

A comparison of binuclear dimethylplatinum(II) complexes with the bridging ligands X(PPh₂)₂, X = CH₂ or NH

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The reaction of [Pt₂Me₄(μ-SMe₂)₂], **1**, with dppa = Ph₂PNHPPH₂ gave the complex [Pt₂Me₄(μ-SMe₂)(μ-dppa)] and, with more dppa, a mixture of the binuclear complex [Pt₂Me₄(μ-dppa)₂] and the mononuclear complex [PtMe₂(dppa)]. In contrast, reaction of [Pt₂Me₄(μ-SMe₂)(μ-dppa)] with dppm = Ph₂CH₂PPh₂ or of [Pt₂Me₄(μ-SMe₂)(μ-dppm)] with dppa gave only the binuclear complex [Pt₂Me₄(μ-dppm)(μ-dppa)]. This unusual complex, which has both bridging dppm and dppa ligands in equivalent positions in an organometallic complex, is more inert to rearrangement to mononuclear complexes, [PtMe₂(dppm)] and [PtMe₂(dppa)], than either symmetrical complex [Pt₂Me₄(μ-dppm)₂] or [Pt₂Me₄(μ-dppa)₂]. A combination of structural and NMR evidence indicates that all binuclear dimethylplatinum(II) complexes adopt a twist boat conformation, and the activation energy for fluxionality *via* a boat intermediate follows the series [Pt₂Me₄(μ-dppm)₂] >> [Pt₂Me₄(μ-dppm)(μ-dppa)] > [Pt₂Me₄(μ-dppa)₂].

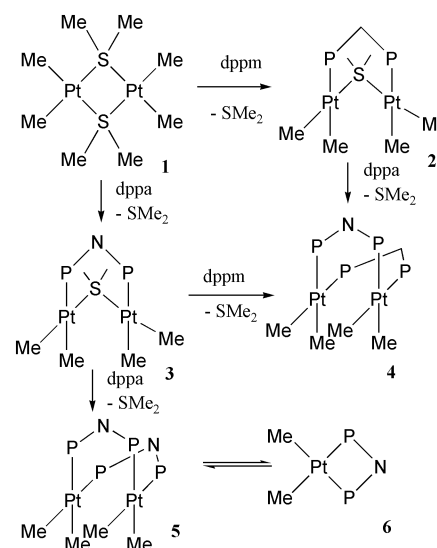
Introduction

The ligands X(PPh₂)₂ with X = CH₂ (dppm), or NH (dppa) are commonly used in stabilizing the types of binuclear organo-transition metal complexes that have given insights into several binuclear bond activation processes. These ligands are easy to obtain and to use and, since their chelate complexes contain strained 4-membered rings, they have a strong tendency to act as bridging ligands. There are several reviews of the applications of both dppm¹ and dppa² in binuclear organometallic and coordination chemistry, and the relative abilities of these ligands to stabilize binuclear *versus* mononuclear complexes has been much debated.³ Two ways to gain insight into this subtle issue are to examine complexes in which there is an equilibrium between monomer and dimer, and to compare structures of pairs of complexes with the two ligands so that the relative strain energies can be assessed. There are many structures of complexes with bridging dppm and dppa ligands, but there appear to be none in which there are bridging dppm and dppa ligands in the same complex and in equivalent bonding sites, though there are several complexes containing both ligands in inequivalent sites.¹⁻³ For example, there is an interesting cluster complex [Pd₄(μ-Cl)₂(μ-dppm)₂(μ-dppa)₂]²⁺, having a rectangle of palladium atoms, in which the dppa ligands span shorter edges with Pd-Pd = 2.61 Å, while dppm ligands span the longer edges with Pd-Pd = 3.72 Å.³ The angles PNP = 113.5° for dppa and PCP = 118.9° for dppm are correspondingly smaller and larger, respectively, compared to the free ligands, with free dppa having PNP = 118.9(2)° and dppm having PCP = 106.2(3)°.^{4,5} This case is an exception to the general rule that the angle PXP is greater in dppa (PNP) than in dppm (PCP) complexes, with typical angles in the region of 119 and 107°, close to the ideal trigonal and tetrahedral angles, respectively.¹⁻⁸ This article reports new binuclear dimethylplatinum(II) complexes with bridging dppa ligands, including the complex [Pt₂Me₄(μ-dppm)(μ-dppa)], in which a direct comparison of dppm and dppa in equivalent positions is possible.

Results

Tetramethyldiplatinum complex chemistry

The synthetic chemistry for tetramethyldiplatinum(II) complexes is outlined in Scheme 1. The conversion of the precursor

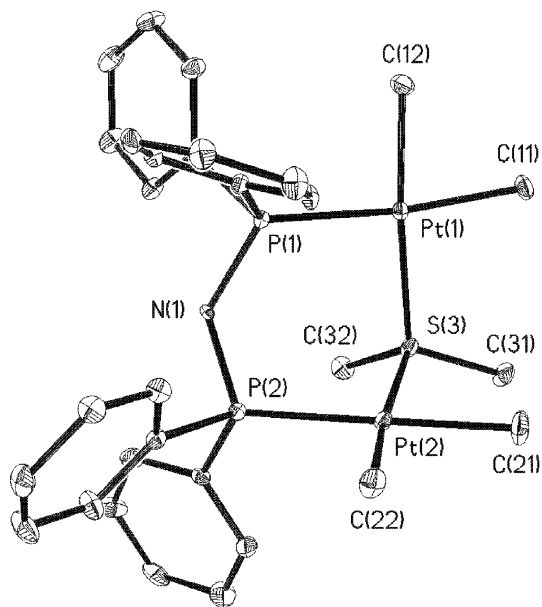


Scheme 1

complex [Pt₂Me₄(μ-SMe₂)₂], **1**,⁹ to the dppm bridged dimer [Pt₂Me₄(μ-SMe₂)(μ-dppm)], **2**, was carried out as reported earlier,^{10,11} and the analogous procedure using dppa gave the complex [Pt₂Me₄(μ-SMe₂)(μ-dppa)], **3**. Complex **3** was fully characterized by its ¹H, ¹³C, ³¹P and ¹⁹⁵Pt NMR spectra. The presence of a single bridging diphosphine ligand was demonstrated most simply by the ¹⁹⁵Pt NMR spectrum, which appeared as a doublet of doublets due to the couplings ¹J(PtP) = 2088 Hz and ³J(PtP) = 31 Hz. The presence of a bridging dimethylsulfide ligand was shown by the appearance of the MeS resonance in the ¹H NMR spectra as a 1 : 8 : 18 : 8 : 1 quintet due to coupling to two adjacent ¹⁹⁵Pt atoms with ³J(PtH) = 20 Hz.¹⁰ The two methylsulfur groups are effectively equivalent by NMR. Finally there were two equal intensity methylplatinum resonances in each of the ¹H and ¹³C NMR spectra; the coupling ¹J(PtC) = 729 Hz for the methyl group *trans* to sulfur was greater than the value ¹J(PtC) = 640 Hz for the methyl group *trans* to phosphorus, and the same trend was observed for the proton resonances (see Experimental). These couplings are strongly influenced by the *trans* ligand with *trans*-influence of P > S. The detailed geometry was confirmed by a structure determination, as shown in Fig. 1 and with selected bond distances and angles in Table 1.

Table 1 Selected bond distances (Å) and angles (°) for complex **3**

Pt(1)–C(12)	2.073(6)	Pt(2)–C(22)	2.048(6)
Pt(1)–C(11)	2.086(5)	Pt(2)–C(21)	2.094(5)
Pt(1)–P(1)	2.276(1)	Pt(2)–P(2)	2.274(1)
Pt(1)–S(3)	2.318(2)	Pt(2)–S(3)	2.341(1)
P(1)–N(1)	1.706(5)	P(2)–N(1)	1.708(4)
C(12)–Pt(1)–C(11)	83.4(2)	C(22)–Pt(2)–C(21)	84.8(3)
C(12)–Pt(1)–P(1)	88.8(2)	C(22)–Pt(2)–P(2)	93.4(2)
C(11)–Pt(1)–P(1)	172.1(2)	C(21)–Pt(2)–P(2)	177.7(2)
C(12)–Pt(1)–S(3)	175.1(2)	C(22)–Pt(2)–S(3)	172.1(2)
C(11)–Pt(1)–S(3)	92.9(2)	C(21)–Pt(2)–S(3)	88.9(2)
P(1)–Pt(1)–S(3)	94.82(5)	P(2)–Pt(2)–S(3)	92.74(5)
N(1)–P(1)–Pt(1)	121.5(1)	N(1)–P(2)–Pt(2)	112.3(2)
Pt(1)–S(3)–Pt(2)	99.87(5)	P(1)–N(1)–P(2)	127.4(3)

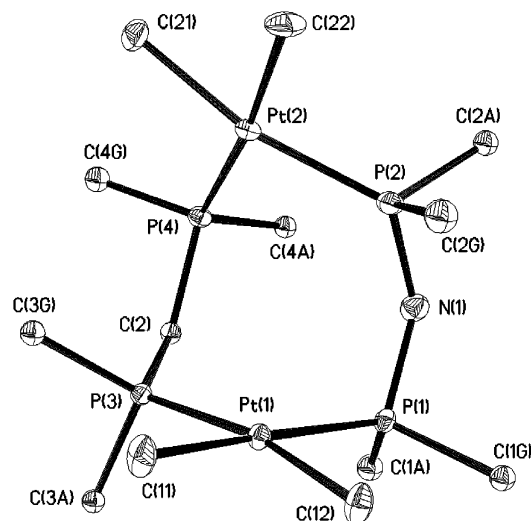
**Fig. 1** A view of the structure of complex **3**.

The platinum atoms are present in a 6-membered ring defined by the atoms Pt(1)S(3)Pt(2)P(2)N(1)P(1), of which all but the sulfur atom are roughly coplanar. Each platinum atom has distorted square planar stereochemistry with *cis*-PtMe₂PS coordination. The geometry of the bridging dimethylsulfide ligand in **3** [PtS = 2.318(2), 2.341(1) Å, PtSPt = 99.87(5)°] is similar to that in [Pt₂Me₄(μ-SMe₂)₂], **1** [PtS = 2.354(3) Å, PtSPt = 100.3(1)°], and the non-bonding Pt ⋯ Pt distances are also similar [3.566 and 3.615 Å in **3** and **1**, respectively].⁹ For the dppa ligand in **3**, the bite separation P1 ⋯ P2 = 3.06 Å is shorter than the separation Pt1 ⋯ Pt2 = 3.566 Å, and the angles PNP = 127.4(3) and NPt = 121.5(1), 112.3(2)° are all greater than tetrahedral in order to accommodate this difference. The distances P–N = 1.706(5), 1.708(4) Å are similar to the distance in the free ligand [1.692(2) Å].⁴

The complex [Pt₂Me₄(μ-dppm)(μ-dppa)], **4**, was prepared in good yield either by reaction of complex **3** with dppm or by reaction of **2** with dppa (Scheme 1). The complex is thermally stable in solution even in boiling benzene and it does not disproportionate to give the symmetrical complexes [Pt₂Me₄(μ-dppm)₂] and [Pt₂Me₄(μ-dppa)₂]. The complex [Pt₂Me₄(μ-dppm)₂] is known to rearrange quantitatively to give the monomer [PtMe₂(dppm)] on heating to 60 °C in benzene solution, containing dimethylsulfide as catalyst, for two days.⁷ Under the same conditions, complex **4** showed no detectable reaction, though on heating to 100 °C in a sealed NMR tube about 5% conversion to a mixture of the monomers [PtMe₂(dppm)] and [PtMe₂(dppa)] occurred in two hours. Complex **4** is thus more inert to rearrangement to the monomers than is the symmetrical complex [Pt₂Me₄(μ-dppm)₂]. The structure of complex **4** was determined and is shown in Fig. 2,

Table 2 Selected bond distances (Å) and angles (°) for complex **4**·CH₂Cl₂

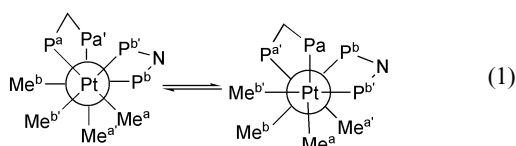
Pt(1)–C(12)	2.09(1)	Pt(1)–C(11)	2.107(9)
Pt(1)–P(1)	2.273(2)	Pt(1)–P(3)	2.290(2)
Pt(2)–C(21)	2.11(1)	Pt(2)–C(22)	2.11(1)
Pt(2)–P(2)	2.270(3)	Pt(2)–P(4)	2.291(2)
P(1)–N(1)	1.727(8)	P(2)–N(1)	1.731(8)
P(3)–C(2)	1.800(8)	P(4)–C(2)	1.816(8)
C(12)–Pt(1)–C(11)	83.2(4)	C(12)–Pt(1)–P(1)	90.0(3)
C(11)–Pt(1)–P(3)	87.8(3)	P(1)–Pt(1)–P(3)	99.21(8)
C(21)–Pt(2)–C(22)	81.1(4)	C(22)–Pt(2)–P(2)	88.4(3)
C(21)–Pt(2)–P(4)	91.9(3)	P(2)–Pt(2)–P(4)	98.35(9)
N(1)–P(1)–Pt(1)	115.0(3)	C(2)–P(3)–Pt(1)	121.5(3)
N(1)–P(2)–Pt(2)	123.0(3)	C(2)–P(4)–Pt(2)	120.7(3)
P(1)–N(1)–P(2)	126.6(5)	P(3)–C(2)–P(4)	123.5(5)

**Fig. 2** A view of the structure of complex **4**, emphasizing the twist-boat conformation. Only the *ipso*-carbon atoms of the phenyl rings are shown, for clarity.

with selected bond parameters listed in Table 2. The conformation of the complex can be described as a twist-boat, in which two square planar *cis*-dimethylplatinum(II) units are bridged by the dppm and dppa ligands. This conformation is similar to that found in [Pt₂Me₄(μ-dppm)₂], but different from the extended chair conformation found in [Pt₂Me₄(μ-dmpm)₂], dmpm = dppm = Me₂CH₂PMe₂.⁷ The conformation can be defined by the torsion angles in the 8-membered ring. For the twist-boat conformation of cyclooctane there are two torsion angles of 38 and 65°, while for [Pt₂Me₄(μ-dppm)₂] the torsion angles cluster around values of 22(1) and 73(1)°. The corresponding torsion angles for complex **4** are 18(3) and 74(4)°, but with a considerably greater range of torsion angles than in [Pt₂Me₄(μ-dppm)₂], as a result of the different bridging ligands. The structure for **4** is thus more distorted. The bite distances of the diphosphine ligands [3.088 Å for dppa, 3.186 Å for dppm] and the Pt ⋯ Pt separation [4.440 Å] in **4** are also similar to those in [Pt₂Me₄(μ-dppm)₂], which has P ⋯ P = 3.18 and 3.20 Å and Pt ⋯ Pt = 4.198 Å.⁷ In the structure of **4** there was disorder of some of the phenyl groups that was resolved. Disorder of the dppm and dppa ligands might be expected, given their similar steric profiles. The bridging N and C atoms were placed based on the better fit with the electron densities, and no disorder was resolved, but it is possible that some unresolved disorder might be present. With the assignment given, the distances in the PNP group with P–N = 1.727(8) and 1.731(8) Å are shorter than the distances in the PCP group of dppm with P–C = 1.800(8) and 1.816(8) Å, consistent with the trend in the free ligands dppa and dppm in which have mean P–N = 1.692(2) Å and P–C = 1.858(5) Å, respectively.⁴ The angle PNP = 126.6(5)° is slightly greater than the angle PCP = 123.5(5)°, as

expected, but the PCP angle is greater than those for $[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})_2]$ of 120(2) and 117(2)°. The two angles NPt = 115.0(3) and 123.0(3) of dppa are significantly different whereas the analogous angles CPt = 121.5(3) and 120.7(3)° are similar, but all of these angles at phosphorus are greater than the ideal tetrahedral angle. These angles are an indication of strain in the complex, perhaps arising from the different preferred geometries of the two bridging ligands. There was no evidence of strong intermolecular interactions in the lattice that might affect the conformation.

Complex **4** was fluxional, as shown by the variable temperature NMR spectra. At room temperature, there was a single resonance in the ^{31}P NMR spectrum for each of the dppm and dppa ligands, but the resonance for the dppa phosphorus atoms was broad (Fig. 3). At lower temperature, the dppa resonance broadened further then split into two resonances at $\delta(^{31}\text{P}) = 45.8$ [$^1J(\text{PtP}) = 2078$ Hz] and 69.0 [$^1J(\text{PtP}) = 2064$ Hz], and then the dppm resonance also broadened and split into two resonances at $\delta(^{31}\text{P}) = 10.4$ [$^1J(\text{PtP}) = 1940$ Hz] and 12.1 [$^1J(\text{PtP}) = 1742$ Hz]. These spectra are readily interpreted in terms of the fluxional process shown in eqn. (1), in which two twist-boat conformers equilibrate through an intermediate boat conformer. In addition, since ^{31}P chemical shifts are strongly influenced by distortions of the angles at phosphorus,¹² the larger difference in ^{31}P chemical shifts for the dppa phosphorus atoms is fully consistent with the solid state structure discussed above, showing greater differences in angles at the two phosphorus atoms of dppa, and suggests that this structure is a good approximation of the ground state solution structure. The activation energy for the fluxional process of eqn. (1) was calculated to be $\Delta G^* =$



42.1(1) kJ mol^{-1} from the coalescence of the dppm resonances at 223 K or the dppa resonances at 249 K. The activation energy is markedly lower than for the similar fluxional process in $[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})_2]$ for which $\Delta G^* = 54.7(4)$ kJ mol^{-1} at 283 K.⁷

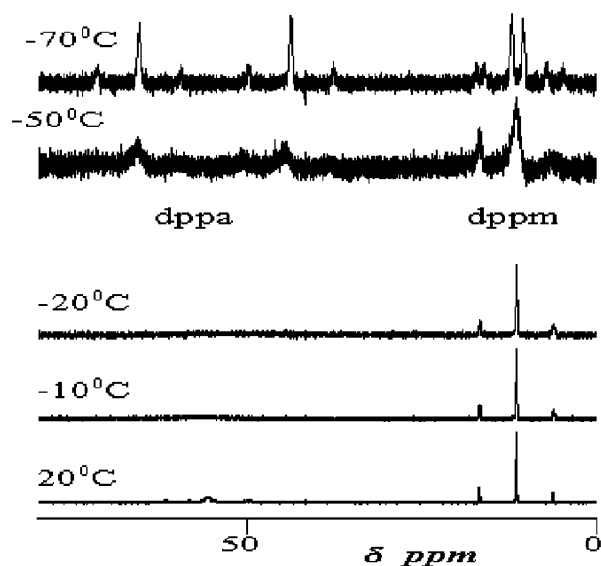


Fig. 3 Variable temperature ^{31}P NMR spectra of complex **4**, showing that at low temperature all phosphorus atoms are non-equivalent.

The reaction of complex **1** with two equivalents of dppa or of complex **3** with one equivalent of dppa gave a mixture of the binuclear complex $[\text{Pt}_2\text{Me}_4(\mu\text{-dppa})_2]$, **5**, and the mononuclear complex $[\text{PtMe}_2(\text{dppa})]$, **6**. Once formed, the composition of

the mixture did not change in solution at room temperature but different syntheses gave varying ratios of products **5** and **6**. It was not possible to separate the mixture by recrystallization and so the compounds were characterized as the isomeric mixture. When a mixture of **5** and **6** in C_6D_6 was heated to 70 °C for one hour in the presence of dimethylsulfide as catalyst, complete conversion to the monomer **6** was observed, as monitored by NMR, and so it is clear that **6** is the thermodynamically stable form. Each complex **5** and **6** gave a single methylplatinum resonance and a single NH resonance in the ^1H NMR spectrum (Fig. 4). There was a particularly large difference in chemical shifts and coupling constants to the platinum of the NH resonances as seen in Fig. 4. This resonance for complex **5** appeared as a 1 : 8 : 18 : 8 : 1 quintet, at $\delta = 3.11$ with $^3J(\text{PtH}) = 21$ Hz, as a result of coupling to two platinum centers. For complex **6**, the NH resonance was at $\delta = 5.56$ with a much larger coupling constant $^3J(\text{PtH}) = 63$ Hz; it appeared as a triplet as a result of coupling to phosphorus with $^2J(\text{PH}) = 9$ Hz and the pattern arising from coupling to ^{195}Pt was a 1 : 4 : 1 triplet as expected for coupling to a single platinum atom. Fig. 5 illustrates the single resonance for each complex in the ^{31}P NMR spectrum at room temperature. The spectra for **5** are broader than for **6**, as a result of fluxionality similar to that described above for the binuclear complexes **4** and $[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})_2]$, and the resonance is split in the spectrum shown at -70 °C (Fig. 5). The activation energy for fluxionality was $\Delta G^* = 40.7(2)$ kJ mol^{-1} , which is slightly lower than that for complex **4** of 42.1(1) kJ mol^{-1} .

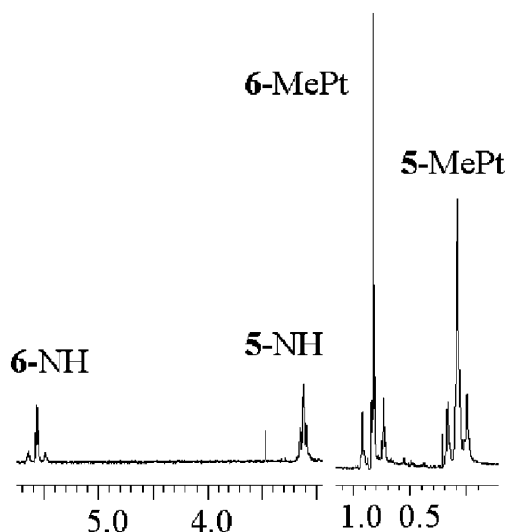


Fig. 4 Characterization of the mixture of complexes **5** and **6** by ^1H NMR spectroscopy at 20 °C. Note the difference in chemical shifts of the NH protons and the different intensities and coupling constants associated with the ^{195}Pt satellite spectra.

The mixture of complexes **5** and **6** was thermally stable but slow hydrolysis occurred in moist solvent. Thus, when a solution containing a mixture of complexes **5** and **6** in benzene was exposed to moist air, crystals of the insoluble complex $[\text{PtMe}(\text{dppa})(\text{PPh}_2\text{O})]$, **7**,¹³ slowly deposited.

Discussion

This work has shown that the ligands dppm and dppa have similar bridging *versus* chelating properties in the complexes $[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})_2]$ and $[\text{Pt}_2\text{Me}_4(\mu\text{-dppa})_2]$, despite the differences in structure and bonding of the free ligands. Thus both complexes rearrange to the respective monomers on heating at 60–80 °C in benzene solution with dimethyl sulfide as catalyst. Curiously, the mixed ligand complex $[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})(\mu\text{-dppa})]$ was less reactive to rearrangement to $[\text{PtMe}_2(\text{dppm})]$

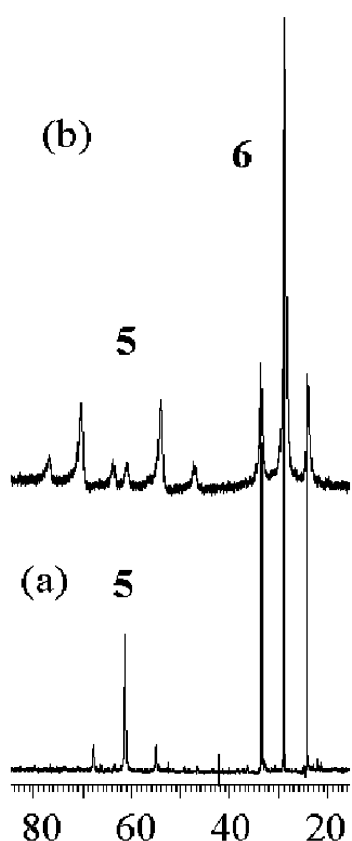


Fig. 5 The ^{31}P NMR spectra of a mixture of complexes **5** and **6**, illustrating the fluxionality of the binuclear complex **5**: (a) spectrum at 20 °C; (b) spectrum at -70 °C.

and $[\text{PtMe}_2(\text{dppa})]$ than either symmetrical complex; it reacted only slowly at 100 °C. The differences appear to be largely kinetic in nature and the chelate monomer is the thermodynamically stable form in solution in each case. All three binuclear complexes adopt a twist-boat conformation and the activation energy for fluxionality by way of a boat (or saddle) intermediate followed the series $[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})_2] \gg [\text{Pt}_2\text{Me}_4(\mu\text{-dppm})(\mu\text{-dppa})] > [\text{Pt}_2\text{Me}_4(\mu\text{-dppa})_2]$, illustrating that there is a significant difference in conformational mobility between bridging dppm and dppa ligands.

Experimental

^1H , ^{13}C and ^{31}P NMR spectra were recorded as solutions in CD_2Cl_2 by using Varian Mercury 400 or Inova 400 spectrometers, while the ^{195}Pt NMR spectrum was recorded using a Bruker Avance DRX 500 MHz spectrometer. The spectra are referenced with respect to TMS (^1H , ^{13}C), H_3PO_4 (^{31}P) or aqueous $\text{K}_2[\text{PtCl}_4]$ (^{195}Pt). The complexes $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$ and $\text{cis,cis-}[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)(\mu\text{-dppm})]$ were prepared by the literature methods.^{9,10}

*cis,cis-}[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)(\mu\text{-dppa})], **3***

A solution of $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$ (1.00 g, 1.73 mmol) and dppa (0.700 g, 1.73 mmol) in C_6H_6 (100 mL) was stirred for 1 h. The solvent was removed and the product was washed with MeOH (2 × 5 mL) and dried under vacuum. Yield: 90%; mp 166–168 °C. Anal. Calcd. for $\text{C}_{30}\text{H}_{39}\text{NP}_2\text{Pt}_2\text{S}$: C, 40.1; H, 4.3; N, 1.6. Found: C, 39.7; H, 4.6; N, 1.5%. NMR in CD_2Cl_2 : $\delta(^1\text{H}) = 0.11$ [m, 6H, $^2J(\text{PtH}) = 85$ Hz, $^3J(\text{PH}) = 10$ Hz, Me *trans* to S]; 0.26 [m, 6H, $^2J(\text{PtH}) = 57$ Hz, $^3J(\text{PH}) = 8$ Hz, Me *trans* to P]; 2.56 [s, 6H, $^3J(\text{PtH}) = 20$ Hz, SMe_2]; 3.10 [m, 1H, $^3J(\text{PtH}) = 28$ Hz, $^2J(\text{PH}) = 8$ Hz, NH]; $\delta(^{13}\text{C}) = 0.0$ [s, $^1J(\text{PtC}) = 729$ Hz, Me *trans* to S]; 11.5 [d, $^1J(\text{PtC}) = 640$ Hz, $^2J(\text{PC}) = 111$ Hz, Me *trans* to P]; 31.2 [s, $^2J(\text{PtC}) = 6$ Hz, MeS]; $\delta(^{31}\text{P}) = 63.9$ [s, $^1J(\text{PtP}) = 2088$ Hz,

$^3J(\text{PtP}) = 31$ Hz, $^2J(\text{PP}) = 47$ Hz, dppa]; $\delta(^{195}\text{Pt}) = -4388$ [dd, $^1J(\text{PtP}) = 2088$ Hz, $^3J(\text{PtP}) = 31$ Hz, Pt].

*cis,cis-}[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})(\mu\text{-dppa})], **4***

A mixture of $\text{cis,cis-}[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)(\mu\text{-dppa})]$, **3**, (150 mg, 0.167 mmol) and dppm (65 mg, 0.167 mmol) in C_6H_6 (20 mL) was stirred for 1 h. The solvent was removed and the product was washed with MeOH (2 × 2 mL) and dried under vacuum. Yield: 84%; mp 205–208 °C. Anal. Calcd. for $\text{C}_{53}\text{H}_{55}\text{NP}_4\text{Pt}_2$: C, 52.2; H, 4.5; N, 1.1. Found: C, 52.5; H, 4.7; N, 0.7%. The synthesis of **4** was also carried out by reaction of $\text{cis,cis-}[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)(\mu\text{-dppm})]$, **2**, and dppa in a similar way. NMR in CD_2Cl_2 at 20 °C: $\delta(^1\text{H}) = 0.11$ [m, 6H, $^2J(\text{PtH}) = 69$ Hz, $^3J(\text{PH}) = 17$ Hz, Me *trans* to dppm]; 0.27 [m, 6H, $^2J(\text{PtH}) = 68$ Hz, $^3J(\text{PH}) = 16$ Hz, Me *trans* to dppa]; 3.50 [br m, 2H, CH_2P_2 of dppm]; 3.70 [t, 1H, $^3J(\text{PtH}) = 27$ Hz, $^2J(\text{PH}) = 8$ Hz, NH of dppa]; $\delta(^{13}\text{C}) = 9.4$ [m, $^2J(\text{PC}) = 100$ Hz, Me *trans* to dppm]; 9.7 [m, $^2J(\text{PC}) = 112$ Hz, Me *trans* to dppa]; 26.2 [t, $^1J(\text{PC}) = 15$ Hz, CH_2P_2 of dppm]; $\delta(^{31}\text{P}) = 11.9$ [m, $^1J(\text{PtP}) = 1832$ Hz, $^3J(\text{PtP}) = 38$ Hz, $^2J(\text{PP}) = 15$ Hz, dppm]; 58.7 [br m, $^1J(\text{PtP}) = 2070$ Hz, dppa]. NMR in CD_2Cl_2 at -70 °C: $\delta(^1\text{H}) = -0.4$ [m, 3H, Me]; 0.0 [m, 3H, Me]; 0.9 [m, 6H, Me]; 2.3 [m, 1H, CH_2P_2 of dppm]; 4.0 [m, 1H, $^3J(\text{PtH}) = 25$ Hz, NH of dppa]; 4.4 [m, 1H, $^3J(\text{PtH}) = 36$ Hz, $^2J(\text{HH}) = 12$ Hz, CH_2P_2 of dppm]; $\delta(^{31}\text{P}) = 10.4$ [m, $^1J(\text{PtP}) = 1940$ Hz, dppm]; 12.1 [m, $^1J(\text{PtP}) = 1742$ Hz, dppm]; 45.8 [m, $^1J(\text{PtP}) = 2078$ Hz, dppa]; 69.0 [m, $^1J(\text{PtP}) = 2064$ Hz, dppa].

*cis,cis-}[\text{Pt}_2\text{Me}_4(\mu\text{-dppa})_2], **5**, and $[\text{PtMe}_2(\text{dppa})]$, **6***

A mixture of $\text{cis,cis-}[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)(\mu\text{-dppa})]$, **3**, (30 mg, 0.033 mmol) and dppa (13 mg, 0.033 mmol) in C_6H_6 (5 mL) was stirred for 1 h. The solvent was removed and the product, identified as a mixture of complexes **5** and **6** in a roughly 1 : 2 molar ratio, was washed with MeOH (2 × 1 mL) and dried under vacuum. Yield: 86%. Anal. Calcd. for $\text{C}_{26}\text{H}_{27}\text{NP}_2\text{Pt}$: C, 51.1; H, 4.4; N, 2.3. Found: C, 51.2; H, 4.4; N, 2.1%. A similar mixture of “isomers” was obtained by reaction of complex **1** with 2 equivalents of dppa. NMR in CD_2Cl_2 at 20 °C: **5**: $\delta(^1\text{H}) = 0.08$ [m, 12H, $^2J(\text{PtH}) = 67$ Hz, MePt]; 3.11 [s, 2H, $^3J(\text{PtH}) = 21$ Hz, NH of dppa]; $\delta(^{13}\text{C}) = 9.9$ [m, $^2J(\text{PC}) = 105$ Hz, MePt]; $\delta(^{31}\text{P}) = 62.1$ [s, $^1J(\text{PtP}) = 2075$ Hz, dppa]; **6**: $\delta(^1\text{H}) = 0.82$ [m, 6H, $^2J(\text{PtH}) = 74$ Hz, MePt]; 5.56 [t, 1H, $^2J(\text{PH}) = 9$ Hz, $^3J(\text{PtH}) = 63$ Hz, NH of dppa]; $\delta(^{13}\text{C}) = -2.3$ [m, $^2J(\text{PC}) = 107$, 8 Hz, $^1J(\text{PtC}) = 632$ Hz, MePt]; $\delta(^{31}\text{P}) = 30.4$ [s, $^1J(\text{PtP}) = 1475$ Hz, dppa]. NMR at -70 °C: **5**: $\delta(^{31}\text{P}) = 53.0$ [s, $^1J(\text{PtP}) = 2135$ Hz, dppa]; 68.7 [s, $^1J(\text{PtP}) = 2012$ Hz, dppa].

When a mixture of **5** and **6** (15 mg) in C_6D_6 (0.4 mL) was heated in a sealed NMR tube at 70 °C for 1 h, complete conversion to **6** occurred as determined by NMR spectroscopy.

$[\text{PtMe}(\text{dppa})(\text{PPh}_2\text{O})]$, **7**

A solution containing a mixture of complexes **5** and **6** in benzene was allowed to evaporate slowly. Decomposition occurred slowly to give crystals of the product **7**. Yield: ca. 20%; mp 208–210 °C (decomp.). Anal. Calcd. for $\text{C}_{37}\text{H}_{34}\text{NOP}_3\text{Pt}$: C, 55.8; H, 4.3; N, 1.8. Found: C, 55.1; H, 4.4; N, 1.9%. The complex was insufficiently soluble to allow NMR characterization.

Structure determinations

Crystals were grown from CH_2Cl_2 /hexane, and were mounted on glass fibres. Data were collected by using a Nonius Kappa-CCD diffractometer with COLLECT (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 SHELXTL-NT V5.1 (Sheldrick, G.M.) suite of programs was used to solve the structure by direct methods.¹⁴ The non-hydrogen atoms were

Table 3 Crystal data and structure refinement

Complex	3	4·CH ₂ Cl ₂
Formula	C ₃₀ H ₃₉ NP ₂ Pt ₂ S	C ₅₄ H ₅₇ Cl ₂ NP ₄ Pt ₂
Formula weight	897.80	1304.97
Temperature/K	200(2)	200(2)
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>P2₁/c</i>
<i>a</i> /Å	21.9630(2)	14.0637(2)
<i>b</i> /Å	17.7423(2)	16.9276(2)
<i>c</i> /Å	15.5770(1)	22.1155(3)
β /°	90	105.437(1)
Volume/Å ³	6069.9(1)	5075.0(1)
<i>Z</i>	8	4
μ /mm ⁻¹	9.403	5.775
Data/restr./param.	8875/0/277	11636/0/268
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0415	0.0601
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0887	0.1127

refined with anisotropic thermal parameters, with the exception of the phenyl carbon atoms for complex **4**, some of which were disordered. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

Complex **4** contained a well-ordered solvate molecule of CH₂Cl₂, but there was disorder in three of the phenyl rings and they were modeled as 50/50, 60/40 and 60/40 mixtures. Details of the crystal data and structure refinement for the complexes are given in Table 3.

CCDC reference numbers 203234–203235.

See <http://www.rsc.org/suppdata/dt/b3/b301419c/> for crystallographic data in CIF or other electronic format.

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