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Organoplatinum(II) complexes with phosphite ligands

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ABSTRACT

The phosphite complexes *cis*-[$PtMe_2L(SMe_2)$] in which L = $P(O^iPr)_3$, **1a**, or L = $P(OPh)_3$, **1b**, were synthesized by the reaction of *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] with 2 equiv. of L. If 4 equiv. of L was used the bis-phosphite complexes *cis*-[$PtMe_2L_2$] in which L = $P(O^iPr)_3$, **2a**, or L = $P(OPh)_3$, **2b**, were obtained. The reaction of *cis*-[$Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2$] with 2 equiv. of L gave the aryl bis-phosphite complexes *cis*-[$Pt(p\text{-}MeC_6H_4)_2L_2$] in which L = $P(O^iPr)_3$, **2a′**, or L = $P(OPh)_3$, **2b′**. Use of 1 equiv. of L in the latter reaction gave the bis-phosphite complex along with the starting complex in a 1:1 ratio.
The complexes failed to react with MeI. The reaction of *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] with 2 equiv. of the phosphine PPh_3 gave *cis*-[$PtMe_2(PPh_3)_2$] and *cis*-[$PtMe_2(PPh_3)(SMe_2)$] along with unreacted starting material. Reaction of *cis*-[$PtMe_2L(SMe_2)$], **1a** and **1b** with the bidentate phosphine ligand bis(diphenylphosphino)methane, dppm = $Ph_2PCH_2PPh_2$, gave [$PtMe_2$(dppm)], **8**, along with *cis*-[$PtMe_2L_2$], **2**. The reaction of *cis*-[$PtMe_2L(SMe_2)$] with 1/2 equiv. of the bidentate N-donor ligand NN = 4,4′-bipyridine yielded the binuclear complexes [$PtMe_2L(\mu\text{-}NN)PtMe_2L$] in which L = $P(O^iPr)_3$, **3a**, or L = $P(OPh)_3$, **3b**.
The complexes were fully characterized using multinuclear NMR (^1H, ^{13}C, ^{31}P, and ^{195}Pt) spectroscopy.

1. Introduction

Phosphorus(III) ligands, especially phosphines and phosphites, have extensively been used as auxiliary ligands in forming transition metal complexes. These ligands are very useful as they present wide varieties of steric effects and electronic properties when coordinated to transition metals. Thus, by changing the substituents at the phosphorus atom, it is possible to greatly manipulate the chemical behavior of their complexes.

Although organoplatinum complexes with phosphines, PR_3, as ligands are widely studied and the complexes have been involved in many chemical transformations, the related organoplatinum complexes with phosphite ligands, $P(OR)_3$, have been far less investigated [1]. One important reason for this disparity is that the phosphites usually perform the "classical" Arbuzov rearrangement during which a phosphonate molecule is formed, and this property is often retained when they are coordinated to a transition metal [2]. Secondly, the platinum–phosphite complexes are usually very soluble in organic solvents and easily form oils [3].

In the present study, using suitable starting materials, we have synthesized some primary organoplatinum(II) complexes containing the phosphite ligands L = $P(O^iPr)_3$ or $P(OPh)_3$, of formula *cis*-[$PtMe_2L(SMe_2)$], *cis*-[$PtMe_2L_2$], or *cis*-[$Pt(p\text{-}MeC_6H_4)_2L_2$]. Some reactions of the complexes, including reactions with the bidentate N-donor, 4,4′-bipyridine, were also investigated.

2. Results and discussion

2.1. Synthesis and reactions of the complexes

The synthetic methods used to prepare the desired complexes are described in Scheme 1. The reaction of organoplatinum(II) precursors *cis*-[$PtR_2(SMe_2)_2$] (R = *p*-MeC_6H_4) or *cis*,*cis*-[$R_2Pt(\mu\text{-}SMe_2)_2PtR_2$] (R = Me) with 2 equiv. or 4 equiv., respectively, of the phosphite ligand L, L = $P(O^iPr)_3$ or $P(OPh)_3$, in benzene gave *cis*-[PtR_2L_2], **2**. When *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] was reacted with 2 equiv. of L, the monosubstituted complexes *cis*-[$PtMe_2L(SMe_2)$], **1**, were formed. Note that reaction of the starting complex *cis*-[$PtR_2(SMe_2)_2$] (R = *p*-MeC_6H_4) with 1 equiv. of L did not give the expected monosubstituted complexes *cis*-[$PtR_2L(SMe_2)$] and instead the corresponding complexes **2** were obtained along with the unreacted starting complex, in a 1:1 ratio. When 2 equiv. of PPh_3 was reacted with 1 equiv. of *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$], the di-substituted complex *cis*-[$PtMe_2(PPh_3)_2$] was formed along with the monosubstituted complex, *cis*-[$PtMe_2(PPh_3)(SMe_2)$] in an approximately 1:2 ratio, and small amount of the starting complex.

All these observations could be explained in terms of the π-acceptor ability or nucleophilicity of the phosphorus ligand. In all these substitution reactions, it is known that they normally proceed via a penta-coordinated intermediate involving bonding of the incoming phosphorus ligand with the empty $6p_z$ orbital of the square-planar starting complex to form a square-pyramidal species [5]. As such, the dimethylplatinum complexes

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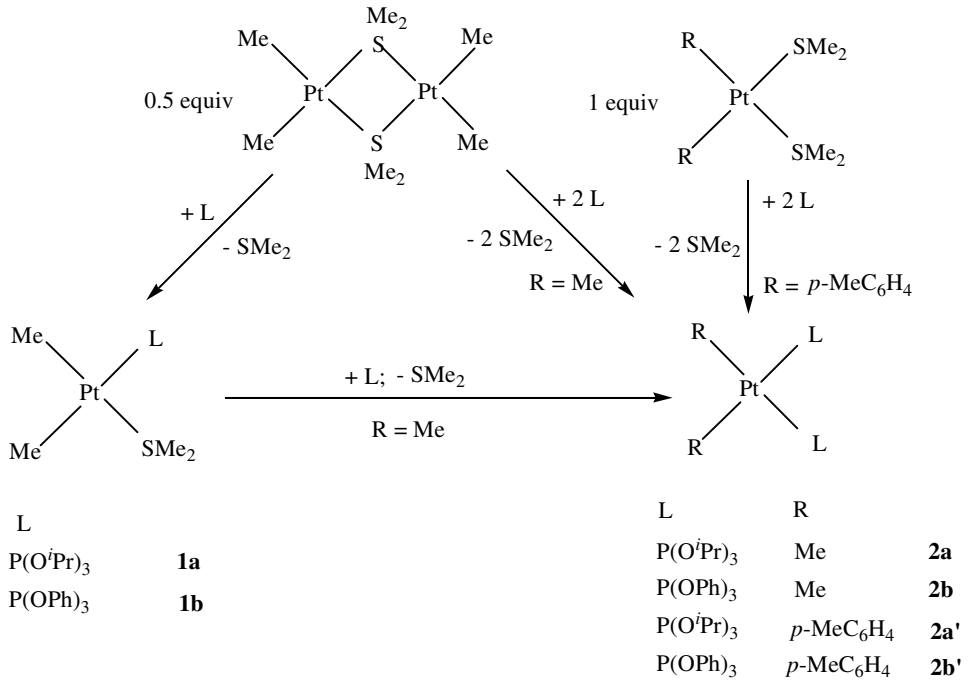
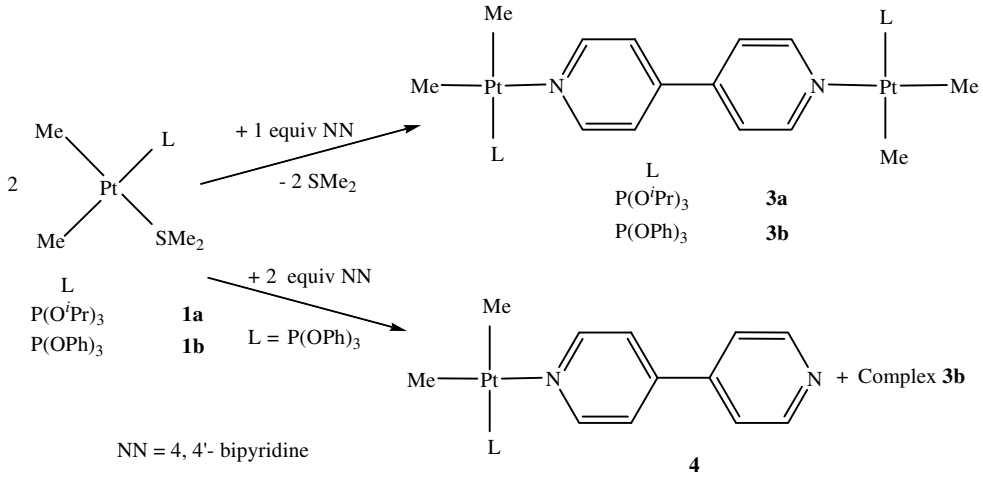


Scheme 1.

cis-[$PtMe_2L(SMe_2)$], **1a** and **1b**, are stable enough to be separated under normal condition; high π-acceptor ability of the phosphite ligands L has stabilized the complexes. However, the related tolyl analogues *cis*-[$Pt(p\text{-}MeC_6H_4)_2L(SMe_2)$] were not formed at the same condition. We believe that in the latter species, the additional π-acceptance implemented by the aryl ligands, as compared to the Me ligands in complexes **1**, has made the metallic center more electrophilic and therefore more prone to attack by the second nucleophile L, i.e. the rate of the substitution of the first L is comparable to that of the second substitution by L. In addition, it has previously been shown that the *trans* influence of tolyl ligand is greater than that of Me ligand [4], and this would further facilitate the displacement of the second SMe_2 labile ligand in the tolyl complexes.

In contrast to complexes *cis*-[$PtMe_2L(SMe_2)$], **1**, the related phosphine complex *cis*-[$PtMe_2(PPh_3)(SMe_2)$] could not be separated and it quickly reacted with the second PPh_3 to form *cis*-[$PtMe_2(PPh_3)_2$]. We attributed this to the lower π-acceptor ability of PPh_3, as compared to that of phosphites, in stabilizing the monosubstituted complex. Besides, it has been shown [5,6] that in this type of substitution reaction involving the attack of a phosphorus donor on a square-planar platinum(II) complex, PPh_3 has a higher σ-donor ability than $P(O^iPr)_3$, and therefore when the lone pair of electrons on PPh_3 is bound to the low lying platinum $6p_z$ orbital to form the initial transition state containing the square-pyramidal metallic center, it is better able to cope with the electron density already present in the filled metal $5d_{z^2}$ orbital [5].

We found that the SMe_2 ligand in complexes *cis*-[$PtMe_2L(SMe_2)$], **1**, could be substituted with N-donor ligands. Thus, as shown in Scheme 2, when each of the complexes **1** was reacted with 1/2 equiv. of the bidentate N-donor, 4,4′-bipyridine(NN), the bimolecular complex [$PtMe_2L(\mu\text{-}NN)PtMe_2L$], **3**, was obtained. However, when complex **1b** was reacted with 1 equiv. of NN, then the complex **4**, in which the NN acts as a monodentate ligand,



Scheme 2.

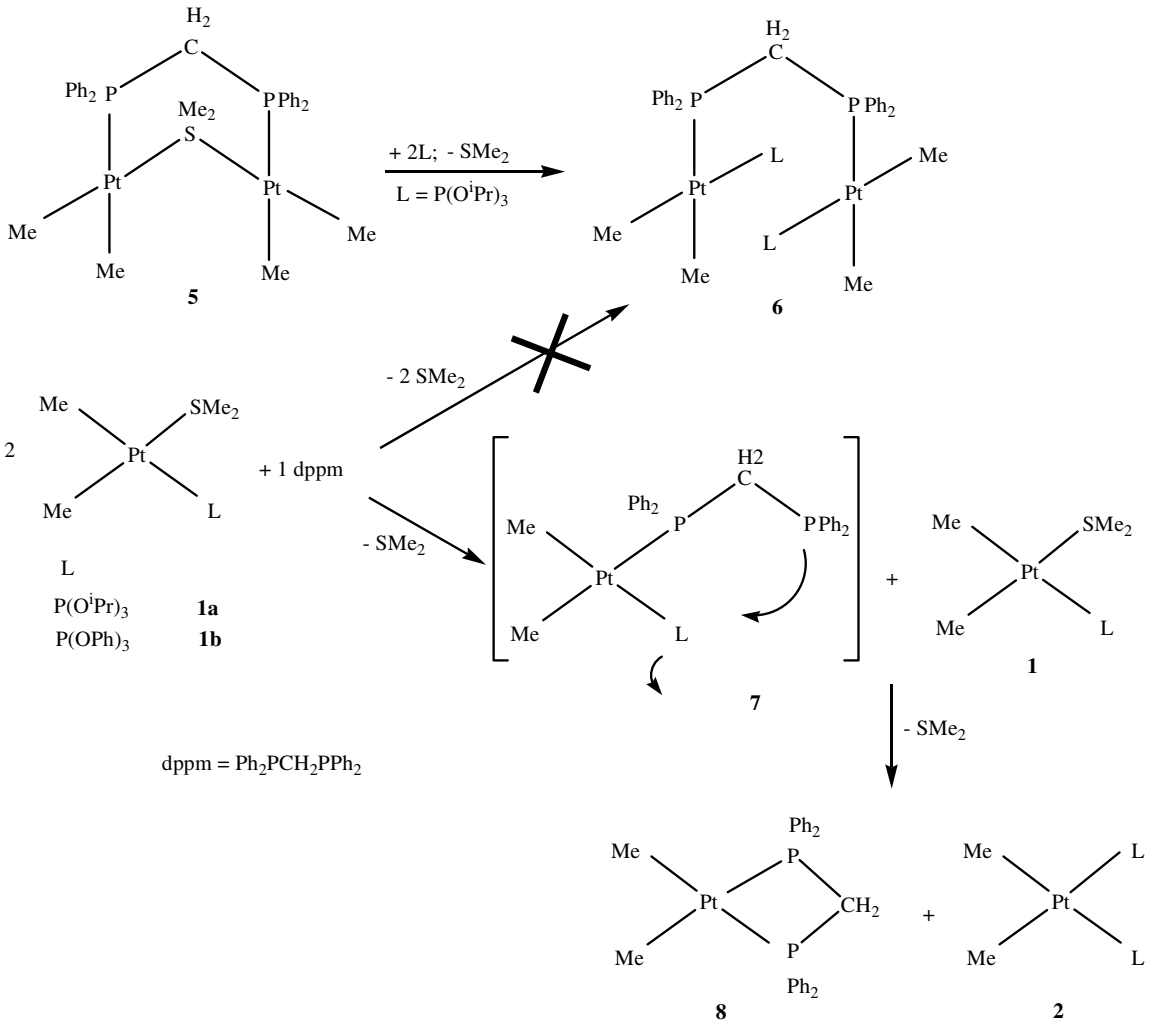
was formed along with the corresponding binuclear complex **3b**.

The reaction of complexes **1** with the bidentate phosphine ligand bis(diphenylphosphino)methane, dppm = $Ph_2PCH_2PPh_2$, was also studied and the results are summarized in Scheme 3. The bidentate ligand dppm has a strong tendency to act both as a chelate or bridging ligand [7], although in some cases it acts as a monodentate (dangling) ligand [8]. As has been reported before [9], when the binuclear complex *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtMe_2$], **5**, is reacted with 2 equiv. of $P(O^iPr)_3$, then the bridging SMe_2 ligand is displaced and the binuclear complex *cis*,*cis*-[$Me_2\{P(O^iPr)_3\}Pt(\mu\text{-dppm})Pt\{P(O^iPr)_3\}Me_2$], **6**, was obtained (see Scheme 3). As can be seen, upon this reaction, the binuclear integrity of the complex in retained. In contrast, in the present work when we started from the mononuclear complex **1** and reacted it with 0.5 equiv. of dppm, the binuclear complex **6** was not formed and instead the known dppm chelate complex [$PtMe_2$(dppm)] [4d], **8**, was obtained along with an equivalent amount of the mononuclear complex *cis*-[$PtMe_2L_2$], **2**. The complex **1** has probably reacted with dppm and by replacing SMe_2, the dppm monodentate intermediate **7** has formed first as a mixture with 1 equiv. of the unreacted complex **1**. The chelate effect has probably resulted in displacement of L by the dangling phosphorus end of the dppm ligand to form the chelate complex **8** and meanwhile the released L has displaced the SMe_2 ligand of the unreacted complex **1** to form complex **2**.

The phosphite complexes **1** and **2** resisted reaction with MeI, even in the presence of excess reagent and long reaction times. We believe that this is related to strong π-acceptor ability of the phosphite ligands, making the complexes poor nucleophiles for an attacking Me group in the oxidative addition reagent MeI, via the usual S_N2 type process. Although steric hindrances are also influential in this kind of reactions, its importance in the reactions involving the present phosphite complexes are ruled out. Note that for example although the Tolman cone angle of $P(O^iPr)_3$, 130°, is smaller than that of $PMePh_2$ (136°), the corresponding dimethyl complex of the latter, *cis*-[$PtMe_2(PMePh_2)_2$], is known to have reacted with MeI to give the Pt(IV) complex [$PtMe_3I(PMePh_2)_2$] [4d].

2.2. Characterization of the complexes

The complexes were fully characterized using multinuclear NMR (^1H, ^{31}P, ^{13}C and ^{195}Pt) spectroscopy. The phosphite complexes **1** and **2** are very soluble in organic solvents and therefore complete removal of solvent at the end of work up stage was not always possible and this has usually been reflected in the microanalytical results.



Scheme 3.

In the ^{1}H NMR spectrum of *cis*-[$PtMe_2${$P(OPh)_3$}(SMe_2)], **1b**, shown in Fig. 1, two doublets (each further coupled with the Pt center) at $\delta = 0.36$ [^2J(PtH) = 65.4 Hz, ^3J(PH) = 10.8 Hz], for Me ligand *trans* to $P(OPh)_3$, and at $\delta = 0.80$ [^2J(PtH) = 85.8 Hz, ^3J(PH) = 8.9 Hz], for Me ligand *trans* to SMe_2, were observed. The considerably lower ^2J(PtH) value for the first signal, as compared to that of the second one, is due to the higher *trans* influence of $P(OPh)_3$ than SMe_2. A singlet at 1.89 accompanied by Pt satellites with ^3J(PtH) = 23.9 Hz was assigned to 2 equiv. Me groups of the terminal SMe_2 ligand. The observation of this 1:4:1 pattern for SMe_2 as well as the overall 2:1:1 relative intensity of the three different Me groups, strongly confirms the monomeric nature of the complex **1b** and rules out the possibility of formation of any binuclear species of type *cis,cis*-[{$P(OPh)_3$}$Me_2Pt(\mu$-SMe_2)$PtMe_2$-{$P(OPh)_3$}], for which the Me groups would be expected to give similar patterns.

Consistent with the ^{1}H NMR data, is the ^{13}C NMR spectrum of *cis*-[$PtMe_2${$P(OPh)_3$}(SMe_2)], **1b**, shown in Fig. 2. A doublet signal at $\delta = -9.8$ with ^2J(CP) = 9 Hz and ^1J(PtC) = 695 Hz was assigned to the Me ligand *trans* to SMe_2 and *cis* to $P(OPh)_3$]. The second Me ligand which is *trans* to $P(OPh)_3$ appeared at $\delta = 8.3$ with a much higher value of ^2J(CP) = 165 Hz, but a lower value of ^1J(PtC) = 637 Hz.

In the ^{31}P NMR spectrum of *cis*-[$PtMe_2${$P(OPh)_3$}(SMe_2)], **1b**, a singlet at $\delta = 116$ with ^1J(PtP) = 3343 Hz was observed for the phosphite ligand. Observation of a doublet at −2677 in the ^{195}Pt NMR spectrum of complex **1b** with ^1J(PtP) = 3352 Hz (very close to the value of ^1J(PtP) = 3343 Hz, obtained from the ^{31}P NMR spectrum) clearly indicated the presence of only one phosphite ligand in the complex. The complex *cis*-[$PtMe_2${$P(O^iPr)_3$}(SMe_2)], **1a**, was similarly identified and the data are summarized in Section 3.

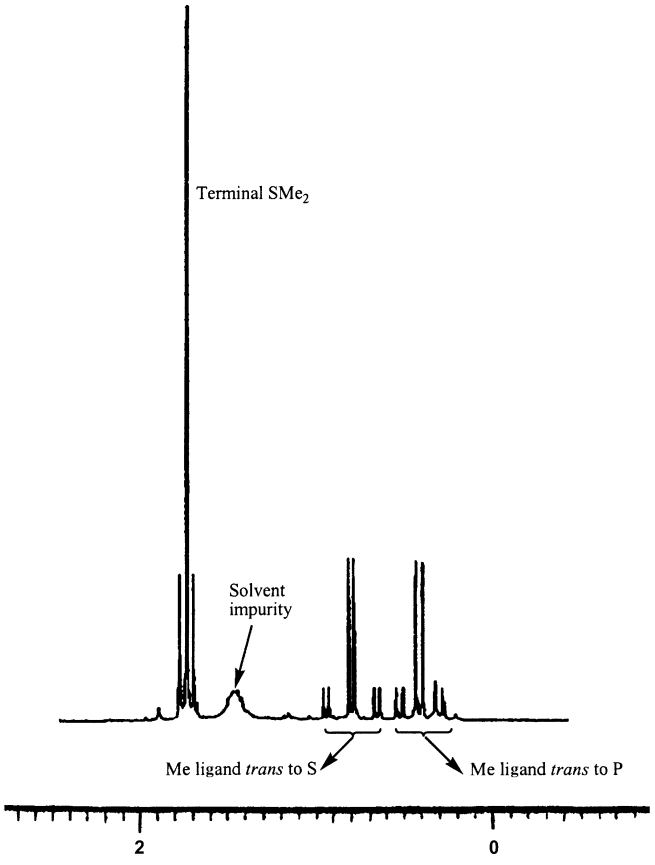


Fig. 1. ^{1}H NMR spectrum of *cis*-[$PtMe_2${$P(OPh)_3$}(SMe_2)], **1b**.

In the ^{1}H and ^{13}C NMR spectra of **1a**, both the Me groups of $P(O^iPr)_3$ ligand, and the corresponding CH groups, each appeared as two sets with relative intensity 2:1. It has been shown [10] that $P(OR)_3$ ligands can take up four different conformations resulting from the relative positions of the R groups. It is also indicated that one of the possibilities in which two of the R groups direct away from phosphorus lone pair and the third R group take up position toward the lone pair, as indicated in Scheme 4, is more likely.

Thus in the ^{13}C NMR spectrum of the latter complex, the Me groups of $P(O^iPr)_3$ ligand appeared as two doublets at $\delta = 23.6$ and $\delta = 24.2$ and the corresponding CH groups were located at $\delta = 68.8$ and $\delta = 68.9$, respectively. Consistently, in the ^{1}H NMR spectrum two doublets (2:1) at $\delta = 1.26$ and $\delta = 1.30$, respectively, were observed for Me groups of $P(O^iPr)_3$ ligand and the related CH groups appeared as multiplet at $\delta = 4.80$. These data support the suggestion that the conformation of phosphite ligand in **1a** is as suggested in Scheme 4.

The ^{1}H NMR spectrum of *cis*-[$PtMe_2${$P(OPh)_3$}$_2$], **2b**, is shown in Fig. 3. The signal at $\delta = 0.14$ due to the 2 equiv. Pt–CH_3 groups which are *trans* to two P ligands, has a complicated pattern [4d], and the Pt satellites gave ^2J(PtH) = 70.6 Hz. The 2 equiv. phosphorus atoms in complex **2b** appeared as a singlet at $\delta = 120$ in the ^{31}P NMR spectrum with platinum satellites with ^1J(PtP) = 3036 Hz. Due to a very high solubility of complex **2b**, it was possible to obtain a very well resolved signal in its ^{1}H coupling ^{195}Pt NMR spectrum, as shown in Fig. 4. This is interesting since the Pt signal, appeared at $\delta = -2899$ and has coupled to 6 equiv. protons of the 2Me ligands to give a septet with ^2J(PtH) = 71 Hz, a value almost identical to the value of 70.6 Hz obtained from the corresponding ^{1}H NMR spectrum, discussed below. The septet is further coupled with 2 equiv. P atoms to give a triplet with a ^1J(PtP) value of 3025 Hz, close to the ^1J(PtP) value of 3036 Hz, obtained in the related ^{31}P NMR spectrum. The complex *cis*-[$PtMe_2${$P(O^iPr)_3$}$_2$], **2a**, was similarly identified and the data are summarized in the experimental. Both di-methyl complexes **2a** and **2b** were also identified by ^{13}C NMR spectroscopy. Typically, as shown in Fig. 2, a doublet of doublets at $\delta = 0.8$ with ^1J(PtC) = 552 Hz, $^2J(CP_{trans})$ = 142 Hz and $^2J(CP_{cis})$ = 14 Hz was observed for the two Pt–Me groups *trans* to $P(O^iPr)_3$ in complex *cis*-[$PtMe_2${$P(O^iPr)_3$}$_2$], **2a**.

In the ^{31}P NMR spectrum of *cis*-[$Pt(p$-$MeC_6H_4)_2${$P(O^iPr)_3$}$_2$], **2a′**, a singlet at $\delta = 121.8$ with ^1J(PtP) = 3119 Hz was observed for the 2 equiv. phosphorous ligands and this is consistent with the observation of a triplet at $\delta = -2940$ in the corresponding ^{195}Pt NMR spectrum with ^1J(PtP) = 3114 Hz. A similar trend was also observed for the analogous complex *cis*-[$Pt(p$-$MeC_6H_4)_2${$P(OPh)_3$}$_2$], **2b′**. The ^{13}C NMR spectra of these di-tolyl complexes gave useful information about the tolyl ligands. The region of C atoms of tolyl ligands directly connected to the platinum center in complex *cis*-[$Pt(p$-$MeC_6H_4)_2${$P(O^iPr)_3$}$_2$], **2a′**, is shown in Fig. 2. The observation of a doublet of doublets at $\delta = 154.4$ with $^2J(CP_{trans})$ = 169 Hz and $^2J(CP_{cis})$ = 20 Hz was assigned to the 2 equiv. C atoms of tolyl ligands (C^i) that further coupled to platinum center to give ^1J(PtC) = 796 Hz. It is interesting to note that this latter coupling is nearly 30% lower than ^1J(PtC) = 552 Hz observed for Me ligands *trans* to $P(O^iPr)_3$ in *cis*-[$PtMe_2${$P(O^iPr)_3$}$_2$], **2a**, discussed above (see also Fig. 2). This is obviously due to the fact that the C atom of tolyl ligand (C^i) has used sp^2 hybrid orbital to bind to the platinum center, as compared with sp^3 hybrid orbital used by C of Me in complex **2a**. This behavior has also been reflected on the $^2J(CP_{trans})$ values and as is expected based on hybrid orbitals. The value for the tolyl complex **2a′** is some 16% greater than the corresponding value for the Me complex **2a** (169 vs. 142). A similar trend, a 30% change in the $^2J(CP_{cis})$ values (20 vs. 14) is observed for the complexes **2a** and **2a′**. Consistently, the ^1J(PtP) value in the ^{31}P NMR spectrum of complex *cis*-[$PtMe_2${$P(O^iPr)_3$}$_2$], **2a**, 3177 Hz, is higher than the value for the complex *cis*-[$Pt(p$-$MeC_6H_4)_2${$P(O^iPr)_3$}$_2$], **2a′**,

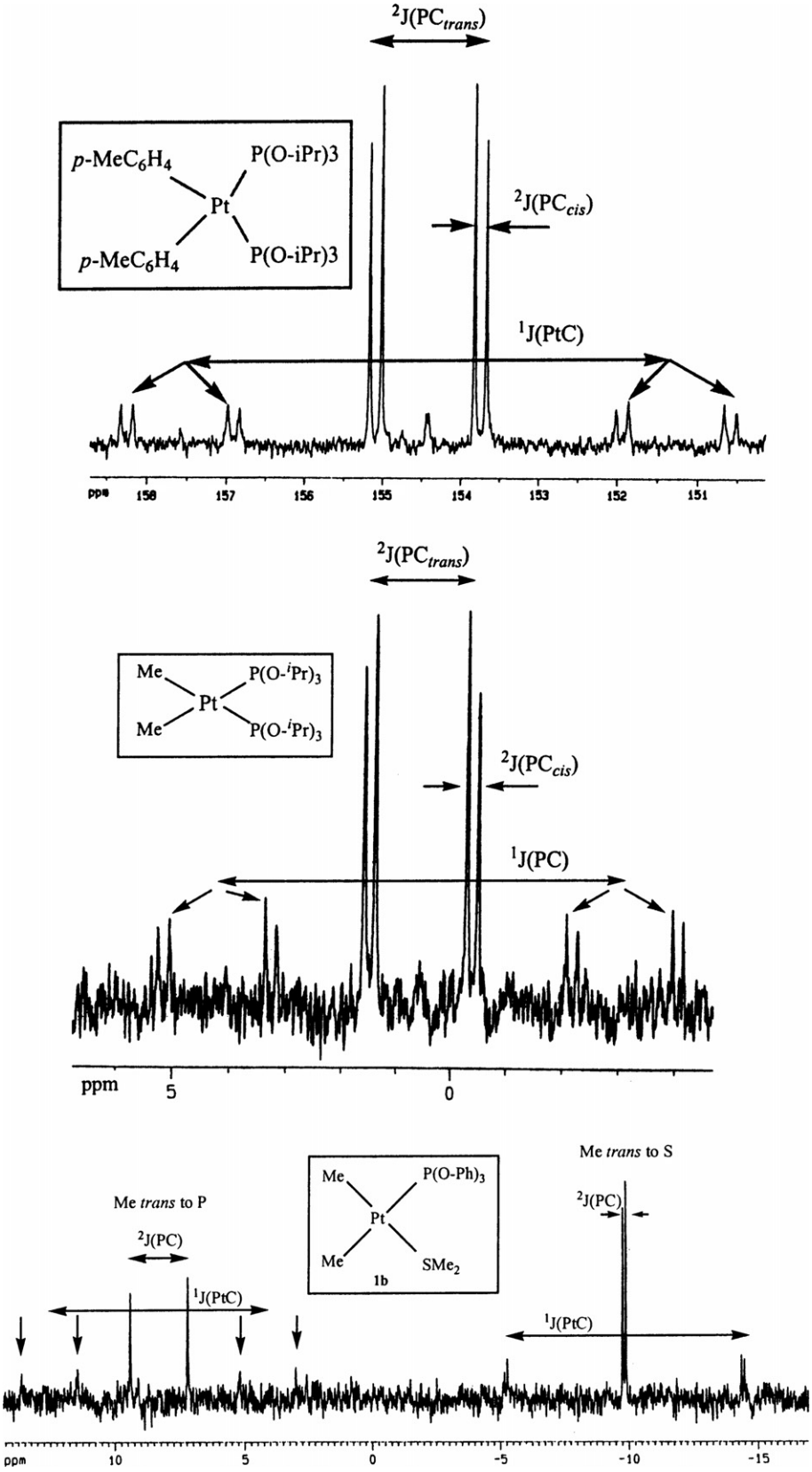
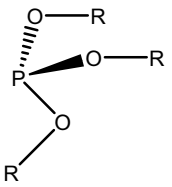


Fig. 2. ^{13}C NMR spectra of complexes: bottom view, the Pt–Me region of *cis*-[$PtMe_2\{P(OPh)_3\}(SMe_2)$], **1b**; middle view, the Pt–Me region of *cis*-[$PtMe_2\{P(O^iPr)_3\}_2$], **2a**; top view, C atoms of tolyl ligands directly connected to Pt center in *cis*-[$Pt(p\text{-}MeC_6H_4)_2\{P(O^iPr)_3\}_2$], **2a′**. The assignments are shown.

3119 Hz. The difference, although modest (≈2%), reflects the higher *trans* influence of tolyl ligand as compared to that of Me ligand [4]. A similar trend of ≈2% difference was observed for the $P(OPh)_3$ complexes **2b** and **2b′**.



Scheme 4.

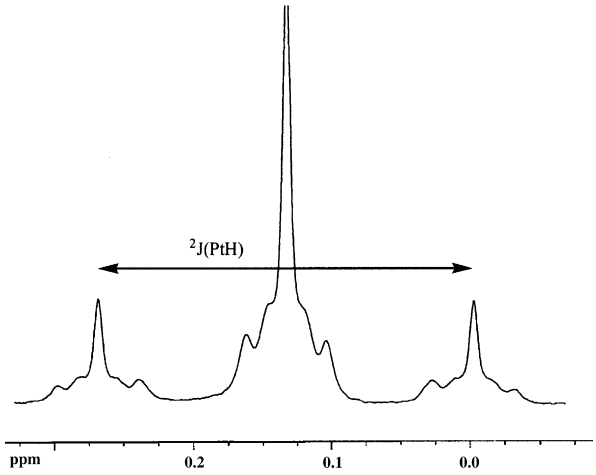


Fig. 3. ^{1}H NMR spectrum of *cis*-[PtMe$_2${P(OPh)$_3$}$_2$], **2b**, in Me region.

The above data also suggest that the phosphite P(O^{i}Pr)$_3$, as compared to P(OPh)$_3$, forms a stronger bond to the platinum center. Thus, the ^1J(PtP) value of 3119 Hz observed in the ^{31}P NMR spectrum of the di-aryl complex *cis*-[Pt(p- MeC$_6$H$_4$)$_2${P(O^{i}Pr)$_3$}$_2$], **2a′**, is some 4% higher than the corresponding value of 2987 Hz observed in the ^{31}P NMR spectrum of the di-aryl complex *cis*-[Pt(*p*-MeC$_6$H$_4$)$_2${P(OPh)$_3$}$_2$], **2b′**. A similar "4% increase" trend was also observed for the di-methyl complexes **2a** and **2b**. The phosphite ligands P(OR)$_3$ are σ-donors as well as rather strong π-acceptors when forming bond with platinum atom. The alkyl group ^{i}Pr in P(O^{i}Pr)$_3$, as compared to the aryl group Ph in P(OPh)$_3$, would obviously make P(O^{i}Pr)$_3$ a stronger σ-donor and a weaker π-acceptor than P(OPh)$_3$. As such it would seem that the σ-donor ability plays a dominating role in forming a bond between platinum and the phosphites. Consistently, the ^{13}C NMR data for P(O^{i}Pr)$_3$ indicates a higher *trans* influence than P(OPh)$_3$. Thus, the ^1J(PtC) value of 552 Hz observed for the Pt–Me group in the ^{13}C NMR spectrum of complex *cis*-[PtMe$_2${P(O^{i}Pr)$_3$}$_2$], **2a**, is some 4% lower than that of the corresponding value of ^1J(PtC) = 575 Hz in complex *cis*-[Me$_2$Pt{P(OPh)$_3$}$_2$], **2b**. A similar "4% decrease" trend was also observed for the ^1J(PtC) coupling between the platinum atom and the C atom of the tolyl ligand directly connected to platinum in di-aryl complexes **2a′** and **2b′**.

The binuclear complexes **3a** and **3b**, containing bridging NN ligand were characterized using ^{1}H and ^{31}P NMR spectroscopy. Typically in the ^{1}H NMR spectrum of [Me$_2${P(O^{i}Pr)$_3$}Pt(μ-NN)Pt-{P(O^{i}Pr)$_3$}Me$_2$], **3a**, a doublet at δ = 0.32 with ^2J(PtH) = 64.7 Hz and ^3J(PH) = 10.3 Hz was assigned to the 2 equiv. Pt–Me groups *trans* to P(O^{i}Pr)$_3$] while the doublet at δ = 0.76 with ^3J(PH) = 8.0 Hz and a considerably higher ^2J(PtH) value of 87.9 Hz was assigned to the 2 equiv. Pt–Me groups *cis* to P(O^{i}Pr)$_3$ and *trans* to N. The ^2J(PtH) values are consistent with a higher *trans* influence of the phosphite ligand than that of the N ligating atom. In the ^{31}P NMR spectrum of [Me$_2${P(OPh)$_3$}Pt(μ-NN)Pt{P(OPh)$_3$}Me$_2$], **3b**, shown in Fig. 5, the observation of a singlet with Pt satellites at δ = 117.5 with ^1J(PtP) = 3341 Hz indicates that each of the two P atoms are situated on one platinum center to give a symmetrical geometry as shown in Scheme 2. A relatively low intensity singlet was observed at δ = 119.5 with ^1J(PtP) = 3043 Hz, which is assigned to a very small amount of the monomeric complex [Me$_2$Pt(NN-*N*)-{P(OPh)$_3$}],**4**, (NN-*N* = monodentate 4,4′-bipyridine). As mentioned in the previous section (see also Scheme 2), a higher concentration of the complex **4** could be obtained when 2 equiv. of NN are reacted with complex **1b**. In the ^{1}H NMR spectrum, two doublets

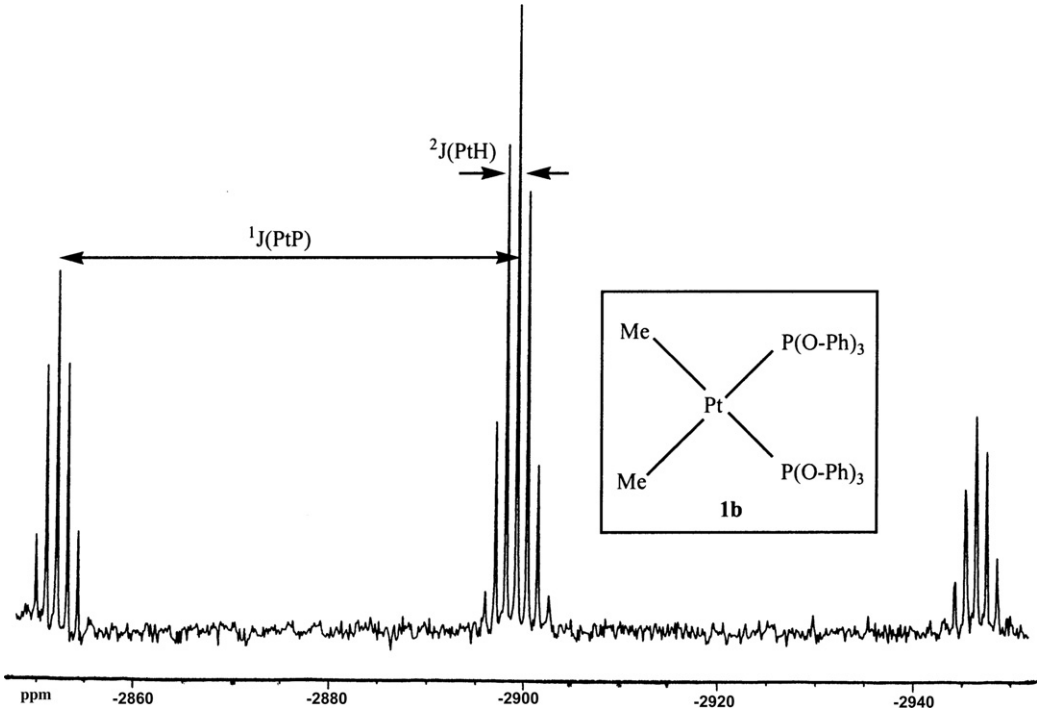


Fig. 4. ^{1}H coupling ^{195}Pt NMR spectrum of *cis*-[PtMe$_2${P(OPh)$_3$}$_2$], **2b**.

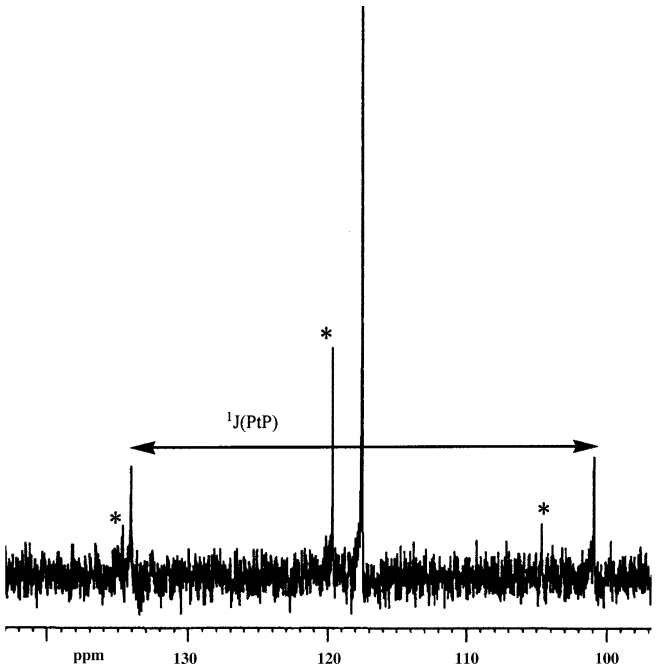


Fig. 5. ^{31}P NMR spectrum of [Me_2{$P(OPh)_3$}Pt(μ-NN)Pt{$P(OPh)_3$}Me_2], **3b**. The signal together with its Pt satellites shown by asterisks is due to a small quantity of the monomeric complex [Me_2Pt(NN-*N*){$P(OPh)_3$}],**4**, (NN-*N* = monodentate 4,4′-bipyridine).

at δ = 0.26 and 0.85 with ^2J(PtH) = 66.8 Hz [^3J(PH) = 11.3 Hz] and ^2J(PtH) = 86.9 Hz [^3J(PH)=9.0 Hz] were assigned to the Me ligand *trans* to $P(OPh)_3$ and the Me ligand *cis* to $P(OPh)_3$ (and *trans* to N), respectively. The binuclear complexes **3a** and **3b** are therefore always contaminated with at least a very small amount of the monomeric complex of type **4** and as such the obtained CNH microanalytical results did not properly match with the calculated quantities.

3. Experimental

The ^{1}H NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer. ^{31}P, ^{13}C and ^{195}Pt NMR spectra were recorded on a Bruker Avance DRX 300 MHz spectrometer. References were TMS (^{1}H, ^{13}C), H_3PO_4 (^{31}P), and aqueous K_2PtCl_4 (^{195}Pt); $CDCl_3$ was used as solvent. All the chemical shifts and coupling constants are in ppm and Hz, respectively. *cis*-[$Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2$] [11] and the dimeric precursor *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] [12] were prepared by the literature methods. The phosphites $P(O^iPr)_3$ and $P(OPh)_3$ were used as purchased from Fluka without any purification. The stock solutions of $P(OR)_3$ were prepared by adding 474 μL of $P(OPh)_3$ or 444 μL of $P(O^iPr)_3$ to 5 mL dried benzene.

3.1. *cis*-[$PtMe_2${$P(O^iPr)_3$}(SMe_2)], ***1a***

Five hundred μL stock solution of $P(O^iPr)_3$ (0.174 mmol) was added to a solution of *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] (50 mg, 0.087 mmol) in dried benzene (10 mL). After stirring at room temperature for 1 h, the solvent was removed under vacuum. The oily product was soluble in many organic solvents. Yield: almost quantitative. Anal. Calc. for $C_{13}H_{33}O_3PPtS$: C, 31.52; H, 6.66. Found: C, 30.86; H, 6.97%. NMR in $CDCl_3$: δ (^{1}H) = 0.32 [d, ^2J(PtH) = 62.4 Hz, ^3J(PH) = 10.2 Hz, 3H, Me ligand *trans* to $P(O^iPr)_3$], 0.64 [d, ^2J(PtH) = 84.0 Hz, ^3J(PH) = 8.1 Hz, 3H, Me ligand *cis* to $P(O^iPr)_3$], 1.26 [d, ^3J(HH) = 6.1 Hz, 12H, 4Me of ^{i}Pr groups], 1.30 [d, ^3J(HH) = 6.1 Hz, 6H, 2Me of ^{i}Pr groups], 2.43 [s, ^3J(PtH) = 24.0 Hz, 6H, 2Me of SMe_2 ligand], 4.80 [m, 3H, 3 CH of ^{i}Pr groups]; δ (^{13}C) = −12.6 [d, ^1J(PtC) = 688 Hz, ^2J(CP) = 9 Hz, Me ligand *cis* to $P(O^iPr)_3$], 6.9 [d, ^1J(PtC) = not resolved, ^2J(CP) = 153 Hz, Me ligand *trans* to $P(O^iPr)_3$], 21.5 [d,^2J(PtC) = 9 Hz, ^3J(CP) = 3 Hz, Me groups of SMe_2 ligand], 23.6 [d, ^3J(CP) = 5 Hz, 4Me groups of ^{i}Pr], 24.2 [d, ^3J(CP) = 4 Hz, 2Me groups of ^{i}Pr], 68.8 [s, ^3J(CPt) = 17 Hz, CH groups of ^{i}Pr], 68.9 [s, ^3J(CPt) = 18 Hz, CH groups of ^{i}Pr]; δ (^{31}P) = 128.1 [s, ^1J(PtP) = 3315 Hz]; δ (^{195}Pt) = −2720 [d, ^1J(PtP) = 3321 Hz].

The complex *cis*-[$PtMe_2${$P(OPh)_3$} (SMe_2)],**1b**, was prepared similarly using 2 equiv. of $P(OPh)_3$. Yield: almost quantitative. Anal. Calc. for $C_{22}H_{27}O_3PPtS$: C, 44.23; H, 4.52. Found: C, 44.59; H, 4.73%. NMR in $CDCl_3$: δ (^{1}H) = 0.36 [d, ^2J(PtH) = 65.4 Hz, ^3J(PH) = 10.8 Hz, 3H, Me ligand *trans* to $P(OPh)_3$], 0.80 [d, ^2J(PtH) = 85.8 Hz, ^3J(PH) = 8.9 Hz, 3H, Me ligand *cis* to $P(OPh)_3$], 1.89 [s, ^3J(PtH) = 23.9 Hz, 6H, 2Me of SMe_2 ligand], 6.84–7.06 [Ph groups on $P(OPh)_3$ ligand]; δ (^{13}C) = −9.8 [d, ^1J(PtC) = 695 Hz, ^2J(CP) = 9 Hz, Me ligand *cis* to $P(OPh)_3$], 8.3 [d, ^1J(PtC) = 637 Hz, ^2J(CP) = 165 Hz, Me ligand *trans* to $P(OPh)_3$], 20.4 [d, ^3J(CP) = 3 Hz, Me groups of SMe_2 ligand], 120.9, 121.0, 124.3, 129.5, 151.5, 151.6 [the Ph protons]; δ (^{31}P) = 116.1 [s, ^1J(PtP) = 3343 Hz]; δ (^{195}Pt) = −2677.3 [d, ^1J(PtP) = 3352 Hz].

3.2. *cis*-[$PtMe_2${$P(O^iPr)_3$}$_2$], ***2a***

One thousand μL stock solution of $P(O^iPr)_3$ (0.348 mmol) was added to a solution of *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] (50 mg, 0.087 mmol) in dried benzene (10 mL) and stirred at room temperature for 1 h. The solvent was removed under reduced pressure to yield a colorless oily product which was soluble in many organic solvents. Yield: almost quantitative. Anal. Calc. for $C_{20}H_{48}O_6P_2Pt \cdot 0.2C_6H_6$: C, 38.63; H, 7.52. Found: C, 38.83; H, 7.49%. NMR in $CDCl_3$: δ (^{1}H) = 0.46 [m, ^2J(PtH) = 66.5 Hz, ^3J(P-PtCH$_3$) = 10.5 Hz, 6H, 2Me ligands], 1.28 [d, ^3J(HH) = 6.2 Hz, 36H, 12Me groups of ^{i}Pr], 4.73 [m, 6H, 6CH groups of ^{i}Pr]; δ (^{13}C) = 0.8 [dd, ^1J(PtC) = 552 Hz, $^2J(CP_{trans})$ = 142 Hz, $^2J(CP_{cis})$ = 14 Hz, 2Me ligands *trans* to $P(O^iPr)_3$], 24.2 [t, ^3J(CP) = 4 Hz, Me groups of ^{i}Pr], 68.7 [s, ^3J(CPt) = 17 Hz, CH groups of ^{i}Pr]; δ (^{31}P) = 131.7 [s, ^1J(PtP) = 3177 Hz]; δ (^{195}Pt) = −2966 [t, ^1J(PtP) = 3170 Hz, ^2J(PtH) = 64 Hz (obtained from the ^{1}H coupling ^{195}Pt NMR spectrum)].

The following complexes were made similarly using *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] and 4 equiv. or *cis*-[$Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2$] and 2 equiv. of the corresponding L group: *cis*-[$PtMe_2${$P(OPh)_3$}$_2$], **2b**. Yield: almost quantitative. Anal. Calc. for $C_{38}H_{36}O_6P_2Pt$: C, 53.84; H, 4.24. Found: C, 53.86; H, 4.24%. NMR in $CDCl_3$: δ (^{1}H) = 0.14 [m, ^2J(PtH) = 70.6 Hz, 6H, 2Me ligands], 6.83–7.15 [Ph groups on $P(OPh)_3$ ligand]; δ (^{13}C) = 1.7 [dd, ^1J(PtC) = 575 Hz, $^2J(CP_{trans})$ = 146 Hz, $^2J(CP_{cis})$ = 15 Hz, 2Me ligands], 120.7, 124.4, 129.4, 151.3 [s, carbons in Ph groups of $P(OPh)_3$]; δ (^{31}P) = 119.8 [s, ^1J(PtP) = 3036 Hz]; δ (^{195}Pt) = −2899 [t, ^1J(PtP) = 3025 Hz, ^2J(PtH) = 71 Hz]. *cis*-[*Pt*(*p*-MeC_6H_4)$_2${$P(O^iPr)_3$}$_2$], **2a′**. Anal. Calc. for $C_{32}H_{56}O_6P_2Pt \cdot 0.5C_6H_6$: C, 50.47; H, 7.14. Found: C, 50.49; H, 7.69%. NMR in $CDCl_3$: δ (^{1}H) = 1.18[d, ^3J(HH) = 6.2 Hz, 36H, 12Me groups of ^{i}Pr], 2.08 [s, 6H, 2Me groups on the *p*-tolyl ligands], 4.54 [m, 6H, 6CH groups of ^{i}Pr]; 6.69 [d, ^3J(HH) = 6.4Hz, 4H^m of tolyl ligands], 7.18 [m, ^3J(PtH) = 55.9 Hz, 4H^o of tolyl ligands]; δ (^{13}C) = 20.8 [s Me groups on the *p*-tolyl ligands]; 24.3 [s, Me groups of ^{i}Pr], 69.5 [s, CH groups of ^{i}Pr],127.6 [t, ^2J(CPt) = 63 Hz, ^3J(CP) = 8 Hz, C^o of tolyl ligands], 129.7 [s, C^p of tolyl ligands], 136.9 [t, ^3J(CPt) = 35 Hz, C^m of tolyl ligands], 154.4 [dd, ^1J(PtC) = 796 Hz, $^2J(CP_{trans})$ = 169 Hz, $^2J(CP_{cis})$ = 20 Hz, C^i of tolyl ligands]; δ (^{31}P) = 121.8 [s, ^1J(PtP) = 3119 Hz]; δ (^{195}Pt) = −2940 [t, ^1J(PtP) = 3114 Hz]. *cis*-[*Pt*(*p*-MeC_6H_4)$_2${$P(OPh)_3$}$_2$], **2b′**. NMR in $CDCl_3$: δ (^{1}H) = 1.82 [s, 6 H, 2Me groups on the *p*-tolyl ligands], 6.27 [d, ^3J(HH) = 7.5 Hz, 4H^m of tolyl ligands], 6.73 [m, *J*(PtH);= not resolved, ^3J(HH) = 31.2 Hz, 4H^o of tolyl ligands]; 6.89–7.1 [Ph groups on $P(OPh)_3$ ligand]. δ (^{13}C) = 20.8[s, Me groups on the

p-tolyl ligands];120.8, 124.6, 129.5, 151.3 [s, aromatic carbons in $P(OPh)_3$]; 127.8 [t, $^2J(CPt) = 65$ Hz, $^3J(CP) = 8$ Hz, C^o of tolyl ligands], 131 [s, C^p of tolyl ligands], 136 [t, $^3J(CPt) = 34$ Hz, C^m of tolyl ligands], 151 [dd, $^1J(PtC) = 830$ Hz, $^2J(CP_{trans}) = 175$ Hz, $^2J(CP_{cis}) = 19$ Hz, C^i of tolyl ligands]; δ (^{31}P) = 111.4 [s, $^1J(PtP) = 2987$ Hz]; δ (^{195}Pt) = −2883 [t, $^1J(PtP) = 2981$ Hz,].

3.3. $[Me_2Pt\{P(O^iPr)_3\}(\mu\text{-}NN)Pt\{P(O^iPr)_3\}Me_2]$, **3a**

To a colorless solution of *cis*-$[PtMe_2\{P(O^iPr)_3\}(SMe_2)]$, **1a**, (86.245 mg, 0.174 mmol) in benzene(10 mL) was added 4,4′-bipyridine (13.5 mg, 0.087 mmol). The mixture was stirred at room temperature for 3 h, during which the color of the solution was changed to yellow. The solvent was removed under reduced pressure and the oily yellow product was washed with n-hexane (2 mL) to give a yellow powder. NMR in $CDCl_3$: δ (^1H) = 0.32 [d, $^2J(PtH) = 64.7$ Hz, $^3J(PH) = 10.3$ Hz, 6H, 2Me ligands *trans* to $P(O^iPr)_3$], 0.76 [d, $^2J(PtH) = 87.9$ Hz, $^3J(PH) = 8.0$ Hz, 6H, 2Me ligands *cis* to $P(O^iPr)_3$], 0.97[d, $^3J(HH) = 6.2$ Hz, 36 H, 12Me groups of ^{i}Pr], 4.85 [br., 6H, 6CH groups of ^{i}Pr], 7.30[d, $^3J(HH) = 7.5$Hz, $4H^m$ of NN ligand], 8.60 [m, $^3J(HH) = 6.5$Hz, 4 H^o of NN ligand]; δ(^{31}P) = 128.3[s, $^1J(PtP) = 3367$ Hz, $P(O^iPr)_3$ ligands].

The complex $[Me_2\{P(OPh)_3\}Pt(\mu\text{-}NN)Pt\{P(OPh)_3\}Me_2]$, **3b**, was prepared similarly using complex **1b**. NMR in $CDCl_3$: δ (^1H) = 0.32 [d, $^2J(PtH) = 58.8$ Hz, $^3J(PH) = 12.5$ Hz, 6H, 2Me ligands *trans* to $P(OPh)_3$], 0.88 [d, $^2J(PtH) = 87.9$ Hz, $^3J(PH) = 9.0$ Hz, 6H, 2Me ligands *cis* to $P(OPh)_3$], 6.9-7.5 [Ph groups on $P(OPh)_3$ ligand], 8.0–8.75 [aromatic region of NN ligand]; δ (^{31}P) = 117.5 [s, $^1J(PtP) = 3341$ Hz].

3.4. $[Me_2Pt(NN\text{-}N)\{P(OPh)_3\}]$, **4**

This was obtained as an approximately 1:1 mixture with complex **3b** by the above procedure used to prepare **3b**, i.e. the reaction of complex *cis*-$[PtMe_2\{P(OPh)_3\}(SMe_2)]$, **1b**, with 2 equiv. of NN. NMR in $CDCl_3$: δ (^1H) = 0.26 [d, $^2J(PtH) = 66.8$ Hz, $^3J(PH) = 11.3$ Hz, 3H, Me ligand *trans* to $P(OPh)_3$], 0.85 [d, $^2J(PtH) = 86.9$ Hz, $^3J(PH) = 9.0$ Hz, 3H, Me ligand *cis* to $P(OPh)_3$], 6.8–7.2 [Ph groups on $P(OPh)_3$ ligand], 7.25–8.75 [aromatic region of NN ligand]; δ(^{31}P) = 119.5 [s, $^1J(PtP) = 3043$ Hz].

3.5. Reaction of *cis*-$[PtMe_2L(SMe_2)]$, **1**, with dppm

In a typical experiment, to a solution of complex *cis*-$[PtMe_2\{P(O^iPr)_3\}(SMe_2)]$, **1a**, (8.6245 mg, 0.0174 mmol) in 10 mL dried benzene was added dppm (3.34 mg, 0.0087 mmol) and the mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure and the resulting oil was washed with *n*-hexane to give a white powder which was identified by ^1H NMR spectroscopy as a 1:1 mixture of $[PtMe_2(dppm)]$ and $[PtMe_2\{P(O^iPr)_3\}_2]$.

3.6. Attempted reaction of MeI with complexes **1** and **2**

In a typical experiment, excess of MeI (1 mL) was added to 10 mg of complex $[PtMe_2\{P(O^iPr)_3\}_2]$, **2a**, (either as solid or in 5 mL of benzene or acetone solutions). The mixture was stirred for 2 h. The solvent was removed and based on the ^1H NMR data of the resulting residue, no reaction had been occurred.

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