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Binuclear dimethylplatinum (II) complexes each containing monodentate phosphine ligands and a bridging diphosphine ligand $X(PPh_2)_2$, X = CH_2 or NH. Molecular structure of *cis*,*cis*-$[Me_2(pyPh_2P)Pt(\mu\text{-}Ph_2PNHPPh_2)Pt(PPh_2py)\ Me_2]\cdot 2CH_2Cl_2$

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Abstract

Displacement of the labile bridging SMe_2 ligand in the organodiplatinum(II) complexes *cis*,*cis*-$[Me_2Pt(\mu\text{-}SMe_2)\{\mu\text{-}X(PPh_2)_2\}PtMe_2]$, in which $X(PPh_2)_2$ is either bis(diphenylphosphino)amine [dppa (X = NH)], **1a**, or bis(diphenylphosphino)methane [dppm (X = CH_2)], **1b**, with 2 equiv of some monodentate phosphine ligands, L, gave a series of organodiplatinum(II) complexes with general formula *cis*,*cis*-$[Me_2LPt(\mu\text{-dppa})PtLMe_2]$[L = PPh_3, **2a**, PPh_2py(2-diphenylphosphinopyridine, PN), **3a**, or $P(O\text{-}^iPr)_3$, **4a**] or *cis*,*cis*-$[Me_2LPt(\mu\text{-dppm})PtLMe_2]$[L = PPh_3, **2b**, PN, **3b**, or $P(O\text{-}^iPr)_3$, **4b**] in good yields. In these complexes the two metallic centers are held together by only one bridging diphosphine ligand with no metal–metal bond. When L is PPh_2Me or $PPhMe_2$, the diplatinum(II) complexes are split to the corresponding monomers, $[PtMe_2\{X(PPh_2)_2\}]$ and *cis*-$[PtMe_2L_2]$. No reaction was observed when L is pyridine or SMe_2. The complexes were fully characterized using multinuclear NMR (^1H, ^{13}C, ^{31}P and ^{195}Pt) methods, and the structure of *cis*,*cis*-$[Me_2(pyPh_2P)Pt(\mu\text{-}Ph_2PNHPPh_2)Pt(PPh_2py)Me_2]\cdot 2CH_2Cl_2$, **3a**, has been determined crystallographically.

Keywords: Platinum; Organoplatinum; Binuclear complexes; Diphosphine ligands

1. Introduction

Binuclear complexes, as the simplest multimetallic systems, are of great interest because the neighboring metals may "cooperate" in promoting difficult reactions, and because electronic interactions between the two metals can lead to distinctive properties [1,2]. In these complexes, the metallic centers are usually held together by two or more bridging ligands and metal–metal bonds may also be involved. Bis(diphenylphosphino)methane (dppm) [3] and the amine analog bis(diphenylphosphino)amine (dppa) [4] are versatile ligands which usually bridge two metal centers in forming binuclear complexes, although there are cases in which they act as chelate or monodentate ligands. There are many similarities, and also some differences, in the coordination chemistry of these two ligands [5]. In the diplatinum complexes containing these ligands, the metallic centers are usually held together by two bridging dppm or dppa ligands and in many cases metal–metal bonds are present as well [3,4,6]. However, recently a number of diplatinum(II) complexes containing two different bridging

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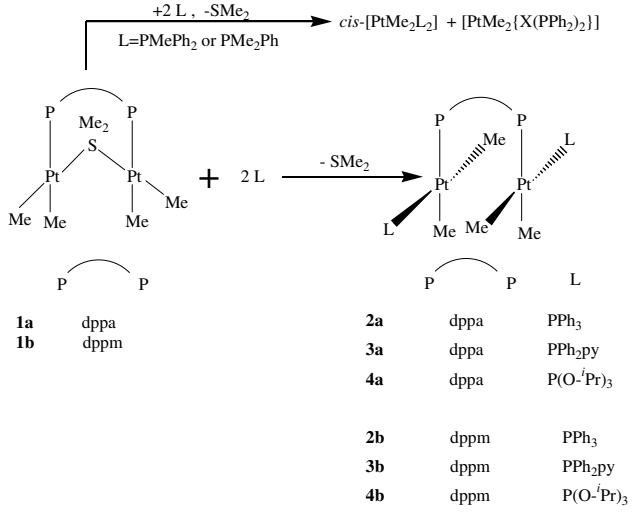
ligands, e.g., *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtMe_2$] [7], [$NBu_4$][$(C_6F_5)_2Pt(\mu\text{-halide})(\mu\text{-}dppm)Pt(C_6F_5)_2$] [8] and a particularly interesting dimeric complex *cis*,*cis*-[$Me_2Pt(\mu\text{-}dppm)(\mu\text{-}dppa)PtMe_2$] (in which a direct comparison of dppm and dppa in equivalent positions was possible) [5], have been reported. In continuation of our interest in making diplatinum complexes of this type, we report a new series of complexes of general formula *cis*,*cis*-[$Me_2LPt\{\mu\text{-}X(PPh_2)_2\}PtLMe_2$], in which $X(PPh_2)_2$ is either dppm($X = CH_2$) or dppa ($X = NH$) and L is a monodentate phosphorus ligand with a relatively large Tolman cone angle, e.g., PPh_3, PPh_2py(2-diphenylphosphinopyridine, PN) or $P(O\text{-}^iPr)_3$ [9]. This indicates that, in this type of dimer, the two metallic centers can be locked together with only one bridging bidentate ligand and with no metal–metal bonding or other bridging ligand present.

2. Results and discussion

2.1. Synthesis of the complexes

As described in Scheme 1, reaction of the dimeric precursors *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppa)PtMe_2$] [5], **1a**, or *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtMe_2$] [7], **1b**, each of which contains a labile bridging SMe_2, with 2 equiv of L (L = PPh_3, PN or $P(O\text{-}^iPr)_3$) in benzene proceeded by displacement of SMe_2 to give after 1 h the desired dimers *cis*,*cis*-[$Me_2LPt\{\mu\text{-}X(PPh_2)_2\}PtLMe_2$], **2**–**4**, in good yields. Note that the reaction with 1 equiv of L gave the same dimer along with 0.5 equiv of unreacted starting dimer. In these unusual dimers, the dinuclear integrity is held by only one bridging ligand $X(PPh_2)_2$ with no metal–metal bonding; each platinum center also bears a monodentate ligand L and two methyl groups.



Scheme 1.

When L is PPh_2Me or $PPhMe_2$ (which have relatively lower cone angles, but higher σ-donor abilities compared to the above mentioned monodentate phosphorus ligands), then the dimers are split into the corresponding monomers [$PtMe_2\{X(PPh_2)_2\}$] and *cis*-[$PtMe_2L_2$]. Pyridine or SMe_2 are unable to displace the bridging labile ligand SMe_2 in complexes **1**, and so no reaction was observed between these reagents and **1**, as monitored by ^1H NMR spectroscopy.

2.2. Characterization of the complexes

The dinuclear complexes were fully characterized by their ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra. In the ^{31}P NMR spectrum of *cis*,*cis*-[$Me_2(Ph_3P)Pt(\mu\text{-}dppa)Pt(PPh_3)Me_2$], **2a** (Fig. 1(b)), the two equivalent phosphorus atoms of dppa resonated as a singlet at $\delta = 60.5$ and showed short range coupling platinum satellites with $^1J(PtP) = 2142$ Hz as well as platinum satellites arising from long range coupling with $^3J(PtP) = 46$ Hz. The splitting in the satellites corresponds to the phosphorus–phosphorus coupling when only one of the platinum atoms is ^{195}Pt with $^2J(PP) = 55$ Hz. No coupling was resolved between the dppa phosphorus and the phosphorus atom of the PPh_3 ligand. A singlet at $\delta = 27.5$ with $^1J(PtP) = 1910$ Hz was assigned to the two phosphorus atoms of the PPh_3 ligands. Note that in ^{31}P NMR spectrum of the dppm analog complex **4b**, *cis*,*cis*-[$Me_2(^iPrO)_3P\}Pt(\mu\text{-}dppm)Pt\{P(O\text{-}^iPr)_3\}Me_2$] (Fig. 1(c)), the coupling between the phosphorus atom of $P(O\text{-}^iPr)_3$ with the phosphorus atom of dppm ($^2J(PP) = 17$ Hz) is also observed. Consistent with these results, the ^{195}Pt NMR spectrum (Fig. 1(a)) showed a doublet of doublets of doublets signal at $\delta = -4672$ that is due the short range coupling of each platinum with two inequivalent phosphorus atoms directly connected to the platinum with $^1J(PtP) = 2148$ Hz and $^1J(PtP) = 1911$ Hz which further couples to the distant dppa phosphorus with $^3J(PtP) = 43$ Hz. In the ^{13}C NMR spectrum of **2a**, the two methyl groups which are attached to the same platinum atom are inequivalent. The carbon atom *trans* to PPh_3 coupled to the *trans* phosphorus and gave a doublet at $\delta = 5.9$ with $^2J(CP_{trans}) = 107$ Hz which further coupled to the *cis* phosphorus of dppa to give a doublet of doublets with $^2J(CP_{cis}) = 8$ Hz. The coupling to ^{195}Pt gave satellites with $^1J(PtC) = 634$ Hz. The carbon atom *trans* to the phosphorus atom of dppa resonated at $\delta = 4.3$ and similarly gave the coupling constants $^1J(PtC) = 634$ Hz and $^2J(CP_{trans}) = 97$ Hz. However, the resonance appeared as a doublet of multiplets (which appeared as a second order pattern) due to the long range coupling to the distant dppa phosphorus atom (4-bond coupling). A similar pattern (Fig. 2) was also observed in the ^{13}C NMR of the $P(O\text{-}^iPr)_3$ analog complex **4a**. The observation of this long range coupling could be attributed to the large PNP angle (see Scheme 2

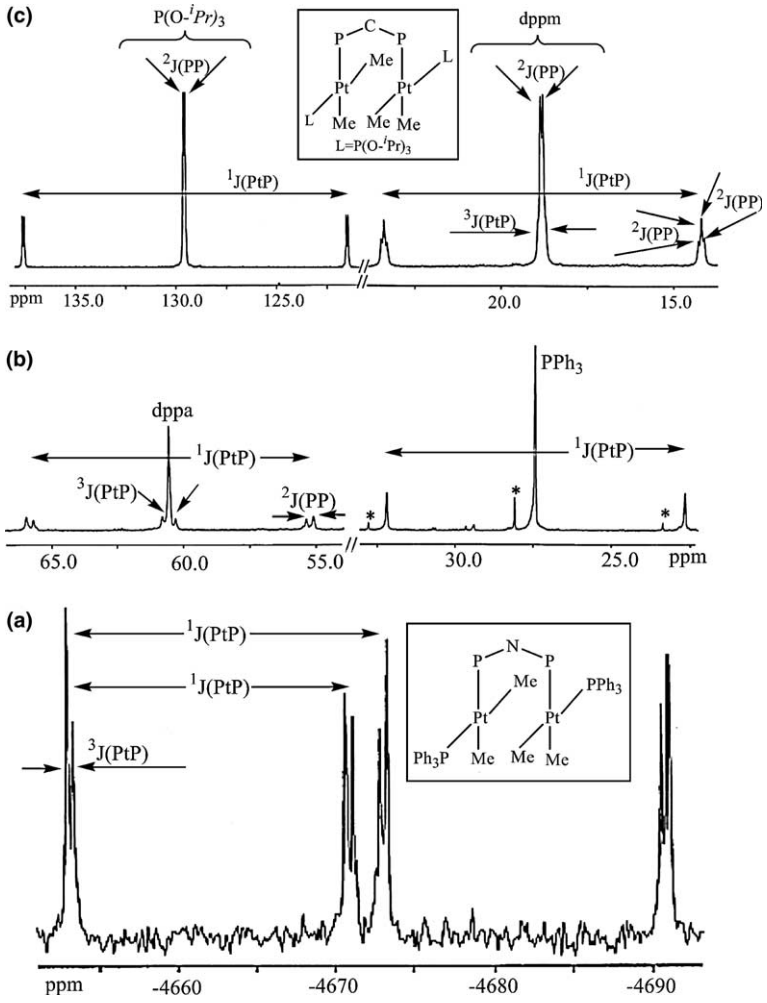


Fig. 1. Selected NMR spectra: (a) the ^{195}Pt resonance for complex **2a** (see the inset) showing the doublet of doublets of doublets pattern arising from two inequivalent ^{1}J(PtP) couplings with further coupling to ^{3}J(PtP); (b) the ^{31}P NMR spectrum for complex **2a** showing two resonances due to the dppa and PPh_3 phosphorus atoms with the corresponding couplings as shown. The asterisks indicate a very small trace of a monomeric impurity and (c) the ^{31}P NMR spectrum for complex **4b** (see the inset) showing the ^{2}J(PP) (phosphorus of P(O-^{i}Pr)$_3$ with phosphorus of dppm) as well.

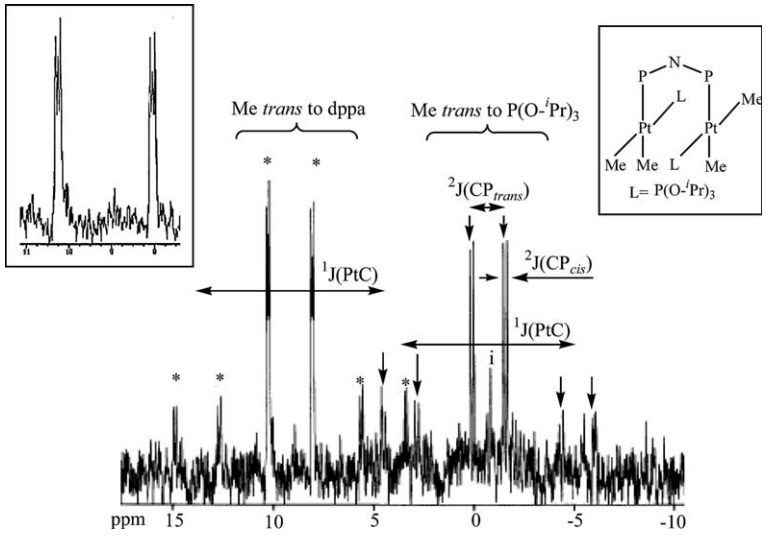
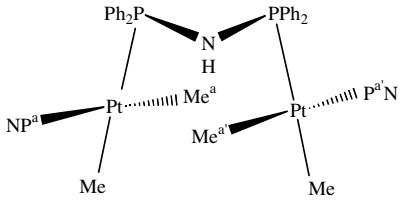


Fig. 2. ^{13}C NMR spectrum of complex **4a** (shown in the right inset). Most of the assignments are indicated. Left inset is the expansion of the region for Me ligand *trans* to dppa. The peak shown by (i) indicates a very small trace of an impurity.



Scheme 2. A Simplified representation of structure of *cis*,*cis*-[Me_2(NP)-Pt(μ-dppa)Pt(PN)Me_2], **3a**.

and the related discussion, which follows shortly). Two triplets with platinum satellites at $\delta = 0.13$[^2J(PtH) = 66.5 Hz and ^3J(PH) = 7.5 Hz] and 0.60[^2J(PtH) = 69.3 Hz and ^3J(PH) = 6.7 Hz] were observed in the ^{1}H NMR spectrum of **2a** for the two inequivalent CH_3 groups on each platinum center. The NH proton resonated as a broad signal at $\delta = 4.87$. The other complexes were similarly characterized and the results are gathered in the experimental section.

The structure of complex *cis*,*cis*-[Me_2(NP)Pt(μ-dppa)-Pt(PN)Me_2], **3a**, was determined crystallographically and is shown in Fig. 3, with selected bond parameters listed in Table 1. Each of the Pt atoms has distorted square planar stereochemistry and the two square planar *cis*-dimethylplatinum(II)-PN units are bridged by the dppa ligand. The distances P–N = 1.684(7) and 1.703(7) Å are similar to the distance in the free ligand dppa [1.692(2) Å] [10]. The two angles NPPt = 104.1(3)° and 105.1(3)° are close to the ideal tetrahedral angle and indicate that there is no significant strain in the complex as opposed to the strain in complex *cis*,*cis*-[Me_2Pt-(μ-dppm)(μ-dppa)PtMe_2] in which the platinum centers are held together by two bridging diphosphine ligands [5]. The angle PNP = 145.1(5)° is very large (cf. the angle PNP = 126.6(5)° in the double bridged dimer just mentioned). This configuration is probably to allow the two very bulky PtP_2C_2 moieties to stay as far away as

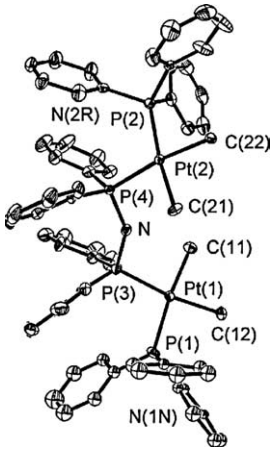


Fig. 3. A view of the structure of *cis*,*cis*-[Me_2(NP)Pt(μ-dppa)Pt(PN)-Me_2], **3a**.

Table 1
Selected bond distances (Å) and angles (°) for complex *cis*,*cis*-[Me_2(NP)Pt(μ-dppa)Pt(PN)Me_2], **3a**

Pt(1)–C(12)	2.097(10)	Pt(1)–C(11)	2.097(9)
Pt(1)–P(1)	2.276(2)	Pt(1)–P(3)	2.309(3)
Pt(2)–C(21)	2.095(8)	Pt(2)–C(22)	2.101(10)
Pt(2)–P(2)	2.287(2)	Pt(2)–P(4)	2.299(2)
P(3)–N	1.684(7)	P(4)–N	1.703(7)
C(12)–Pt(1)–C(11)	83.3(4)	C(12)–Pt(1)–P(1)	89.9(3)
C(11)–Pt(1)–P(3)	88.7(3)	P(1)–Pt(1)–P(3)	98.14(10)
C(21)–Pt(2)–C(22)	84.8(4)	C(22)–Pt(2)–P(2)	87.3(3)
C(21)–Pt(2)–P(4)	88.4(3)	P(2)–Pt(2)–P(4)	99.50(9)
N–P(3)–Pt(1)	105.1(3)	N–P(4)–Pt(2)	104.1(3)
P(3)–N–P(4)	145.1(5)		

possible from each other. This may also be responsible for a nearly 50% increase in the ^3J(PtP) value in the ^{31}P NMR spectrum(see above) as compared to the same coupling in *cis*,*cis*-[Me_2Pt(μ-SMe_2)(μ-dppa)PtMe_2] (46 Hz vs 31 Hz). As expected therefore, the bite separation P3...P4 = 3.23 Å, and the non-bonding Pt...Pt distance of 5.68 Å are greater than the corresponding separations in the double bridged complexes *cis*,*cis*-[Me_2Pt(μ-SMe_2)(μ-dppa)PtMe_2] (3.06 and 3.57 Å, respectively) and *cis*,*cis*-[Me_2Pt(μ-dppm)(μ-dppa)PtMe_2] (3.09 Å and 4.44 Å, respectively). A simplified representation of structure of *cis*,*cis*-[Me_2(NP)Pt(μ-dppa)Pt(PN)Me_2], **3a**, is shown in Scheme 2. The central N atom of PNP ligand is directed towards one of the terminal PN ligands and therefore, as indicated, some of the ligating atoms are inequivalent. However, these atoms appear equivalent in the NMR time scale in the corresponding spectra discussed above. It therefore seems that the simple umbrella like inversion of the ligands about the N atom of PNP can take place in solution to make the whole molecule more symmetrical.

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 500 MHz. References were TMS (^{1}H, ^{13}C), H_3PO_4 (^{31}P), and aqueous K_2PtCl_4 (^{195}Pt), and unless otherwise stated, $CDCl_3$ was used as solvent. All the chemical shifts and coupling constants are in ppm and Hz, respectively. The dimeric precursors *cis*,*cis*-[Me_2Pt(μ-SMe_2)(μ-dppa)PtMe_2] [5], **1a**, and *cis*,*cis*-[Me_2Pt(μ-SMe_2)(μ-dppm)PtMe_2] [7], **1b**, were prepared by the literature methods.

3.1. *cis,cis-[Me₂(Ph₃P)Pt(μ-dppa)Pt(PPh₃)Me₂],* **2a**

A mixture of *cis*,*cis*-[Me_2Pt(μ-SMe_2)(μ-dppa)PtMe_2], **1a**, (70 mg, 0.078 mmol) and PPh_3 (40.89 mg, 0.156 mmol) in benzene (10 ml) was stirred at room

temperature for 1 h. The solvent was removed and the product was washed with *n*-hexane (5 ml) and dried under vacuum. Yield: 77%; m.p. 171–172 °C (decomp.). Anal. Calcd. for $C_{64}H_{63}NP_4Pt_2$: C, 56.51; H, 4.67; N, 1.03. Found: C, 56.8; H, 4.7; N, 1.0%. NMR in $CDCl_3$: $\delta(^1H) = 0.13$ [t, $^2J(PtH) = 66.5$ Hz, $^3J(PH) = 7.5$ Hz, 6H, 2 Me ligands], 0.60 [t, $^2J(PtH) = 69.3$ Hz, $^3J(PH) = 6.7$ Hz, 6 H, 2 Me ligands], 4.87 [br., 1H, NH]; $\delta(^{13}C) = 4.3$ [m, $^1J(PtC) = 634$ Hz, $^2J(CP_{trans}) = 97$ Hz, 2 Me ligands *trans* to dppa], 5.9 [dd, $^1J(PtC) = 634$ Hz, $^2J(CP_{trans}) = 107$ Hz, $^2J(CP_{cis}) = 8$ Hz, 2 Me ligands *trans* to PPh_3]; $\delta(^{31}P) = 27.5$ [s, $^1J(PtP) = 1910$ Hz, PPh_3 ligands], 60.5 [s, $^1J(PtP) = 2142$ Hz, $^3J(PtP) = 46$ Hz, $^2J(PP) = 55$ Hz (dppa-PP), dppa]; $\delta(^{195}Pt) = -4672$ [ddd, $^1J(PtP) = 2148$ Hz, $^1J(PtP) = 1911$ Hz, $^3J(PtP) = 43$ Hz].

The following complexes were made similarly using *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppa})PtMe_2$], **1a**, or *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtMe_2$, **1b**, and 2 equiv of the corresponding L group: *cis*,*cis*-*[Me_2(NP)Pt-(μ-dppa)Pt(PN)Me_2]*, **3a**. Yield: 73%; m.p. 146 °C (decomp.). Anal. Calcd. for $C_{62}H_{61}N_3P_4Pt_2$: C, 54.58; H, 4.47; N, 3.08. Found: C, 54.2; H, 4.2; N, 2.8%. NMR in CD_2Cl_2: $\delta(^1H) = 0.10$ [m, $^2J(PtH) = 66.5$ Hz, $^3J(PH) = 8.2$ Hz, 6H, 2 Me ligands], 0.64 [m, $^2J(PtH) = 69.3$ Hz, $^3J(PH) = 7.4$ Hz, 6H, 2 Me ligands], 5.00 [m, $^3J(PtH) \approx 10$ Hz, $^2J(PH) \approx 5$ Hz, 1H, NH of dppa], 8.15 [d, $^3J(HH) = 4.0$ Hz, 1H, H^6 of PN]; $\delta(^{31}P) = 27.7$ [s, $^1J(PtP) = 1917$ Hz, PN ligands], 63.7 [s, $^1J(PtP) = 2119$ Hz, $^3J(PtP) = 46$ Hz, $^2J(PP) = 56$ Hz (dppa-PP), $^2J(PP) = 6$ Hz, dppa]. *cis*,*cis*-[Me_2(^{i}Pr-O)$_3P$}Pt(μ-dppa)Pt {$P(O\text{-}^i\text{Pr})_3$}$Me_2$], **4a**. Yield: 57%; m.p. 152 °C (decomp.). Anal. Calcd. for $C_{46}H_{75}NO_6P_4Pt_2$: C, 44.12; H, 6.04; N, 1.12. Found: C, 44.6; H, 5.8; N, 1.1%. NMR in $CDCl_3$: $\delta(^1H) = 0.35$ [t, $^2J(PtH) = 60.0$ Hz, $^3J(PH) = 7.0$ Hz, 12H, 4 Me ligands], 0.72 [d, $^3J(HH) = 6.1$ Hz, 24H, 6 Me groups of ^{i}Pr groups], 4.31 [br., 6H, 6 CH groups of ^{i}Pr groups], 4.93 [br., 1H, NH]; $\delta(^{13}C) = -0.8$ [dd, $^1J(PtC) = 560$ Hz, $^2J(CP_{trans}) = 106$ Hz, $^2J(CP_{cis}) = 11$ Hz, 2 Me ligands *trans* to $P(O\text{-}^i\text{Pr})_3$], 9.1 [m, $^1J(PtC) = 588$ Hz, $^2J(CP_{trans}) = 139$ Hz, 2 Me ligands *trans* to dppa]; $\delta(^{31}P) = 65.0$ [s, $^1J(PtP)$=2078 Hz, $^3J(PtP) = 23$ Hz, $^2J(PP) = 14$ Hz, $^2J(PP) = 58$ Hz, dppa], 131.4 [s, $^1J(PtP) = 3242$ Hz, $^2J(PP) = 14$ Hz, $P(O\text{-}^i\text{Pr})_3$ ligands]; $\delta(^{195}Pt) = -4599$ [dd, $^1J(PtP) = 3247$ Hz, $^1J(PtP) = 2107$ Hz]. *cis*,*cis*-[Me_2(Ph_3P)Pt(μ-dppm)Pt-(PPh_3)Me_2], **2b**. Yield: 81%; m.p. 164–176 °C (decomp.). Anal. Calcd. for $C_{65}H_{64}P_4Pt_2$: C, 57.44; H, 4.75. Found: C, 58.2; H, 4.8%. NMR in $CDCl_3$: $\delta(^1H) = 0.31$ [t, $^2J(PtH) = 68.8$ Hz, $^3J(PH) = 9.7$ Hz, 6H, 2 Me ligands], 0.37 [t, $^2J(PtH) = 55.7$ Hz, $^3J(PH) = 6.7$ Hz, 6H, 2 Me ligands], 3.14 [m, $^3J(PtH) \approx 32$ Hz, $^2J(PH) = 8.1$ Hz, 2H, CH_2 of dppm]; $\delta(^{13}C) = 7.0$ [dd, $^1J(PtC) = 621$ Hz, $^2J(CP_{trans}) = 106$ Hz, $^2J(CP_{cis})$ = not measured, 2 Me ligands], 7.9 [dd, $^1J(PtC) = 637$ Hz, $^2J(CP_{trans}) = 104$ Hz, ^2J(CPtextsubscript*cis*) = not measured, 2 Me ligands], 24.7 [br. s, CH_2 of dppm]; $\delta(^{31}P) = 27.3$ [m, $^1J(PtP) = 1880$ Hz, $^2J(PP) = 9$ Hz, PPh_3ligands], 17.6 [s, $^1J(PtP) = 1904$ Hz, $^3J(PtP) = 18$ Hz, $^2J(PP) = 9$ Hz, $^2J(PP) = 21$ Hz(dppm-PP), dppm]; $\delta(^{195}Pt) = -4718$ [t, $^1J(PtP) = 1892$ Hz]. *cis*,*cis*-[Me_2(*NP*) *Pt*(μ-dppm)*Pt*(*PN*)-Me_2], **3b**. Yield: 86%. NMR in $CDCl_3$: $\delta(^1H) = 0.00$ [m, $^2J(PtH) = 66.0$ Hz, $^3J(PH) = 7.9$ Hz, 6H, 2 Me ligands], 0.13 [m, $^2J(PtH) = 69.3$ Hz, $^3J(PH) = 7.7$ Hz, 6H, 2 Me ligands], 3.37 [m, $^3J(PtH) = 18.0$ Hz, $^2J(PH) = 9.0$ Hz, 2H, CH_2 of dppm], 8.10 [d, $^3J(HH) = 4.2$ Hz, 1H, H^6 of PN]; $\delta(^{31}P) = 18.4$ [s, $^1J(PtP) = 1924$ Hz, $^3J(PtP)$ = not resolved, $^2J(PP) = 20$ Hz (dppm-PP), dppm], 26.8 [s, $^1J(PtP) = 1873$ Hz, PN ligands]; $\delta(^{195}Pt) = -4720$ [dd, $^1J(PtP) = 1914$ Hz, $^1J(PtP) = 1882$ Hz]. *cis*,*cis*-[Me_2(^{i}Pr-O)$_3P$}Pt(μ-dppm)Pt {$P(O\text{-}^i\text{Pr})_3$}$Me_2$], **4b**. Yield: 52%; m.p. 154 °C (decomp.). Anal. Calcd. for: $C_{47}H_{76}O_6P_4Pt_2$: C, 45.12; H, 6.12. Found: C, 45.0; H, 6.0%. NMR in $CDCl_3$: $\delta(^1H) = 0.13$ [t, $^2J(PtH) = 64.5$ Hz, $^3J(PH) = 8.9$ Hz, 6H, 2 Me ligands], 0.42 [t, $^2J(PtH) = 70.8$ Hz, $^3J(PH) = 7.1$ Hz, 6H, 2 Me ligands], 0.84 [d, $^3J(HH) = 5.9$ Hz, 24 H, 6 Me groups of ^{i}Pr groups], 4.41 [br., 6H, 6 CH groups of ^{i}Pr groups], 3.96 [m, $^3J(PtH) = 20.0$ Hz, $^2J(PH) = 9.8$ Hz, 2H, CH_2 of dppm]; $\delta(^{13}C) = -2.8$ [dd, $^1J(PtC) = 584$ Hz, $^2J(CP_{trans}) = 99$ Hz, $^2J(CP_{cis}) = 11$ Hz, 2 Me ligands *trans* to $P(O\text{-}^i\text{Pr})_3$], 8.9 [dd, $^1J(PtC) = 586$ Hz, $^2J(CP_{trans}) = 142$ Hz, $^2J(CP_{cis}) = 7$ Hz, 2 Me ligands *trans* to dppm]; $\delta(^{31}P) = 18.8$ [s, $^1J(PtP) = 1860$ Hz, $^3J(PtP)$ = not resolved, $^2J(PP) = 18$ Hz (dppm-PP), $^2J(PP) = 17$ Hz (phosphorus of $P(O\text{-}^i\text{Pr})_3$with phosphorus of dppm), dppm], 129.7 [s, $^1J(PtP) = 3232$ Hz, $^2J(PP) = 17$ Hz (phosphorus of $P(O\text{-}^i\text{Pr})_3$ with phosphorus of dppm), $P(O\text{-}^i\text{Pr})_3$ ligands]; $\delta(^{195}Pt) = -4635$ [dd, $^1J(PtP) = 1860$ Hz, $^1J(PtP) = 3226$ Hz].

3.2. Reaction of *cis,cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppa})PtMe_2$], **1a**, with $PPhMe_2$

A mixture of *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppa})PtMe_2$], **1a**, (50 mg, 0.056 mmol) and $PPhMe_2$(17 μl, 0.111 mmol) in benzene (15 ml) was stirred at room temperature for 1 h. The solvent was removed and the product was washed with *n*-hexane (5 ml) and dried under vacuum. The product was identified as an equivalent mixture of the monomers *cis*-[$PtMe_2(PPhMe_2)_2$] and [$PtMe_2$(dppa)] as confirmed by its ^1H NMR spectrum [5,11].

Similar results were obtained for the reactions of complex **1a** with PPh_2Me and complex *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtMe_2$, **1b**, with PPh_2Me and the resulting monomers were identified by their ^1H NMR spectra [11,12].

Table 2
Crystal data and structure refinement for **3a**

Formula	$C_{62}H_{61}N_3P_4Pt_2$
Formula weight	1362.20
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pca2*(1)
a (Å)	16.2101(2)
b (Å)	18.3159(2)
c (Å)	18.6612(3)
β (°)	90
Volume (Å^3)	5540.56(13)
Z	4
D(calc) (Mg m^{-3})	1.633
Absorption coefficient (mm^{-1})	5.202
F(000)	2680
Number of reflections	58499
Number of independent reflections	12248 [*R*(int) = 0.100]
Absorption correction	Integration
GOOF (F^2)	0.994
R_1, wR_2 [$I > 2\sigma(I)$]	0.0491, 0.0990
R_1, wR_2 (all data)	0.0928, 0.1124

3.3. X-ray structure determination

Crystals of *cis*,*cis*-[Me_2(NP)Pt(μ-dppa)Pt(PN)Me_2], **3a**, were grown from a concentrated methylene chloride solution by slow diffusion of hexane. A colourless shoebox was mounted on a glass fiber. Data were collected at 200 K using a Nonius Kappa-CCD diffractometer with COLLECT software (Nonius B.V., 1998). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO (Nonius B.V., 1998). The data were scaled using SCALEPACK (Nonius B.V., 1998). The crystal data and structure refinement parameters are listed in Table 2. The reflection data and systematic absences were consistent with an orthorhombic space group: *Pca2* (1).

The SHELXTL-NT V5.1 (Sheldrick, G.M.) suite of programs was used to solve the structure by Patterson. Subsequent difference Fouriers allowed the remaining atoms to be located. The molecule was reasonably well behaved. There was some disorder of the aromatic rings on P1. Each of the three rings was modeled as a 50/50 mixture of isotropic atoms. All of the remaining non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. N2R (not C2N) was determined to be the nitrogen atom by examining the thermal parameters when both were refined as carbon atoms. The absolute structure parameter refined to a value of 0.50(1).

The largest residue electron density peak (3.008) was associated with one of the platinum atoms. Full-matrix least squares refinement on F^2 gave $R_1 = 4.91$ for 2σ data and $wR_2 = 11.24$ for all data (GOOF = 0.994).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 256450. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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