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The steric effect of *o*-tolyl ligand on the fluxionality behavior of some binuclear organoplatinum(II) complexes with bis(diphenylphosphino)methane as bridging ligand

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Abstract

A series of binuclear organoplatinum(II) complexes of general formula *cis*,*cis*-[$R_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)Pt(o\text{-}MeC_6H_4)_2$], **3a**–**3d**, in which R = Ph, *p*-MeC_6H_4, *m*-MeC_6H_4 or *p*-$MeOC_6H_4$, were prepared by the reaction of monomeric precursors [$Pt(o\text{-}MeC_6H_4)_2(dppm)$] and *cis*-[$PtR_2(SMe_2)_2$]. The binuclear dialkyl analogs, in which R = Me (**3e**) or R_2 = {$(CH_2)_4$} (**3f**), were prepared by the reaction of *cis*-[$Pt(o\text{-}MeC_6H_4)_2(SMe_2)_2$] and [$PtR_2$ (dppm)]. The complexes were fully characterized by multinuclear (^1H, ^{13}C, ^{31}P, ^{195}Pt) NMR spectroscopy each as a mixture of *syn* and *anti* isomers (depending on the relative orientations of Me substituents on *o*-tolyl ligands) and each isomer was shown to have a rigid structure. Other binuclear analogs *cis*,*cis*-[$R_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtR'_2$], **3g**–**3j**, in which R is a less steric demanding aryl groups *m*-MeC_6H_4 or *p*-$MeOC_6H_4$, and R′ = Me or R'_2 = {$(CH_2)_4$}, were prepared by the reaction of *cis*-[$PtR_2(SMe_2)_2$] and [PtR'_2(dppm)], and shown to have fluxional structures.
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Keywords: Organoplatinum complexes; Binuclear Platinum complexes

1. Introduction

Dinuclear complexes are of great importance in chemistry, catalysis and medicine. Diplatinum complexes have been well known for many years and bis(diphenylphosphino)methane (dppm) and related ligands have been widely used to hold the platinum centers together [1–3]. The dinuclear complexes containing two different bridging ligands in transition metal chemistry are not common. An unusual organodiplatinum(II) complex with two different biphosphine bridging ligands, a dppm and a dppa (bis(diphenylphosphino)amine), [$Me_2Pt(\mu\text{-}dppm)(\mu\text{-}dppa)PtMe_2$], has recently been reported [4]. We also have recently reported a series of uncommon diplatinum fluxional complexes of general formula *cis*,*cis*-[$R_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtR'_2$] (in which R and R′ are alkyl or simple aryl groups) [5,6]. These complexes are interesting in that while a bridging dppm group holds the dinuclear integrity, the other labile bridging group, SMe_2, could create an interesting chemistry. In this article, a series of unsymmetrical complexes of this type containing substituted aryl ligands, especially *o*-tolyl ligands, are synthesized and the effect of the substituents on the complex formation and fluxionality behavior is studied. Shaw and coworkers [7] have prepared a bis(μ-dppm)$_2$ complex [$Me_2Pt(\mu\text{-}dppm)_2$ $Pt(o\text{-}tolyl)_2$] and shown that depending on the relative positions of the *ortho* methyl substituents, two isomers are formed.

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2. Results and discussion

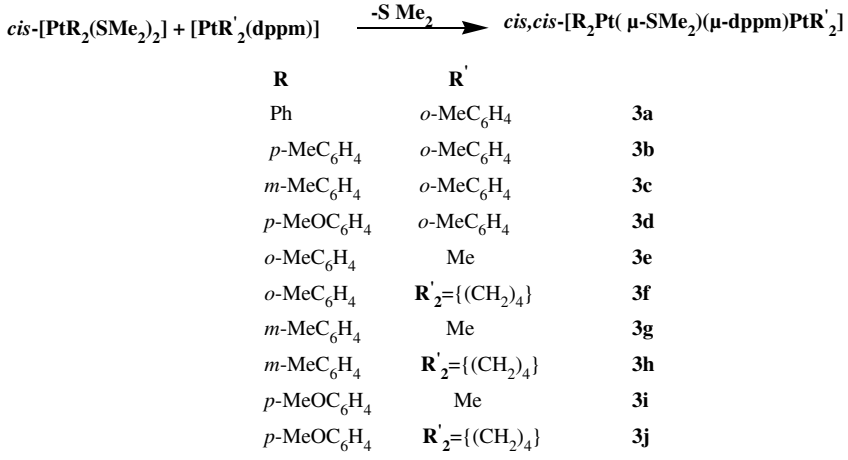
2.1. Synthesis of the complexes

As described in Scheme 1, the reaction of organoplatinum(II)sulfide monomers with the appropriate organoplatinum(II)(dppm) complexes gave a variety of the desired organoplatinum(II) dimers of general formula *cis*, *cis*-$[R_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtR'_2]$ in good yields by displacement of one SMe_2 ligand. The complex **3a** was also made by the reaction of $[PtPh_2(dppm)]$ with *cis*-$[Pt(o\text{-}MeC_6H_4)_2(SMe_2)_2]$. When R or R′ is *o*-$MeC_6H_4$, the reactions were rather slow and carried out at room temperature in CH_2Cl_2 for 3 days, while for other complexes the reactions were performed in CH_2Cl_2 or C_6H_6 for 8 h.

2.2. Characterization of complexes

All the complexes were fully characterized by multinuclear (^1H, ^{13}C, ^{31}P, ^{195}Pt) NMR spectroscopy (Tables 1–5) and microanalysis (Table 6).

Each of the diplatinum(II) complexes **3a**–**3f**, in which one of the aryl ligands is *o*-MeC_6H_4, was characterized as an approximately 2:1 mixture (for di-*o*-tolyl-diaryl complexes **3a**–**3d**) or 1:1 mixture (for di-*o*-tolyl-dialkyl complexes **3e**–**3f**) of two isomers **X** and **Y** as shown in Scheme 2. The major isomer was assigned structure **X**,



Scheme 1.

Table 1
^{31}P NMR data for complexes *cis*, *cis*-$[R_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtR'_2]$, **3a**–**3j**, in $CDCl_3$

Complex[a]	$\delta(P^a)$	$^1J(Pt^aP^a)(^3J(Pt^bP^a))$	$\delta(P^b)$	$^1J(Pt^bP^b)(^3J(Pt^aP^b))$	$^2J(P^aP^b)$
3a	15.8 [15.6]	1812 (b) [1784 (b)]	12.9 [13.4]	1839 (b) [1836 (b)]	43 [48]
3b	15.6 [15.4]	1802 (b) [1779 (b)]	12.6 [13.1]	1832 (b) [1832 (b)]	43 [47]
3c	15.4[c]	1780 (b)	13.7[c]	1815 (b)	(b)
3d	15.7 [15.5]	1809 (b) [1779 (b)]	13 [13.5]	1842 (b) [1842 (b)]	43 [46]
3e	19 [17.1]	1898 (b) [1908 (b)]	13.5 [13.1]	1778 (b) [1806 (b)]	47 [48]
3f	18.2 [16.2]	1837 (b) [1844 (b)]	14.6 [14.4]	1789 (b) [1804 (b)]	51 [52]
3g	21.8	1879(38)	14.0	1791(26)	48
3h	21.0	1805(40)	15.3	1793(29)	51
3i	22.0	1879(35)	13.3	1814(24)	47
3j	21.2	1805(39)	14.6	1815(26)	51

[a] Values in the brackets are for the isomer **Y**.
[b] Not resolved.
[c] Broad peak.

Table 2
^{195}Pt NMR data for complexes, *cis*, *cis*-[$R_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtR'_2$], **3a–3f**, in $CDCl_3$

Complex[a]	$\delta(Pt^a)$	$^1J(Pt^aP^a)$ ($^3J(Pt^aP^b)$)	$\delta(Pt^b)$	$^1J(Pt^bP^b)$ ($^3J(Pt^bP^a)$)
3a	−4295 [−4255]	1828 (b) [1774 (b)]	−4283 [−4265]	1849 (b) [1840 (b)]
3b	−4274 [−4255]	1828 (b) [1785 (b)]	−4287 [−4266]	1828 (b) [1828 (b)]
3c	−4296 [−4252]	1817 (b) [1820 (b)]	−4283 [−4263]	1840 (b) [1840 (b)]
3d	−4262 [−4253]	1810 (b) [1785 (b)]	−4265 [−4278]	1850 (b) [1850 (b)]
3e	−4340 [−4370]	1892 (37) [1903 (23)]	−4264 [−4241]	1828 (b) [1731 (b)]
3f	−4462 [−4437]	1828 (b) 1839 (b)	−4236 [−4257]	1806 (b) [1806 (b)]

[a] Values in the brackets are for the isomer **Y**.
[b] Not resolved.

Table 4
^{1}H NMR data for the complexes *cis*,*cis*-[$R_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)Pt(o\text{-}MeC_6H_4)_2$], **3a**–**3d**, in $CDCl_3$

Complex[b]	SMe_2[a]	dppm	CH_3 on *o*-MeC_6H_4	CH_3 on R
	δ(Me)(^3J(PtH))	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(CH_3)$
3a	1.52 (18.2) 1.65 (18.8) [1.60 (19)] [1.76 (19.4)]	3.3	1.98, 2.12 [2.29, 2.39]	–
3b	1.64 (18.5) 1.51 (19) [1.74 (17)] [1.59 (20)]	3.3	1.97–2.38	1.97–2.38
3c	1.5 (18.1) 1.59 [1.56] [1.72 (20)]	3.4	2.0–2.4	2.0–2.4
3d	1.5–1.7	3.3	2.23, 2.3 [2.38, 2.46]	3.54–3.62

[a] Appeared as a quintet with relative intensity 1:8:18:8:1.
[b] Values in the brackets are for isomer **Y**.

Table 3
^{13}C NMR data for the complexes *cis*, *cis*-[$R_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtR'_2$], in $CDCl_3$

Complex[c]	SMe_2	dppm	$PtCH_2^{\alpha}$ or $PtCH_3$ (*trans* to P)	$PtCH_2^{\alpha}$ or $PtCH_3$ (*trans* to SMe_2)	$PtCH_2^{\beta}$ (*trans* to P)	$PtCH_2^{\beta}$ (*trans* to SMe_2)	Ar[a]	X[b]
	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(CH_2)$ or $\delta(CH_3)$	$\delta(CH_2)$ or $\delta(CH_3)$	$\delta(CH_2)$	$\delta(CH_2)$	$\delta(C^1)$	$\delta(CH_3)$
	(^4J(PC))	(^1J(PC))	(^1J(PtC), ^2J(PC))	(^1J(PtC), ^2J(PC))	(^2J(PtC), ^3J(PC))	(^2J(PtC), ^3J(PC))	(^1J(PtC), ^2J(PC))	(^3J(PtC), ^4J(PC))
3a	25.2 (4) 25.5 (4) [23.3 (4)] [24.5 (4)]	23.0 (16) [24.7 (15)]	–	–	–	–	165.1, 163.8, 163.3, 162.0 [164.8, 163.0, 162.0, 160.2]	28.6[d] (91, –) [27.4[d] (80, –)] 27.7[e] (70, 3) [25.9[e] (64, 3)]
3b	25.1 (4) 24.8 (4) [24.2 (4)] [22.9 (4)]	22.9 (15) [24.6 (16)]	–	–	–	–	163.0, 162.1, 160.0, 159.1 [161.3, 160.3, 159.8, 158.8]	28.2[d] (80, –) [27.0[d] (83, –)] 27.3[e] (76, 4) [25.6[e] (56, 3)]
3g	24.2	22.6 (16)	6.9 (661, 106)	−4.6 (748, 4)	–	–	144.7[d] (1041, 8) 163.6[e] (905, 115)	21.8 (–, –) 21.9 (–, –)
3h	24.9	22.7 (15)	36.8 (700, 93)	28.6 (768, –)	38.5 (32,14)	34.7 (56, 5)	145.3[d] (1036, 8) 163.5[e] (902, 116)	21.9 (–, –) 22.0 (–, –)
3i	24.4	22.7 (15)	7.0 (661, 106)	−4.5 (747, 4)	–	–	134.7[d] (1059, 9) 153.9[e] (927, 119)	54.9 (–, –) 55.6 (–, –)
3j	25.1	22.8 (16)	36.8 (698, 94)	28.6 (774, 2)	38.5 (29, 14)	34.7 (55, 5)	135.0[d] (1062, 9) 153.8[e] (922, 120)	55.3 (–, –) 55.6 (–, –)

[a] C^1 is aryl carbon directly attached to Pt.
[b] X is CH_3 or OCH_3 substitution on aryl ligands.
[c] The values in the brackets are for isomer **Y**.
[d] Aryl ligand trans to SMe_2.
[e] Aryl ligand trans to P.

Table 5
^{1}H NMR data for the complexes *cis*,*cis*-[$R_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtR'_2$], **3e–3j**, in $CDCl_3$

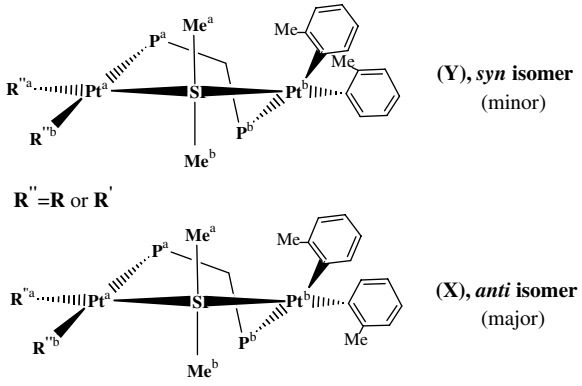
Complex	SMe_2[a]	dppm	$PtCH_3$ (*trans* to P)	$PtCH_3$ (*trans* to SMe_2)	CH_2 protons of platinacycle ring	X[b]
	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(CH_3)$
	(^3J(PtH))	(^2J(PH))	(^2J(PtH), ^3J(PH))	(^2J(PtH), ^3J(PH))		
3e	1.59(19.7) [1.63(19.8)][d]	3.2(c)	–0.013(66.7, 6.7) [0.098(c, 6.8)][d]	0.21(86.8, 8.8)	–	1.8–2.0
3f	1.77(18)	3.4(c)	–	–	0.90–2.4	2.0–2.4
3g	1.76(18.8)	3.33(7.5)	0.12(66.4, 7.4)	0.38(86.5, 9.1)	–	1.76, 2.01
3h	1.87(17.7)	3.42(7.3)	–	–	0.90–1.62	1.82, 2.10
3i	1.66(19.3)	3.25(c)	0.01(66.5, 7.4)	0.27(84.9, 9.1)	–	3.36, 3.42
3j	1.94(17.4)	3.47(7.3)	–	–	0.90–1.69	3.61, 3.67

[a] Appeared as a quintet with a relative intensity 1:8:18:8:1.
[b] CH_3 substitution on aryl ligands.
[c] Not resolved.
[d] Values in the brackets are for isomer **Y**.

Table 6
Characterization data for complexes *cis*,*cis*-[$R_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtR'_2$], **3a–3j**

Complex	Yield (%)	m.p.[a] (°C)	Elemental analysis[b] (%)	
			C	H
3a	75	132	53.7 (54.3)	4.6 (4.4)
3b	73	130	54.6 (55)	4.8 (4.7)
3c	77	126	54.8 (55)	4.8 (4.7)
3d	57	132	53.4 (53.6)	4.4 (4.5)
3e	45	162	49.8 (49.2)	4.3 (4.6)
3f	35	176	50.4 (50.3)	4.6 (4.6)
3g	86	142	49.2 (49.2)	4.6 (4.6)
3h	85	140	50.4 (50.3)	4.7 (4.6)
3i	80	135	48 (47.8)	4.5 (4.4)
3j	86	140	49.2 (48.8)	4.3 (4.5)

[a] Decomposed.
[b] Found (calc.).



Scheme 2. Complexes **3a**–**3f**.

anti isomer, in which the *o*-tolyl ligands are in an *anti* configuration while in the minor *syn* isomer **Y**, the two *o*-tolyl ligands are in a *syn* configuration. These assignments are based on the expected steric requirements, although the opposite assignment is not impossible.

In the ^{31}P NMR spectrum of the *o*-tolyl containing complex **3d**, *cis*,*cis*-[(p-$MeOC_6H_4$)$_2$Pt(μ-SMe_2)(μ-dppm)Pt(o-MeC_6H_4)$_2$] (Fig. 1), for each isomer the two phosphoros atoms are inequivalent and appeared as an AB pattern and showed short-range coupling platinum satellites, while the long-range coupling satellites were not resolved. The phosphoros P^b (in each of the isomers **X** or **Y**), which is *trans* to *o*-tolyl ligand, is resonated at higher field (δ around 13) with $^1J(Pt^bP^b) = 1842$ Hz. The phosphoros P^a appeared around $\delta = 15$ with $^1J(Pt^aP^a)$ values 1779 Hz (isomer **X**) and 1809 Hz (isomer **Y**). It therefore appears that *o*-tolyl ligand exerts a relatively lower *trans* influence compared to p-MeC_6H_4 or p-$MeOC_6H_4$. The ^{31}P NMR spectra of other complexes **3b**–**3f** were similarly assigned. However, in the ^{31}P NMR spectrum of the complex *cis*,*cis*-[(m-MeC_6H_4)$_2$Pt(μ-SMe_2)(μ-dppm)Pt(o-MeC_6H_4)$_2$], **3c**, two broad peaks centered at δ 13.7($^1J(Pt^bP^b) = 1830$ Hz) and δ 15.4($^1J(Pt^aP^a) = 1767$ Hz) were observed (see Fig. 1). This probably suggests that the two main isomers **X** and **Y** are formed (see also the ^{195}Pt NMR data presented below), but the two *m*-tolyl groups can take up different configurations and therefore a mixture of many isomers is formed causing the broadening of the signals. A typical $^2J(P^aP^b)$ value of 42–52 Hz was observed in all the complexes. For the remaining diplati-

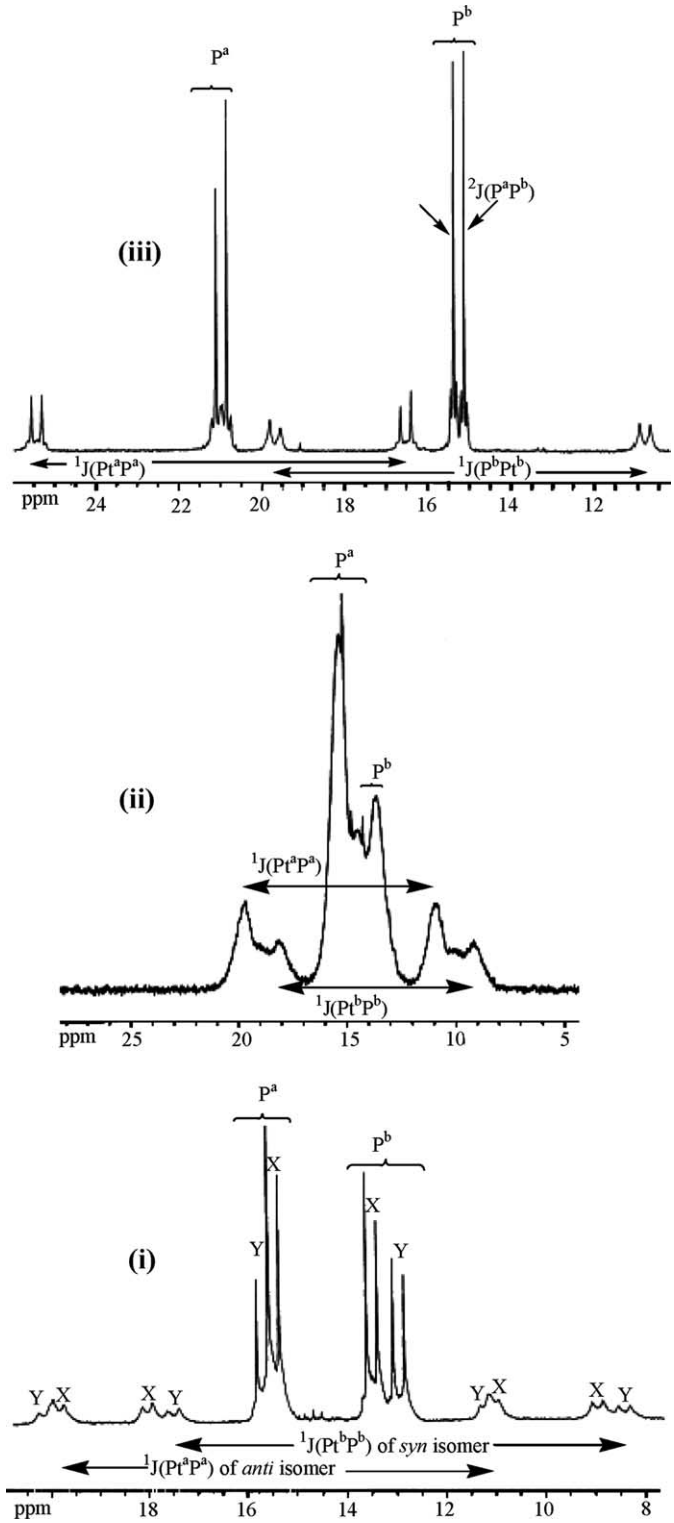
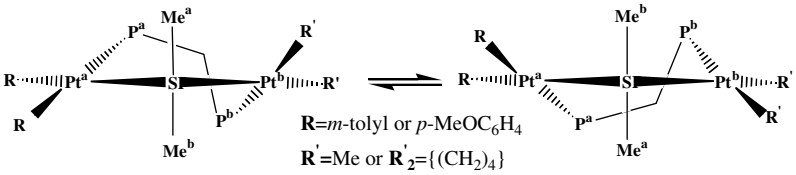


Fig. 1. ^{31}P NMR spectra (202.5 MHz) of (i) *cis*,*cis*-[(*p*-$MeOC_6H_4)_2Pt(\mu$-dppm)(μ-SMe_2)Pt(*o*-$MeC_6H_4)_2$], **3d**; major isomer **X** and minor isomer **Y**, (ii) *cis*,*cis*-[(*m*-$MeC_6H_4)_2Pt(\mu$-SMe_2)(μ-dppm)Pt(*o*-$MeC_6H_4)_2$], **3c**, and (iii) *cis*,*cis*-[(*m*-$MeC_6H_4)_2$ $Pt(\mu$-SMe_2)(μ-dppm)Pt{$(CH_2)_4$}], **3h**. Some of the assignments are shown.

num(II) complexes **3g**–**3j**, in each of which one platinum center carries aryl ligands *m*-MeC_6H_4 or *p*-$MeOC_6H_4$ and the other platinum center carries alkyl ligands Me or {$(CH_2)_4$}, the structure and fluxionality behavior given in Scheme 3 is suggested. It seems that in this type of diplatinum complexes, only when the more steric



Scheme 3. Structure and fluxionality mechanism for complexes **3g**–**3j**.

demanding ligands *o*-MeC_6H_4 exist at least on one of the platinum(II) centers, then the potential fluxionality stops and the two isomers involved are observable.

In the ^{31}P NMR spectrum of each of the complexes **3g**–**3j**, the two phosphoros atoms are inequivalent (Scheme 3), appeared as two doublet signals and showed short-range as well as long range platinum satellites (Fig. 1). The first signal was appeared around δ 13.3–15.3 (with $^1J(Pt^bP^b)$ = 1791–1815 Hz and $^3J(Pt^aP^b)$ = 24–29 Hz) and assigned to P^b, which is connected to $Pt(aryl)_2$ moiety. The second signal (around δ 21–22) has $^1J(Pt^aP^a)$ = 1879 Hz when *trans* to Me($^3J(Pt^bP^a)$ = 35–38 Hz) and 1805 Hz when *trans* to CH_2 group of metallacycle ($^3J(Pt^bP^a)$ = 39–40 Hz). This modest difference of 26 Hz is ascribed to chelating $\{(CH_2)_4\}$ ligand in the latter that exerts a significantly higher *trans* influence than the methyl group [8,9]. A $^2J(P^aP^b)$ value of 47–51 Hz was observed in each case.

Based on the above data and those of our previous works [5,6], the following approximate *trans* influence series for the involved organic ligands is presented:

m-MeC_6H_4 > Ph ≈ *p*-MeC_6H_4 > CH_2 of $\{(CH_2)_4\}$ group > *p*-$MeOC_6H_4$ > *o*-MeC_6H_4 > Me

The ^{195}Pt NMR spectrum of each of the non-fluxional *o*-MeC_6H_4 containing complexes **3a**–**3f** (Fig. 2), as expected on the basis of the above ^{31}P NMR results, contains two doublets (with separations $^1J(Pt^aP^a)$ and $^1J(Pt^bP^b)$) for isomer **X** and similarly two doublets for isomer **Y**. The $^3J(Pt^aP^b)$ and $^3J(Pt^bP^a)$ couplings were not usually observed. It is interesting to note that in the spectrum of *cis*,*cis*-[(*m*-$MeC_6H_4)_2Pt(\mu$-$SMe_2)(\mu$-dppm)Pt(*o*-$MeC_6H_4)_2$], **3c**, a similar pattern was observed, but the peaks were rather broad. This again confirms that the two main isomers **X** and **Y** are formed (see the ^{31}P NMR spectrum presented above), but the two *m*-tolyl groups can take up different configurations and therefore a mixture of many isomers is formed causing the broadening of the signals.

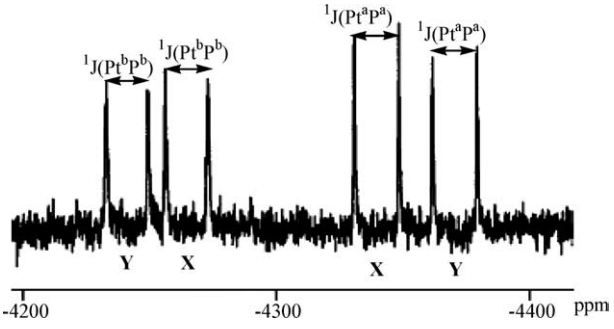


Fig. 2. Pt NMR spectrum (107 MHz) of *cis*,*cis*-[$Me_2Pt(\mu$-dppm)(μ-$SMe_2)Pt(o$-$MeC_6H_4)_2$], **3e**; major isomer **X** and minor isomer **Y**. The assignments are shown.

^{13}C NMR spectra of *o*-MeC_6H_4 containing complexes were also very useful in identification of isomers **X** and **Y** in the product mixture. In the ^{13}C NMR spectrum of *cis*,*cis*-[$Ph_2Pt(\mu$-$SMe_2)(\mu$-dppm)Pt(*o*-Me $C_6H_4)_2$], **3a**, for each isomer two signals were observed for methyl substituents on the *o*-MeC_6H_4 ligands. The first one is for the ligand *trans* to SMe_2 (δ = 28.6 or 27.4, for isomers **X** or **Y**, respectively), which couples to the attached platinum (with ^{3} J(PtC) = 91 or 80 Hz for isomers **X** or **Y**, respectively). The second signal is for the *o*-MeC_6H_4 ligand *trans* to phosphoros atom (δ = 27.7 or 25.9, for isomers **X** or **Y**, respectively), which couples to the attached platinum as well as the *trans* phosphoros atom (with ^3J(PtC) = 70 Hz, ^4J(PC) = 3 Hz or ^3J(PtC) = 64 Hz, ^4J(PC) = 3 Hz, for isomers **X** or **Y**, respectively). The ^3J(PtC) value for the first signal is some 30% higher than the value for the second signal, which is reflection of the higher *trans* influence of phosphoros ligand compared to SMe_2 ligand. For the major isomer **X,** two doublets at δ 25.2 ($^4J(C^aP^b)$ = 4 Hz) and 25.5 ($^4J(C^bP^a)$ = 4 Hz) were assigned to Me^a and Me^b carbons, respectively, of the SMe_2 ligand. For isomer **Y**, these were appeared at δ 23.3 ($^4J(C^aP^b)$ = 4 Hz) and 24.5 ($^4J(C^bP^a)$ = 4 Hz) for Me^a and Me^b carbons, respectively. It therefore seems that Me^a or Me^b carbons of the SMe_2 ligand in each isomer are only coupled to the transoid phosphoros atoms, i.e., P^b or P^a, respectively, and give rise to doublets. As expected, a total of eight signals around δ 160–165 were observed for C^1 aryl carbons directly attached to platinum, although no PtC coupling values could be measured properly. The CH_2 carbon of dppm resonated at δ 23.0 (^1J(PC) = 16 Hz), for the major isomer **X**, and at δ 24.7 (^1J(PC) = 15 Hz), for the minor isomer **Y**. The complex **3b** was similarly assigned.

In the ^{13}C NMR spectrum of the fluxional complex *cis*,*cis*-[(*m*-$MeC_6H_4)_2Pt(\mu$-$SMe_2)(\mu$-dppm)$PtMe_2$], **3g**, the isomers are not distinguished and Me^a and Me^b carbons of the SMe_2 ligand become equivalent and appeared at δ = 24.2 with no coupling to platinum or

phosphoros atoms. A signal at $\delta = 22.6$ (^1J(PC) = 16 Hz) was assigned to the CH_2 carbon of dppm. Two signals were clearly assigned to the two different carbons of Me ligands. The first signal due to Me group *trans* to phosphoros atom was appeared at $\delta = 6.9$ with ^1J(PtC) = 661 Hz and ^2J(PC) = 106 Hz. The second signal appeared at $\delta = -4.5$ and was assigned to Me group *trans* to SMe_2, which has a higher ^1J(PtC) value of 748 Hz due to the higher *trans* influence of phosphoros ligand compared to SMe_2 ligand. As expected, this signal has a *cis* coupling to phosphoros with a ^2J(PC) value of only 4 Hz.

The metallacycle analog *cis*,*cis*-[(*m*-$MeC_6H_4)_2$Pt(μ-SMe_2)(μ-dppm)Pt{$(CH_2)_4$}], **3h**, was similarly assigned, except that the two different CH_2^{α} carbon atoms of platinacycle moiety were appeared at $\delta = 36.8$ (*trans* to phosphoros, with ^1J(PtC) = 700 Hz and ^2J(PC) = 93 Hz) and at $\delta = 28.6$ (*trans* to SMe_2, with ^1J(PtC) = 768 Hz and no observable coupling to the *cis* phosphoros). The ^1J(PtC) value for CH_2^{α} carbon atoms of platinacycle in **3h** is 20–39 Hz larger than the ^1J(PtC) values for Me groups in**3g** and this reflects the higher donor ability of CH_2 groups of the metallacycle compared to Me groups[6,8]. The signals for the different CH_2^{β} carbons of the platinacycle were appeared at $\delta = 38.5$ (^2J(PtC) = 32 Hz and ^3J(PC) = 14 Hz, for CH_2^{β} *trans* to phosphoros) and at $\delta = 34.7$ (^2J(PtC) = 56 Hz and ^3J(PC) = 5 Hz, for CH_2^{β} *trans* to SMe_2). The other fluxional molecules **3i** and **3j** were similarly assigned.

In the ^{1}H NMR spectrum of *cis*,*cis*-[Ph_2Pt(μ-SMe_2)-(μ-dppm)Pt(*o*-$MeC_6H_4)_2$], **3a**, Table 4, four signals each having the appearance of a quintet with relative intensity 1:8:18:8:1 with a ^3J(PtH) value close to 19 Hz were observed. Although some of the peaks were overlapped, these quintets are characteristic of SMe_2 acting as bridging ligand between platinum centers, but with unusual chemical shift $\delta = 1.52$–1.76 [5,10]. Thus, each of the isomers **X** or **Y** gives two signals for Me^a and Me^b protons of SMe_2 ligand. The CH_2 protons of dppm ligand in both isomers were overlapped and appeared at $\delta = 3.3$. As expected, two signals at $\delta = 1.98$ and 2.12 for isomer **X** and two signals at $\delta = 2.29$ and 2.39 for isomer **Y** were assigned to the different *ortho*-methyl substituents on *o*-MeC_6 H_4 ligands. Other similar non-fluxional complexes **3b**–**3d** were assigned similarly.

For the non-fluxional di-*o*-MeC_6H_4, dimethyl–diplatinum analog **3e** (Table 5), the signals for Me groups of SMe_2 ligands were mostly overlapped. For the Me ligand *trans* to phosphoros in isomer **X**, a signal at $\delta = -0.01$ with ^2J(PtH) = 66.7 Hz and ^3J(PH) = 6.7 Hz was observed. For isomer **Y**, this signal appeared at $\delta = 0.10$ with ^3J(PH) = 6.8 Hz and no resolvable platinum satellites. The Me ligand *trans* to SMe_2 for both isomers was overlapped and appeared at $\delta = 0.21$ with ^2J(PtH) = 86.8 Hz and ^3J(PH) = 8.8 Hz. In the metallacycle analog **3f**, the overlapping was more extensive and the CH_2 protons of the platinacycle moiety appeared around $\delta = 0.90$–2.4.

The ^{1}H NMR spectra of the fluxional analogs **3g**–**3j** (Table 5) were more clear-cut. A signal around δ 1.8 was assigned to the Me groups of SMe_2 ligands. For the dimethyl analogs **3g** and **3i**, in each case, a signal close to δ 0.1 with ^2J(PtH) = 66.4 Hz and ^3J(PH) = 7.4 Hz was assigned to the Me ligand *trans* to phosphoros and the signal for Me ligand *trans* to SMe_2 was appeared at $\delta = 0.38$ (for **3g**) or 0.27 (for **3i**) with a ^2J(PtH) value of 86.5 Hz (for **3g**) or 84.9 Hz (for **3i**) and ^3J(PH) = 9.1 Hz. As expected on the basis of the higher *trans* influence of phosphine compared to SMe_2, the ^2J(PtH) value for the Me ligand *trans* to SMe_2 is some 30% higher than the ^2J(PtH) value for Me ligand *trans* to the phosphoros atom. The CH_2 protons of the platinacycle moiety appeared as overlapping of multiplets around $\delta = 0.90$–1.69.

3. Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer. ^{31}P and ^{195}Pt 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 (^{19}5Pt), and $CDCl_3$ was used as solvent in all cases. All the chemical shifts and coupling constants are in ppm and Hz, respectively.

The monomeric precursors *cis*-[PtR_2 $(SMe_2)_2$], R = Ph,*p*-MeC_6H_4, *m*-MeC_6H_4 and *p*-$MeOC_6H_4$ were made by the known methods [5,10,11]. The complex *cis*-[Pt(*o*-$MeC_6H_4)_2$ $(SMe_2)_2$] was prepared as follows: In a typical experiment, a freshly prepared solution of *o*-MeC_6H_4 Li (10 mL of 1 M solution in diethylether) (prepared from *o*-MeC_6H_4 Br and Li metal) was added slowly to a stirred, ice-cold solution of [$PtCl_2$ $(SMe_2)_2$] (500 mg; 1.25 mmol) in dry ether (20 mL) under Ar atmosphere. The reaction mixture was stirred for 2 h at 0 °C and subsequently hydrolyzed with a few mL saturated solution of NH_4Cl in water. Separation of organic layer, extraction with ether, and evaporation of solvent gave a mixture of *cis*-[Pt(*o*-$MeC_6H_4)_2$ $(SMe_2)_2$] and [Pt_2(*o*-$MeC_6H_4)_4$(μ-$SMe_2)_2$]. The white residue was treated with SMe_2 (1 mL) in CH_2Cl_2 (20 mL) in order to convert the coexisted dimeric species into the monomer. The solvent was evaporated and the residue was washed with a few mL of dry ether. Yield 58%; m.p. = 160 °C (d); ^{1}H NMR ($CDCl_3$): $\delta = 2.27$ (broad, 12 H, SMe_2), 2.8 (s, 12 H, $ArCH_3$), 7.5 (s, $^3J_{PtH} = 70.4$ Hz, *ortho* H of Ar), 6.8 (m, the other H of Ar); ^{13}C NMR ($CDCl_3$): $\delta = 21$ (SMe_2), 27.6 ($ArCH_3$), 145.8 ($^1J_{PtC} = 1116$, C^1 of Ar), 141.3, 135.5, 128.6, 124.7, 123.2 (the other C of Ar groups).

The dppm containing monomers [$PtPh_2$(dppm)], [Pt(*p*-$MeC_6H_4)_2$(dppm)], [Pt(*m*-$MeC_6H_4)_2$ (dppm)],

[Pt(*p*-$MeOC_6H_4$)$_2$(dppm)], [$PtMe_2$(dppm)] and [Pt{$(CH_2)_4$}(dppm)] were made by the known methods [5,12–15].

[Pt(*o*-MeC_6H_4)$_2$ (dppm)] was prepared by a similar method as described for [Pt(*p*-MeC_6H_4)$_2$ (dppm)] [12]. Yield: 78%; mp 234 ° C. Anal. Calc. for [Pt(*o*-MeC_6H_4)$_2$ (dppm): C, 55.2 ; H, 4.7%. Found: C, 55.6; H, 4.5%. NMR ($CDCl_3$): δ (^{1}H) = 2.62 [s, 6 H of 2 Me substituents on *o*-tolyl ligands], 4.56 [t, ^2J(PH) = 9.3 Hz, ^3J(PtH) = 18.8 Hz, CH_2P_2]; δ (^{13}C) = 27.2 [s, ^3J(PtC) = 73 Hz, Me substituents on *o*-tolyl ligands], 45.3 [t, ^1J(PC) = 26 Hz, CH_2P_2], 158.4 [dd, $^2J(PC_{trans})$ = 117 Hz, $^2J(PC_{cis})$ = 8 Hz, ^1J(PtC) = 939 Hz, C^1 of *o*-tolyl ligands, directly connected to platinum], the other C of *o*-tolyl groups: [122.2 s], 124.4 [t, ^3J(PC) = 3 Hz, ^2J(PtC) = 70 Hz], 128.5 [t, ^3J(PC) = 3 Hz, ^2J(PtC) = 44 Hz], 137 [s, ^3J(PtC) = 35 Hz], 143.3 [t, ^4J(PC) = 3 Hz, ^3J(PtC) = 27 Hz]; δ (^{31}P) = −42 [s, ^1J(PtP) = 1376 Hz].

*3.1. cis,cis-[Ph_2 Pt(μ-SMe_2)(μ -dppm)Pt(o-MeC_6H_4)$_2$], **3a***

A mixture of *cis*-[$PtPh_2$ (SMe_2)$_2$] (62 mg, 0.13 mmol) and [Pt(*o*-MeC_6H_4)$_2$ (dppm)] (100 mg, 0.13 mmol) in CH_2Cl_2 was stirred at room temperature for 3 days. The solvent was removed and the residue was washed with acetone (4 ml) and dried in vacuo.

A similar procedure using an equimolar mixture of [$PtPh_2$ (dppm)] and *cis*-[Pt(*o*-MeC_6H_4)$_2$(SMe_2)$_2$] gave the same product.

The other dimers **3b**–**3j** were made similarly using the appropriate mononuclear complexes.

4. Conclusions

The dimeric organoplatinum(II) complexes *cis*, *cis*-[R_2Pt(μ-SMe_2)(μ-dppm)PtR'_2] are fluxional when R or R′ are alkyl or simple aryl groups and a mechanism of fluxionality as shown in Scheme 3 is suggested. However, in complexes **3a**–**3f** where R or R′ is an *o*-MeC_6H_4 group, then the steric effects created by *ortho*-methyl substituents on *o*-MeC_6H_4 ligands freeze the fluxionality and rigid structures are identified. In each of these complexes, depending on the relative orientations of *ortho*-methyl substituents, a mixture of *syn* and *anti* isomers as indicated in Scheme 2 is formed.

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