in [$Pt_2Me_8(\mu\text{-}SMe_2)_2$] or by the reaction of [$PtMe_3$I(dppa)], **5a**, with MeLi. In the ^{31}P NMR spectrum of **6**, a singlet at $\delta = 1.1$ with $^1J(PtP) = 979$ Hz was observed for the two equivalent phosphorus atoms. In the ^{1}H NMR spectrum of **6**, a triplet at $\delta = -0.14$ with $^3J(PH) = 6.9$ Hz accompanied by platinum satellite with $^2J(PtH) = 45.2$ Hz was assigned to the two equivalent Me ligands *trans* to each other and equivalently *cis* to two phosphorus atoms. The unusually low value of $^2J(PtH)$ is consistent with the very high *trans* influence of the Me ligand. The Me ligands *trans* to phosphorus atoms were located at $\delta = 0.82$ as a multiplet with platinum satellites with $^2J(PtH) = 63.9$ Hz and $^3J(PH) + {}^3J(P'H) = 7.5$ Hz. The NH proton of dppa appeared as a broad signal at $\delta = 5.67$ which coupled with platinum with $^3J(PtH) = 52.5$ Hz. The ^{13}C NMR spectrum of **6** is also very informative and gave a triplet at $\delta = -5.7$ for the Me groups *trans* to each other and *cis* to two equivalent phosphorus atoms with $^2J(CP) = 4$ Hz, with coupling to platinum with a considerably lower $^1J(CPt)$ value of 398 Hz due to the very high *trans* influence of the Me ligand. The Me ligands *trans* to phosphorus ligands appeared at $\delta = 0.4$ as a doublet of doublets with $^2J(CP_{cis}) = 3$ Hz and $^2J(CP_{trans}) = 131$ Hz with coupling to platinum with $^1J(CPt) = 567$ Hz. The PtC coupling values for complex **6** are almost identical to the values obtained for the dppm analogue complex [$PtMe_4$(dppm)],[19] which indicate that dppa and dppm have probably exerted the same *trans* influence. However, based on the above ^{31}P NMR data, the $^1J(PtP)$ value of 979 Hz for complex **6** is nearly 5% higher than the corresponding value of $^1J(PtP) = 936$ Hz for the dppm analogue complex [$PtMe_4$(dppm)].[19] The difference, although modest, confirms that in the dppa analogue the four-membered chelate ring experiences less strain.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer. ^{31}P and ^{195}Pt NMR spectra were recorded on a Bruker Avance DRX 500 MHz. References were TMS (^{1}H and ^{13}C), H_3PO_4 (^{31}P), and aqueous K_2PtCl_4 (^{195}Pt), and $CDCl_3$ was used as solvent in all cases. All chemical shifts and coupling constants are in ppm and Hz, respectively.

The complexes, *cis*-[Pt(*p*-$MeC_6H_4)_2(SMe_2)_2$],[23] *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$],[24] *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)$(μ-dppa)$PtMe_2$], **3a**,[6] [$PtCl_2$(dppa)],[7] [Pt(dppa)$_2$][Cl]$_2$[7] and [$Pt_2Me_8(\mu\text{-}SMe_2)_2$],[25] were prepared by methods described in the literature.

[$PtMe_2$(dppa)], 1a

A solution of MeLi (10 ml) was slowly added to a stirred ice-cold solution of [$PtCl_2$(dppa)] (335 mg; 0.514 mmol) in dry ether (40 ml) under Ar atmosphere. The reaction mixture was stirred for 2 h and then hydrolyzed with water (4 ml). Separation of the organic layer, extraction with CH_2Cl_2, drying over $MgSO_4$ and evaporation of the organic solvents gave an off-white powder which was washed with ether (5 ml) and the product was dried under vacuum. Yield: 86%; mp 175 °C (decomp.). Anal. Calcd. for $C_{26}H_{27}NP_2Pt$: C, 51.2; H, 4.5; N, 2.3. Found: C, 51.3; H, 4.6; N, 2.2%. NMR in $CDCl_3$: δ (^{1}H) = 0.61 [m, $^3J(PtH) = 74.7$ Hz, 6H, 2 Me ligands], 5.28 [t, $^3J(PtH) = 62.3$ Hz, $^2J(PH) = 9.0$ Hz, 1H, NH of dppa].

[Pt(*p*-$MeC_6H_4)_2$(dppa)], 1b

A mixture of *cis*-[Pt(*p*-$MeC_6H_4)_2(SMe_2)_2$] (200 mg; 0.398 mmol) and dppa (153.6 mg; 0.398 mmol) in dry benzene (30 ml) was stirred at room temperature for 2 h. The solvent was removed and the product was washed with *n*-hexane (2 ml) and then ether (2 ml) and dried under vacuum. Yield: 92%; mp 200 °C (decomp.). Anal. Calcd. for $C_{38}H_{35}NP_2Pt$: C, 59.8; H, 4.6. Found: C, 60.6; H, 4.7%. NMR in $CDCl_3$: δ (^{1}H) = 2.18 [s, 6H, 2 Me groups on the tolyl ligands], 5.4 [br., $^3J(PtH) = 65$ Hz, $^2J(PH) =$ not resolved, 1H, NH], 6.64 [d, $^3J(HH) = 6.8$ Hz, 4 H^m of tolyl ligands], 7.18 [m, $^3J(PtH) = 53$ Hz, 4 H^o of tolyl ligands]; $\delta(^{31}P) = 30.6$ [s, $^1J(PtP) = 1463$ Hz].

[$PtMe_2$(dppa-*P*)$_2$], 2a

A mixture of [$PtMe_2$(dppa)], **1a**, (30 mg, 0.049 mmol) and dppa (18.9 mg, 0.049 mmol) in dry benzene (10 ml) was stirred at room temperature for 10 min. The solvent was removed and the residue was washed with n-hexane (2 × 2 ml) and dried under vacuum. Yield: 88%. Anal. Calcd. for $C_{50}H_{48}N_2P_4Pt$; C, 60.3; H, 4.9; N, 2.8; Found: C, 60.3; H, 4.9: N, 2.7%. ^{1}H NMR data in C_6D_6: δ 0.7–1.1 (overlapping multiplets, Me ligands), 4.86 [dd, $^2J(P^bH) = 7.5$ Hz; $^2J(P^aH) = 14.8$ Hz, NH of minor isomer], 3.84 [dd, $^2J(P^bH) = 7.3$ Hz; $^2J(P^aH) = 13.0$ Hz, NH of major isomer]; ^{31}P NMR in C_6D_6: major isomer: $\delta = 64.2$[m, $^1J(PtP^b) = 2064$ Hz, P^b], 30.8 [m, $^3J(PtP^a) = 43$ Hz, N = $^2J(P^bP^a) + {}^4J(P^bP^a) = 19$ Hz, P^a]; minor isomer: $\delta =$ P^b overlapped under P^b of major isomer], 31.3 [m, $^3J(PtP^a) = 29$ Hz, N = $^2J(P^bP^a) + {}^4J(P^bP^a) = 14$ Hz P^a].

[Pt(*p*-$MeC_6H_4)_2$(dppa-*P*)$_2$], 2b

A mixture of [Pt(*p*-$MeC_6H_4)_2$(dppa)], **1b**, (100 mg; 0.131 mmol) and dppa (50.5 mg; 0.131 mmol) in dry benzene (30 ml) was stirred at room temperature for 3 h. The solvent was removed and the product was washed with *n*-hexane (2 × 3 ml) and then dried under vacuum. Yield: 51%, mp 146 °C (decomp.). Anal. Calcd. for $C_{62}H_{56}N_2P_4Pt$: C, 64.9; H, 4.9. Found: C, 65.0; H, 5.0%. NMR in $CDCl_3$: δ (^{1}H) = 2.0 [s, 6H, 2 Me groups on the tolyl ligands], 3.9 [dd, $^2J(PH) = 7.5$ and 5.0 Hz, 2H, NH groups of the 2 dppa

ligands]; $\delta(^{31}P) = 25.2$ [d, $^{3}J(PtP^{a}) = 74$ Hz, $^{2}J(P^{b}P^{a}) = 17$ Hz, 2 P^{a}], 52.2 [d, $^{1}J(PtP^{b}) = 2062$ Hz, $^{2}J(P^{b}P^{a}) = 17$ Hz, 2 P^{b}.

cis,*cis*-[(*p*-$MeC_6H_4)_2Pt(\mu$-$SMe_2)(\mu$-dppa)Pt(*p*-$MeC_6H_4)_2$], 3b

A mixture of *cis*-[$Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2$] (200 mg; 0.398 mmol) and dppa (76.8 mg; 0.199 mmol) in dry benzene (30 ml) was stirred at room temperature for 2 h. The solvent was removed and the product was washed with n-hexane (5 ml) and then methanol (3 ml) and dried under vacuum. Yield: 62%; mp 115 °C (decomp.). Anal. Calcd. for $C_{54}H_{55}NP_2SPt_2$: C, 54.0; H, 4.6; N, 1.2. Found: C, 54.1; H, 4.7; N, 1.2%. NMR in $CDCl_3$: δ (^{1}H) = 1.5[m, $^{3}J(PtH) =$ 23.5 Hz, 6H, 2 Me groups of SMe_2 ligand], 1.9 and 2.0 [s, 2 Me groups on the tolyl ligands], 2.6 [br, $^{3}J(PtH)$ and $^{2}J(PH) =$ not resolved, 1H, NH of dppa]; $\delta(^{31}P) = 63.8$ [s, $^{1}J(PtP) = 2067$ Hz, $^{3}J(PtP) = 33$ Hz, $^{2}J(PP) = 47$ Hz, dppa]; $\delta(^{195}Pt) = -4256$ [dd, $^{1}J(PtP) = 2097$ Hz, $^{3}J(PtP) = 33$ Hz].

Reaction of *cis*-[$Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2$] with dppa in NMR tube

A small sample (20 mg, 0.039 mmol) of *cis*-[$Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2$], was dissolved in $CDCl_3$ in a sealed NMR tube, and dppa (7.68 mg, 0.0195 mmol) was added. The reaction was followed by ^{1}H NMR spectroscopy.

Reaction of *cis*,*cis*-[(*p*-$MeC_6H_4)_2Pt(\mu$-$SMe_2)(\mu$-dppa)Pt(*p*-$MeC_6H_4)_2$], 3b, with dppa in an NMR tube

A small sample (20 mg, 0.016 mmol) of *cis*, *cis*-[$(p\text{-}MeC_6H_4)_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppa)Pt(p\text{-}MeC_6H_4)_2$], **3b**, was dissolved in $CDCl_3$ in a sealed NMR tube, and dppa (6.41 mg, 0.016 mmol) was added. The reaction was followed by ^{1}H and ^{31}P NMR spectroscopy.

Reaction of [$Pt(p\text{-}MeC_6H_4)_2$(dppa-*P*)$_2$], 2b, with *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$]

A mixture of [$Pt(p\text{-}MeC_6H_4)_2$(dppa-*P*)$_2$] (200 mg, 0.174 mmol) and *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] (50 mg, 0.087 mmol) in dry benzene (30 ml) was stirred at room temperature for 1 h. The solvent was removed and the product was washed with *n*-hexane (3 ml) and dried under vacuum.

[$Me_3Pt(\mu$-dppa)$(\mu$-I$)_2PtMe_3$], 4

To a solution of [$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppa)PtMe_2$], **3a**, (70 mg, 0.078) mmol) in benzene (10 ml) at 0 °C, was added excess MeI (2 ml) and the reaction mixture was stirred for 3 h. The solvent and excess MeI was removed and the residue was washed twice with methanol (2 ml) to give the product as a white solid which was dried under vacuum. Yield: 50%; mp 215–220 °C (decomp.). Anal. Calcd. for $C_{30}H_{39}I_2NP_2Pt_2 \cdot 0.3C_6H_6$: C, 33.4; H, 3.6; N, 1.2. Found: C, 33.4; H, 3.8; N, 1.0%. NMR in $CDCl_3$: δ (^{1}H) = 0.72 [d, $^{3}J(PH) = 7.7$ Hz, $^{2}J(PtH) = 74.4$ Hz, 6H, Me ligands *trans* to I], 1.83 [d, $^{3}J(PH) = 8.1$ Hz, $^{2}J(PtH) = 59.4$ Hz, 3H, Me ligand *trans* to phosphorus], 4.0 [br, 1H, NH proton of dppa ligand]; $\delta(^{31}P) =$ 36.8 [s, $^{1}J(PtP) = 1181$ Hz, $^{3}J(PtP) =$ not resolved, $^{2}J(PP) =$ 4.6 Hz, dppa]; $\delta(^{195}Pt) = -3744$ [d, 1J(PtP) = 1209 Hz]; $\delta(^{13}C) =$ 9.7 [d, $^{2}J(CP) = 133$ Hz, $^{1}J(CPt) = 507$ Hz, Me groups *trans* to phosphorus], 12.3 [s, $^{1}J(CPt) = 652$ Hz, Me groups *trans* to I].

[$PtMe_3$I(dppa)], 5a

The complex [$PtMe_2$(dppa)], **1a**, (100 mg), in neat MeI was stirred for 2 h. The solvent was removed and the residue was washed with *n*-hexane (2 × 2 ml) and dried under vacuum. Yield: 73% (90 mg); m.p 165° C (dec.). Anal. Calcd. for $C_{27}H_{30}INP_2Pt$; C, 43.1; H, 4.0; N, 1.9; Found: C, 44.2; H, 4.2: N, 1.9%. NMR in $CDCl_3$: $\delta(^{1}H) =$ 0.74 [t, $^{2}J(PtH) = 70.0$ Hz, $^{3}J(PH) = 8.1$ Hz, 3H, Me ligand *trans* to I], 1.50 [m, $^{2}J(PtH) = 63.0$ Hz, 6H, 2 Me ligands *trans* to P], 5.67 [t, $^{3}J(PtH) = 42.0$ Hz, $^{2}J(PH) = 3.7$ Hz, 1H, NH of dppa]; $\delta(^{31}P) = 10.5$ [s, $^{1}J(PtP) = 927$ Hz, dppa].

When the reaction time was 15 min, the above complex **5a** was accompanied by a second species with the NMR data in $CDCl_3$: δ (^{1}H) = 0.44 [t, $^{2}J(PtH) = 73.0$ Hz, $^{3}J(PH) = 8.2$ Hz, 3H, Me ligand *trans* to I], 1.26 [m, $^{2}J(PtH) = 62.0$ Hz, $^{3}J(PH) + {}^{3}J(P'H) =$ 12.5 Hz, 6H, 2 Me ligands *trans* to P], 5.51 [t, $^{3}J(PtH) = 40.3$ Hz, $^{2}J(PH) = 3.7$ Hz, 1H, NH of dppa]; $\delta(^{31}P) = 1.0$ [s, $^{1}J(PtP) =$ 933 Hz, dppa].

[$Pt(p\text{-}MeC_6H_4)_2$MeI(dppa)], 5b

The complex [$Pt(p\text{-}MeC_6H_4)_2$(dppa)], **1b**, (100 mg) in neat MeI was stirred for 8 h. The solvent was removed and the residue was washed with dry ether (2 × 2 ml) and dried under vacuum. Yield: 71% (85 mg); mp 231 °C (dec). Anal. Calcd. For $C_{39}H_{38}INP_2Pt$; C, 51.8; H, 4.2; N, 1.5; Found: C, 51.9; H, 4.5: N, 1.6%. NMR in $CDCl_3$: δ (^{1}H) = 1.39 [t, $^{2}J(PtH) = 67.7$ Hz, $^{3}J(PH) = 7.8$ Hz, 3H, Me ligand *trans* to I], 2.09 [s, 6H, 2 Me groups on the tolyl ligands], 5.66 [br, $^{3}J(PtH) = 46.6$ Hz, 1H, NH of dppa], 6.65 [d, $^{3}J(HH) = 6.2$ Hz, 4 H^{m} of tolyl ligands], 7.17 [m, $^{3}J(PtH) = 42$ Hz, 4 H^{o} of tolyl ligands]; $\delta(^{31}P) = 2.6$ [s, $^{1}J(PtP) = 964$ Hz, dppa].

[$PtMe_4$(dppa)], 6

(i) A mixture of [$Pt_2Me_8(\mu\text{-}SMe_2)_2$] (127 mg, 0.2 mmol) and dppa (154 mg, 0.4 mmol) in dry ether (30 ml) was stirred at room temperature. After 6 h a colorless solid precipitated. The precipitate was isolated by filtration, washed with ether (2 ml), and dried under vacuum. Yield: 78% (200 mg); mp 140 °C (dec.). Anal. Calcd. for $C_{28}H_{33}NP_2Pt$; C, 52.5; H, 5.2; N, 2.2; Found: C, 52.0; H, 5.3: N, 1.8%. NMR in $CDCl_3$: δ (^{1}H) = −0.14 [t, $^{2}J(PtH) = 45.2$ Hz, $^{3}J(PH) = 6.9$ Hz, 6H, Me ligands *trans* to Me], 0.82 [m, $^{2}J(PtH) = 63.9$ Hz, $^{3}J(PH) + {}^{3}J(P'H) = 7.5$ Hz, 6H, Me ligands *trans* to phosphorus], 5.67[br, $^{3}J(PtH) = 52.5$ Hz, 1H, NH of dppa]. $\delta(^{31}P) = \delta$ 1.1 [s, ^{1}J (PtP) = 979 Hz, dppa]. $\delta(^{13}C) =$ −5.7 [t, $^{1}J(CPt) = 398$ Hz, $^{2}J(CP) = 4$ Hz, 2C *trans* to C], 0.4 [dd, $^{1}J(CPt) = 567$ Hz, $^{2}J(CP_{cis}) = 3$ Hz, $^{2}J(CP_{trans}) = 131$, 2C *trans* to P].

(ii) MeLi (6 ml) was added slowly to a suspension of [$PtMe_3$I(dppa)] (0.5 g, 0.66 mmol) in anhydrous ether (30 ml) at 0 °C under Ar atmosphere. The reaction mixture was stirred for 1 h and then hydrolyzed carefully with saturated aqueous ammonium chloride solution (10 ml). The ether layer was separated, dried over $MgSO_4$, and evaporated under vacuum. The product washed with ether (5 ml) and dried under vacuum. Yield: 70%.

X-Ray structure determination

Single crystals of [$PtMe_3$I(dppa)], **5a**, were grown from a concentrated methylene chloride solution by slow diffusion of hexane. A

Table 2 Crystal data, data collection and structure refinement details for $[PtMe_3I(dppa)]\cdot CH_2Cl_2$, **5a**

Formula	$C_{28}H_{32}Cl_2INP_2Pt$
Formula weight	837.38
Temperature/K	100(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
a/Å	10.6200(11)
b/Å	14.2098(5)
c/Å	19.5531(14)
β/°	94.577(8)
Vol/Å^3	2941.3(4)
Z	4
D(calc)/Mg m^{-3}	1.891
Abs. coeff./mm^{-1}	6.129
F(000)	1608
No. of reflns	55 094
No. of independent reflns	6474 [R(int) = 0.0445]
No. of observed reflns [$I > 2\sigma(I)$]	5631
T_{min}, T_{max}	0.337, 0.612
Gof (F^2)	1.314
$R1$, $wR2$ [$I>2\sigma(I)$]	0.0277, 0.0670
$R1$, $wR2$ (all data)	0.0378, 0.0702

colorless needle of approximate 0.25 × 0.09 × 0.08 mm in size was coated with protective perfluoro polyalkyether and mounted on a glass fiber. Data were collected at 100 K on a Bruker-Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator). The data were corrected for Lorentz and polarization effects, a semiempirical absorption correction based on multiple scans was carried out using SADABS.[26] The structure was solved by direct methods and refined using full-matrix least-squares procedures on F^2 with the SHELXTL NT 6.12 software.[27] Crystal data, data collection and structure refinement details are listed in Table 3. All hydrogen atoms are in positions of idealized geometry, their isotropic displacement parameters were tied to the equivalent isotropic displacement parameters of the corresponding C and N carrier atoms by a factor of 1.2 or 1.5.

CCDC reference number 632285. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700009j

Conclusions

The ^1J(PtP) values in the ^{31}P NMR spectra of chelating organoplatinum(II) complexes $[Pt(p\text{-}MeC_6H_4)_2(dppa)]$, **1b**, and $[Pt(p\text{-}MeC_6H_4)_2(dppm)]$, are 1463 and 1392 Hz,[4b] respectively. A similar trend was also observed in the methyl analogues $[PtMe_2(dppa)]$, **1a**, ^1J(PtP) = 1475 Hz, and $[PtMe_2(dppm)]$, ^1J(PtP) = 1434 Hz.[20] Overall the ^1J(PtP) couplings for the dppa analogues are some 3–5% more than those of the dppm analogues. The difference, although modest, might indicate that in these chelating diphosphine complexes, the four-membered chelate ring experiences less strain in the dppa complexes compared to those in the dppm ones. Note that in accord with this, when the dimeric complex *cis*,*cis*-$[Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2]$ is reacted with 2 mol of dppm, only the dimeric product *cis*,*cis*-$[Me_2Pt(\mu\text{-}dppm)_2PtMe_2]$ is formed,[21] while when it is reacted with 2 mol of dppa, the dimeric product *cis*,*cis*-$[Me_2Pt(\mu\text{-}dppa)_2PtMe_2]$ is formed as a mixture with a considerable amount of the monomeric form $[PtMe_2(dppa)]$.[6] We therefore synthesized the latter monomeric complex in pure form from the reaction of $[PtCl_2(dppa)]$ with MeLi. This provides a nice contrast with the work of Braunstein *et al.*, who demonstrated that deprotonation of the NH moiety with strong bases was possible.[8] Similarly, in the chelating organoplatinum(IV) complexes, the ^1J(PtP) values are more than 3% greater in the dppa analogues. Thus, the ^1J(PtP) values for phosphorus atoms *trans* to Me in $[PtMe_3I(dppa)]$, **5a**, and $[PtMe_3I(dppm)]$[19] are 927 and 897 Hz, respectively. Despite this, based on the ^{13}C NMR data, it is possible to show that both dppa and dppm exert a similar *trans* influence in their complexes. Thus, for the platinum(IV) complexes $[PtMe_4(dppa)]$, **6**, and $[PtMe_4(dppm)]$[19] the ^1J(CPt) values for the Me ligands *trans* to phosphorus for both complexes are 567 Hz. Similarly, it has been shown that for the diplatinum(II) complexes with the general formula *cis*,*cis*-$[Me_2LPt(\mu\text{-}PP)PtLMe_2]$, L = P(O-^{i}Pr)$_3$, in which the bridging PP ligand is either dppa or dppm, the ^1J(CPt) values for the Me ligands *trans* to PP are almost the same (588 or 586 Hz, respectively).[2d]

The complexes $[PtR_2(dppa\text{-}P)_2]$, **2**, in which R is Me or tolyl ligand, are easily prepared at room temperature in pure form and good yields from the reaction of $[PtR_2(dppa)]$, **1**, with one equiv. of dppa, while in a similar procedure, the dppm analogue $[PtR_2(dppm\text{-}P)_2]$ is formed at very low temperatures and in equilibrium with the chelating starting materials, $[PtR_2(dppm)]$.[4b] This indicates that the tendency of dppa to act as monodentate ligand is greater than that of the dppm. This is confirmed by the observation of the dppa intermediate $[PtR_2(dppa\text{-}P)_2]$, **2**, in the reaction of the dimer *cis*,*cis*-$[R_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppa)PtR_2]$, **3a**, with one equiv. of dppa, as shown in Scheme 2; in a similar reaction using the dppm analogous complex *cis*,*cis*-$[R_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtR_2]$, no formation of such an intermediate was observed.[2b] The reaction of the complex $[PtR_2(dppa\text{-}P)_2]$, **2**, with, for example, *cis*,*cis*-$[Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2]$, in an attempt to form the dimeric complexes $[Me_2Pt(\mu\text{-}dppa)_2PtR_2]$, gave instead a mixture of the monomeric forms $[PtR_2(dppa)]$, **1**, and $[PtMe_2(dppa)]$. In contrast, using this type of reaction, the dppm complexes $[PtR_2(dppm\text{-}P)_2]$ have been widely used to systematically synthesize a wide variety of dimeric complexes such as $[Me_2Pt(\mu\text{-}dppm)_2Pt(o\text{-}tolyl)_2]$.[12] As mentioned before, this again is consistent with the greater chelating preference of dppa as compared to that of dppm.

The organoplatinum(IV) complexes containing dppa behaved very similarly compared to the analogous complexes containing dppm,[19] except for the formation of intermolecular hydrogen bonding of type N–H···I–Pt, both in solution and the solid state, in $[PtMe_3I(dppa)]$, **5a**, which caused the complex to undergo self-assembly. Although the corresponding hydrogen bonding involving chlorine, *i.e.* N–H···Cl–Pt, has already been observed,[22] hydrogen bonding of the type N–H···I–Pt, involving the less electronegative iodine with weaker proton acceptor ability, is not common and to the best of our knowledge, only one weak intermolecular hydrogen bonding of this type has recently been reported for $[PtIMe_3(DPA)]$, in which DPA is di-2-pyridylamine.[28]

Acknowledgements

We thank the Shiraz University Research Council for financial support through the Grant No. 85-GR-SC-18. The generous loan of platinum metal salts by Johnson Matthey PLC is also gratefully appreciated. We also would like to thank Professor D. Mohadjer for his useful suggestions.

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