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Unsymmetrical organodiplatinum(II) and organodiplatinum(IV) complexes containing bis(diphenylphosphino)methane as bridging ligand: general approaches for synthesis and characterization by multinuclear NMR studies

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Abstract

Reaction of *cis*-[$PtR_2(SMe_2)_2$] (R = Ph or *p*-MeC_6H_4) with [$PtMe_2$(dppm)] or [Pt{$(CH_2)_4$}(dppm)] (dppm = $Ph_2PCH_2PPh_2$) gave the unsymmetrical *cis,cis*-diaryl-dialkyl diplatinum(II) complexes *cis,cis*-[$R_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtMe_2$], **1a** and **2a**, or *cis,cis*-[$R_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})Pt\{(CH_2)_4\}$], **1b** and **2b**, respectively. Complexes **1a** and **2a** were also prepared by reaction of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] with [$PtR_2$(dppm)]. The unsymmetrical complex *cis,cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})Pt\{(CH_2)\}_4$] (**3b**) was prepared by the same method using [Pt{$(CH_2)_4$}(dppm)] and [$Pt_2Me_4(\mu\text{-}SMe_2)_2$]. The symmetrical complex *cis,cis*-[$Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtMe_2$] (**3a**) was prepared by reaction of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] with either one equivalent of dppm or [$PtMe_2$(dppm)]. The complexes **2** and **3** reacted with MeI to give the unsymmetrical diplatinum(IV) complexes *fac,fac*-[$R_2MePt(\mu\text{-}I)_2(\mu\text{-dppm})PtMeR'_2$] (**4a**, R = R′ = Me; **4b**, R = Me, $R'_2 = (CH_2)_4$; **5a**, R = *p*-MeC_6H_4, R′ = Me; **5b**, R = *p*-MeC_6H_4, $R'_2 = (CH_2)_4$). The reactions probably occurred by a S_N2-type mechanism and the entering Me groups stereoselectively remained in the equatorial positions (Pt–P taken as axial direction), unless for *fac*-$PtMe_3$ moiety that Me scrambling was taken place. Reaction of *cis,cis*-dialkyl-dialkyl diplatinum(II) complexes **3** with one equivalent of dppm gave bis(dppm-bridged) complexes *cis,cis*-[$R_2Pt(\mu\text{-dppm})_2PtR'_2$] (**6a**, R = R′ = Me; **6b**, R = Me, $R'_2 = (CH_2)_4$). The complexes were fully characterized using multinuclear (^1H-, $^{13}C\{^1H\}$-, $^{31}P\{^1H\}$-, $^{195}Pt\{^1H\}$-) NMR spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Platinum; Organodiplatinum(II); Organodiplatinum(IV)

1. Introduction

It is well known that two metals kept in close proximity could react cooperatively with substrate molecules and thus there has been a great interest in developing ligand systems able to lock two metals in such a position [1,2]. In this regard there has been a great interest in bis(diphenylphosphino)methane (dppm = $Ph_2PCH_2PPh_2$) as a versatile ligand which usually bridges two metal centers forming homo or heterobinuclear complexes, although there are cases in which it acts as a chelate or a monodentate ligand [3,4]. Most platinum complexes that contain dppm acting as bridging ligand contain $M_2(\mu\text{-dppm})_2$ units, and in many cases metal–metal bonds are present as well [3,4]. Uncommon anionic dinuclear platinum(II) complexes with general formula [NBu_4][$(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-dppm})Pt(C_6F_5)_2$] and a corresponding neutral complex [$(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-dppm})Pt(C_6F_5)_2$] have recently been synthesized and structurally characterized [5,6]. Also a simple route has been developed recently to synthesize a series of diplatinum(II) complexes of general formula *cis,cis*-[$Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtAr'_2$], in which Ar and Ar′ are identical or different aryl ligands Ph, *p*-MeC_6H_4, *m*-MeC_6H_4 or *p*-$MeOC_6H_4$ [7]. These uncommon complexes each contain two neutral bridging ligands, a dppm and a dimethylsulfide. It has been shown in the present study that the route could be extended to synthesize corresponding unsymmetrical *cis,cis*-diaryl-dialkyl or *cis,cis*-dialkyl-dialkyl diplatinum(II) complexes with general formula *cis,cis*-[$R_2Pt(\mu$-

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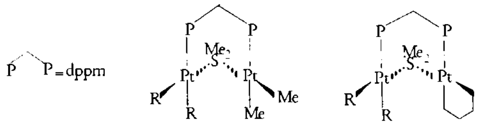
$SMe_2)(\mu\text{-dppm})PtR'_2]$ (**1**–**3**). These are expected to be interesting in the sense that while a bridging dppm group holds the dinuclear integrity, the other labile bridging group, SMe_2, could create an interesting chemistry. Thus in this article, oxidative addition of MeI to the diplatinum(II) complexes, which is accompanied by displacement of SMe_2, has been shown to be a suitable general route to organodiplatinum(IV) complexes of general formula *fac*,*fac*-$[MeR_2Pt(\mu\text{-I})_2(\mu\text{-dppm})PtMeR'_2]$ (**4** and **5**). Also, where R and R′ are alkyl groups, the organodiplatinum(II) complexes undergo reaction with dppm to displace SMe_2 and present a new route to bis(dppm-bridged)diplatinum(II) complexes, $[R_2Pt(\mu\text{-dppm})_2PtR'_2]$.

2. Results and discussion

2.1. Synthesis of organodiplatinum(II) complexes containing dppm and SMe_2 as bridging ligands

The reaction of dialkyl complexes $[PtMe_2(dppm)]$ or $[Pt\{(CH_2)_4\}(dppm)]$ with diaryl complexes *cis*-$[PtR_2(SMe_2)_2]$, R = Ph or *p*-MeC_6H_4, gave unsymmetrical *cis*,*cis*-diaryl-dialkyl diplatinum(II) complexes **1a** and **2a** or **1b** and **2b**, respectively. The dimethyl complexes **1a** and **2a** were also prepared by reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with two equivalents of the corresponding diaryl complexes $[PtR_2(dppm)]$.

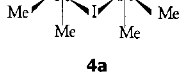


R		
Ph	**1a**	**1b**
p-MeC_6H_4	**2a**	**2b**
Me	**3a**	**3b**

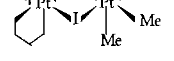
The *cis*,*cis*-dimethyl-dimethyl complex **3a** was prepared by the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with either two equivalents of $[PtMe_2(dppm)]$ or one equivalent of dppm. The dimethylplatinum-platinacycle complex **3b** was prepared by reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with two equivalents of $[Pt\{(CH_2)_4\}(dppm)]$. The above reactions were carried out at room temperature in CH_2Cl_2 or C_6H_6 for several hours.

2.2. Reactions of the organodiplatinum(II) complexes

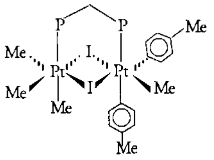
The reactions of the dialkyl-dialkyl diplatinum(II) complexes **3a** or **3b** with MeI in CH_2Cl_2 and at 0 °C gave organodiplatinum(IV) complexes **4a** or **4b**, respectively. Although for **4b** a more symmetrical isomer, in which two ring α-carbon atoms coordinate the positions *trans* to I and Me group on the same platinum center occupies the position *trans* to phosphorus, is possible, only the indicated isomer **4b** was formed. The known complex **4a** has been prepared by the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with MeI followed by the addition of dppm [8]. The diaryl-dialkyl complexes **2a** or **2b** reacted with neat MeI at 0 °C and gave organodiplatinum(IV) complexes **5a** or **5b**, respectively, only with the isomeric forms shown, although other isomeric forms are possible.



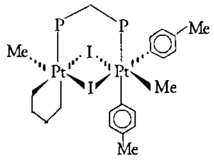
4a



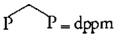
4b



5a

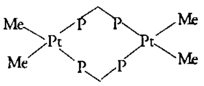


5b

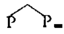


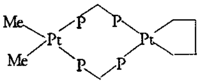
When reactions were carried out at higher temperatures, e.g. room temperature, considerable decomposition took place. For the reactions of complexes **2** one clear decomposition product in both cases was $[Pt(p\text{-}MeC_6H_4)_2MeI(dppm)]$ as confirmed by the $^{31}P\{^1H\}$-NMR data [9]. Also, complex **5b** when dissolved in $CDCl_3$ was, to some extent, converted to some unidentified compounds. Deuterium labeling studies using CD_3I (see ^1H-NMR data in Section 2.3) suggest that in these reactions, CD_3I reacts in a S_N2-type manner, whereby the metal centers in complexes **2** and **3** (shown by the general formula *cis*,*cis*-$[R_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtR'_2]$) attack the carbon atom of CD_3I to afford the transient cationic dinuclear intermediate of the type $[CD_3R_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtR'_2CD_3]^{2+}$. The anions I^- then enter the coordination spheres from the *trans* positions of attacking CD_3 followed by the displacement of SMe_2 to form the platinum(IV) complexes **4** and **5**. When R or R′ are Me groups, the scrambling of CD_3 and Me groups takes place in the *fac*-trimethylplatinum moiety, whereas when R is *p*-MeC_6H_4 or R'_2 is $(CH_2)_4$, the scrambling of CD_3 group is ceased by steric effects or ring constraints, respectively, and the entering CD_3 groups remain in the equatorial positions (Pt–P taken as axial direction). The studies are consistent with the stereoselective formation of complexes **4b** and **5a** exclusively with the indicated less symmetrical isomers. Also on this basis, it is not surprising to observe that the Me groups remain in the equatorial positions in complex **5b** to exclusively form the indicated isomer.

When dialkyl–dialkyl complexes **3** reacted with one equivalent of dppm, bis(dppm-bridged) complexes **6** were formed by displacement of SMe$_2$. The symmetrical diplatinum(II) complexes **6a** or [{Pt{(CH$_2$)$_4$}(μ-dppm)}$_2$] have been prepared [10,11] by reaction of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] or [{Pt{(CH$_2$)$_4$}(μ-SEt$_2$)}$_2$] with two equivalents of dppm. We believe that in these reactions, **3a** or [{Pt{(CH$_2$)$_4$}}$_2$(μ-SEt$_2$)(μ-dppm)], respectively, should have been formed as intermediates.



6a





6b

2.3. Characterization of complexes

The complexes were fully characterized using multinuclear (^{1}H-, ^{13}C{^{1}H}-, ^{31}P{^{1}H}-, ^{195}Pt{^{1}H}-) NMR spectroscopy (Tables 1–4) and microanalysis (Table 5).

2.3.1. Organodiplatinum(II) complexes 1–3

In the ^{31}P{^{1}H}-NMR spectra of each of the unsymmetrical complexes **1** and **2** (Fig. 1a), the two phosphorus atoms are inequivalent, appeared as two doublet signals, and showed short-range as well as long-range coupling platinum satellites. The first signal has parameters (δ around 13–15; $^1J_{PPt} \cong 1800$ Hz and

Table 1
^{1}H-NMR data for diplatinum(II) complexes **1**–**3**, diplatinum(IV) complexes **4**, **5** and bis(dppm-bridged)diplatinum(II) complex **6b** in CDCl$_3$

Complex	SMe$_2$ [a]	dppm	Pt–CH$_3$ (*trans* to P)	Pt–CH$_3$ (*trans* to SMe$_2$)	CH$_2$ protons of platinacycle ring	X [b]
	δ(CH$_3$) ($^3J_{PtH}$)	δ(CH$_2$) ($^2J_{PH}$, $^3J_{PtH}$)	δ(CH$_3$) ($^3J_{PtH}$, $^2J_{PH}$)	δ(CH$_3$) ($^2J_{PtH}$, $^3J_{PH}$)	δ(CH$_2$)	δ(CH$_3$)
1a	1.65 (19.0)	3.2 (7.5, [c])	0.01 (66.2, 7.2)	0.28 (86.4, 9.1)	–	–
1b	1.97 (17.8)	3.49 (7.3, [c])	–	–	1.04–1.75	–
2a	1.84 (19.2)	3.38 (7.5, [c])	0.19 (66.5, 7.2)	0.45 (87.3, 9.1)	–	2.00, 2.06
2b	1.91 (18.1)	3.43 (7.3, [c])	–	–	0.96–1.67	2.02, 2.10
3a	2.38 (19.3)	3.17 (8.7, 17.9)	0.15 (66.0, 7.5)	0.19 (85.5, 9.1)	–	–
3b	2.38 (18.3)	3.15 (8.4, 17.5)	0.35 (66.2, 10.2)	0.4 (86.9, 7.0)	1.1–1.8	–
			Pt–CH$_3$ (*trans* to I) δ(CH$_3$) ($^2J_{PtH}$, $^3J_{PH}$)	Pt–CH$_3$ (*trans* to P) δ(CH$_3$) ($^2J_{PtH}$, $^3J_{PH}$)		
4a	–	5.0 (2H) ([c])	0.92 (12H) (74.5, 7.0)	2.1 (6H) (61.5, 8.5)	–	–
4b	–	4.0 (1H), 4.7 (1H) ([c])	0.8 (3H) (74.5, 7.4)	2.0 (3H) (60.2, 7.3)	3.8 (1α-H) (^2J(PtH) = 97)	–
			1.1 (6H) [d] (77.9, 7.3)		Other protons 1–2.6 m	
5a	–	4.6 (1H), 5.0 (1H) ([c])	0.4 (3H) (73.2, 7.6)	1.9 (3H) (59.4, 7.6)		1.9
			1.1 (3H) (75.1, 7.5) 1.3 (3H) [d] (72.4, 7.4)			2.1
5b	–	4.9 (1H), 5.4 (1H) ([c])	1.6 (3H) (77.2, 7.6)	–	4.4 (1α-H) (^2J(PtH) = 92)	2.4
			1.77 (3H) (73.8, 6.6)	–	Other protons 1–3 m	2.5
			Pt–CH$_3$ (*trans* to P$_A$) δ(CH$_3$) ($^2J_{PtH}$, $^3J_{PH}$)	Pt–CH$_3$ (*trans* to P$_C$) δ(CH$_3$) ($^2J_{PtH}$, $^3J_{PH}$)		
6b [e]	–	2.7 (2H), 4.2 (2H) ([c])	−0.28 (3H) (70.2, 8.9)	0.67 (3H) (68.7, 8.1)	0.5–2 (separated signals)	–

[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] Intensity (3H) was lost when the diplatinum(IV) complex was prepared from CD$_3$I. The relative intensities of Me groups on *fac*-PtMe$_2$(CD$_3$) moiety of course remained 1:1:1 due to scrambling of different methyl groups.

[e] At −60 °C, using a Bruker Avance DRX 500 MHz NMR spectrometer. The data at room temperature: $\delta = 3.96$ and 2.69 (CH$_2$ of dppm); $\delta = 0.1$ (very broad, methyl groups); $\delta = 0.5$–2 (very broad, platinacycle ring protons).

Table 2
$^{13}C\{^1H\}$-NMR data for diplatinum(II) complexes **1**–**3**, diplatinum(IV) complex **4b** and bis(dppm-bridged)diplatinum(II) complex **6b** in $CDCl_3$

Complex	SMe_2	dppm	$PtCH_2^\alpha$orPtCH$_3$ (*trans* to P)	$PtCH_2^\alpha$orPtCH$_3$ (*trans* to SMe_2)	$PtCH_2^\beta$ (*trans* to P)	$PtCH_2^\beta$ (*trans* to SMe_2)	C^{1}ofAr [a] (*trans* to P)	C^{1}ofAr [a] (*trans* to SMe_2)	X [b]	
	$\delta(CH_2)$	$\delta(CH_2)$, ($^1J_{PC}$)	$\delta(CH_2)$ or $\delta(CH_3)$, ($^1J_{PtC}$, $^2J_{PC}$)	$\delta(CH_2)$ or $\delta(CH_3)$, ($^1J_{PtC}$, $^2J_{PC}$)	$\delta(CH_2)$, ($^2J_{PtC}$, $^3J_{PC}$)	$\delta(CH_2)$, ($^2J_{PtC}$, $^3J_{PC}$)	$\delta(C^1)$, ($^1J_{PtC}$, $^2J_{PC}$)	$\delta(C^1)$, ($^1J_{PtC}$, $^2J_{PC}$)	$\delta(CH_3)$	
1a	24.3	22.8 (15)	7.0 (661, 106)	−4.5 (748, 4)	–	–	163.9 (896, 116)	145.1 (1044, 8)	–	
1b	25.0	22.8 (17)	36.9 (701, 94)	28.6 (777, 3)	38.6 (31, 14)	34.7 (55, 5)	163.8 (920, 116)	154.6 (1116, 8)	–	
2a	24.3	22.8 (15)	7.0 (661, 106)	−4.5 (747, 4)	–	–	159.7 (908, 117)	140.5 (1060, 8)	21.4, 21.6	
2b	25.0	22.8 (15)	36.8 (701, 94)	28.5 (784, 3)	38.8 (31, 14)	34.6 (56, 5)	159.5 (917, 117)	141.0 (1041, 8)	21.0, 21.3	
3a	25.3	21.7 (14)	7.2 (634, 106)	−5.1 (737, [c])	–	–	–	–	–	
3b	25.1	21.0 (14)	6.3 [d] (660, 106) 36 [e] (700, 94)	−5.9 [d] (740, 4) 27.4 [e] (780, 3)	37.7 (32, 13)	33.5 (54, 5)	–	–	–	
			α-CH_2 (*trans* to P) $\delta(CH_2)$, ($^1J_{PtC}$, $^2J_{PC}$)	α-CH_2 (*trans* to I) $\delta(CH_2)$, ($^1J_{PtC}$) [f]	β-CH_2 (*trans* to P) $\delta(CH_2)$, ($^1J_{PtC}$, $^3J_{PC}$)	β-CH_2 (*trans* to I) $\delta(CH_2)$, ($^2J_{PtC}$, $^3J_{PC}$)	Pt–CH_3 (*trans* to I) $\delta(CH_3)$, ($^1J_{PtC}$) [f]			Pt–CH_3 (*trans* to P) $\delta(CH_3)$, ($^1J_{PtC}$, $^2J_{PC}$)
4b	–	35.9 (11)	39.9 (533, 108)	44.6 (663)	36.5 (19, 12)	35.5 (30, 6)	13.4 (654)	10.1 (657)	8.7 (721)	10.6 (520, 123)
			α-CH_2 $\delta(CH_2)$ ($^1J_{PtC}$, $^2J_{PC}$)	β-CH_2 $\delta(CH_2)$	Pt–CH_3 $\delta(CH_3)$					
6b [g]		28.5	40.5 (658, 90)	37	10.4					

[a] C^1 is aryl carbon directly attached to Pt.

[b] X is CH_3 substitution on aryl ligands.

[c] Not resolved.

[d] Pt–CH_3 group.

[e] Pt–$^\alpha CH_2$ group.

[f] $^2J_{PC}$ not resolved.

[g] The data at −60 °C (using a Bruker Avance DRX 500 MHz NMR spectrometer) are: the two Me carbons were appeared at $\delta(CH_3) = 8.5$ ($^2J_{PC} = 100$ Hz) and $\delta = 11.8$ ($^2J_{PC} = 100$ Hz); other signals were not resolved due to low intensity.

Table 3
$^{31}P\{^1H\}$-NMR data for diplatinum(II) complexes **1**–**3**, diplatinum(IV) complexes **4**, **5** and bis(dppm-brigded)diplatinum(II) complex **6b** in $CDCl_3$

Complex	P (phosphorus *trans* to aryl)		P (Phosphorus *trans* to alkyl)		$^2J_{PP}$
	δ(P), ($^1J_{PtP}$,$^3J_{PtP}$)		δ(P), ($^1J_{PtP}$,$^3J_{PtP}$)		
1a	13.3 (1801, 23)		22.3 [a] (1879, 38)		47
2a	13.0 (1798, 24)		22.0 [a] (1879, 38)		47
3a	–		17.5 [a] (1896, 29)		50
1b	14.6 (1800, [c])		21.3 [b] (1807, 29)		51
2b	14.4 (1798, 26)		21.1 [b] (1805, 37)		51
3b	–		18.2 [a] (1887, 31) 17.4 [b] (1819, 31)		53
4a [d]	–		−21.9 [a] (1056, –)		–
4b	–		−19.3 [a] (1069, –) −19.1 [b] (1006, –)		15
5a	−19.8 (996, –)		−20.6 [a] (1104, –)		6
5b	−19.6 (991, –)		−21.6 [b] (1037, –)		9
	Phosphorus *trans* to methyl		Phosphorus *trans* to CH_2 of metallacycle		
	$\delta(P_A)$ ($^1J_{PtP}$) ($^2J_{PAPB}$) ($^2J_{PAPC}$)	$\delta(P_C)$ ($^1J_{PtP}$) ($^2J_{PCPD}$) ($^2J_{PCPA}$)	$\delta(P_B)$ ($^1J_{PtP}$) ($^2J_{PBPA}$) ($^2J_{PBPD}$)	$\delta(P_D)$ ($^1J_{PtP}$) ($^2J_{PDPC}$) ($^2J_{PDPB}$)	
6b [e]	5.8 (1864) (43) (10)	11.5 (1815) (44) (11)	12.5 (1807) (43) (11)	6.1 (1810) (45) (10)	

[a] *Trans* to CH_3 group.
[b] *Trans* to CH_2 group of platinacycle.
[c] Not resolved.
[d] Taken from Ref. [8].
[e] At −60 °C.

$^3J_{PPt} \cong 25$ Hz) close to those found in aryldiplatinum(II) complexes *cis*,*cis*-[$Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2$] and therefore was assigned to the phosphorus atom of dppm which is connected to the R_2Pt (R = aryl) moiety [7]. The second signal (around $\delta = 21-22$) was assigned to the dialkyl Pt moiety. This has a $^1J_{PtP}$ value of 1879 Hz for complexes **1a** and **2a** (where alkyl is Me) which is higher than the $^1J_{PtP}$ value of 1806 Hz for complexes **1b** and **2b** (where dialkyl is $(CH_2)_4$). This difference, although modest, could be due to chelating $(CH_2)_4$ ligand in the latter that exerts a significantly higher *trans* influence than the methyl group [12,13].

In the $^{31}P\{^1H\}$-NMR spectrum of **3b**, the two inequivalent phosphorus atoms appeared as an AB pattern, and as expected the $^1J_{PtP}$ for the phosphorus *trans* to methyl group is higher than the $^1J_{PtP}$ for the phosphorus *trans* to CH_2 group of platinacycle. The two equivalent phosphorus atoms in the symmetrical complex **3a** resonated as a singlet and showed short-range as well as long-range coupling platinum satellites.

The $^{195}Pt\{^1H\}$-NMR spectra of the typical complexes **2** and **3b** each contains two doublet of doublets signals due to the two inequivalent platinum atoms with $^1J_{PtP}$ values close to the values obtained from the $^{31}P\{^1H\}$-NMR data described above. Also, each signal is accompanied by platinum satellites with $^2J_{PtPt}$ around 150 Hz due to coupling with the adjacent inequivalent platinum atom through the bridging SMe_2 ligand.

In the $^{13}C\{^1H\}$-NMR spectra of dimethyl complexes **1a** and **2a**, in each case, the two methyl groups which are attached to the same platinum center are inequiva-

Table 4
$^{195}Pt\{^1H\}$-NMR data for diplatinum(II) complexes **2** and **3**, diplatinium(IV) complexes **4b**, **5**, and bis(dppm-bridged)diplatinum(II) complex **6b** in $CDCl_3$

Complex	Pt (attached to aryls)	Pt (attached to alkyls)	J_{PtPt}
	δ(Pt),($^1J_{PtP}$, $^3J_{PtP}$)	δ(Pt), ($^1J_{PtP}$, $^3J_{PtP}$)	
2a	−4535 (1788, 43)	−4612 [a] (1863, 32)	143
2b	−4529 (1788, 43)	−4705 [b] (1798, 32)	150
3a		−4642 (1885, –)	–
3b	–	−4636 [a] (1894, 32) −4734 [b] (1820, 32)	150
4b	–	−3935 [a] (1060, –) −4015 [b] (996, –)	–
5a	−3371 (996, –)	−3975 [a] (1104, –)	–
5b	−3360 (996, –)	−4050 [b] (1038, –)	–
6b [c]	–	−49 143 [a] (1831, –) −4964 [b] (1820, –)	–

[a] Attached to Me group.
[b] Attached to CH_2 group of platinacycle.
[c] At −60 °C.

Table 5
Characterization data for diplatinum complexes **1**–**6**

Complex	Yield (%)	Melting point [a](°C)	Elemental analysis [b] (%)	
			C	H
1a	90	145	47.7 (48.2)	4.3 (4.3)
1b	88	160	48.7 (49.3)	4.4 (4.4)
2a	92	142	48.6 (49.2)	4.6 (4.5)
2b	89	162	49.5 (50.2)	4.6 (4.6)
3a	82	170	41.7 (41.5)	4.4 (4.4)
3b	74	135	42.7 (42.9)	4.4 (4.5)
4b	80	215	34.3 (34.4)	3.6 (3.6)
5a	75	155	40.6 (40.6)	4.0 (3.8)
5b	70	165	41.8 (41.6)	3.8 (4.0)
6b	85	205	53.8 (54.0)	4.7 (4.6)

[a] Decomposed.

[b] Found (calculated).

lent. Thus, the carbon atoms *trans* or *cis* to phosphorus appeared at $\delta = 7$ ($^2J_{PC(trans)} = 106$ Hz) and $\delta = -4.5$ ($^2J_{PC(cis)} = 4$ Hz), respectively. Also, $^1J_{PtC}$ for the carbon atom *trans* to phosphorus atom is about 87 Hz lower than $^1J_{PtC}$ for the carbon atom *trans* to SMe_2 due to the higher *trans* influence of phosphorus over sulfur. In the $^{13}C\{^1H\}$ spectra of the metallacycle complexes **1b** and **2b** again two signals with similar coupling patterns were observed for the two inequivalent α-CH_2Pt groups of the platinacycle ring. Also, in these complexes two signals at δ 38.6 and δ 34.7 were assigned to the two inequivalent β-CH_2 groups of ring *trans* to phosphorus ($^2J_{PtC} = 31$ Hz and $^3J_{PC} = 14$ Hz) and *cis* to phosphorus ($^2J_{PtC} = 55$ Hz and $^3J_{PC} = 5$ Hz), respectively. The aryl carbon atoms attached directly to the platinum center in R_2Pt moiety of complexes **1** and **2**, appeared further downfield from the other aromatic carbons and showed that the two aryl groups are inequivalent. Thus, the carbon atoms *trans* or *cis* to phosphorus atom gave $^2J_{PC(trans)} = 116$ Hz and $^2J_{PC(cis)} = 8$ Hz, respectively. As expected, the $^1J_{PtC}$ for the carbon atom *trans* to the phosphorus atom is some 150 Hz lower than the $^1J_{PtC}$ for the carbon atom *trans* to SMe_2.

The unsymmetrical complex **3b** contains both $PtMe_2$ and $Pt\{(CH_2)_4\}$ moieties and therefore its $^{13}C\{^1H\}$-NMR spectrum contained signals expected for these moieties with similar coupling patterns as discussed above for complexes **1** and **2**. Similarly the $^{13}C\{^1H\}$-NMR spectrum of the symmetrical complex **3a** confirmed that the two Me groups attached to the same platinum atom are inequivalent.

In the ^1H-NMR spectra of each of the diaryl–dialkyl complexes **1** and **2**, a quintet with relative intensity 1:8:18:8:1 was observed, which is characteristic of SMe_2 acting as bridging ligand between platinum centers, but with the unusual chemical shift $\delta = 1.65–1.94$ [7,8]. However, for dialkyl–dialkyl complexes **3**, the bridging SMe_2 signal appeared at the usual chemical shift of $\delta = 2.38$. In the spectra of dimethyl complexes **1a**–**3a** and **3b**, two signals in the region $\delta = 0–0.4$ were assigned to Me group *trans* to phosphorus atom ($^2J_{PtH} =$ ca. 66 Hz, $^3J_{PH} =$ ca. 7.4 Hz) and Me group *trans* to SMe_2 ($^2J_{PtH} =$ ca. 86 Hz, $^3J_{PH} = 9.1$Hz). For metallacy-

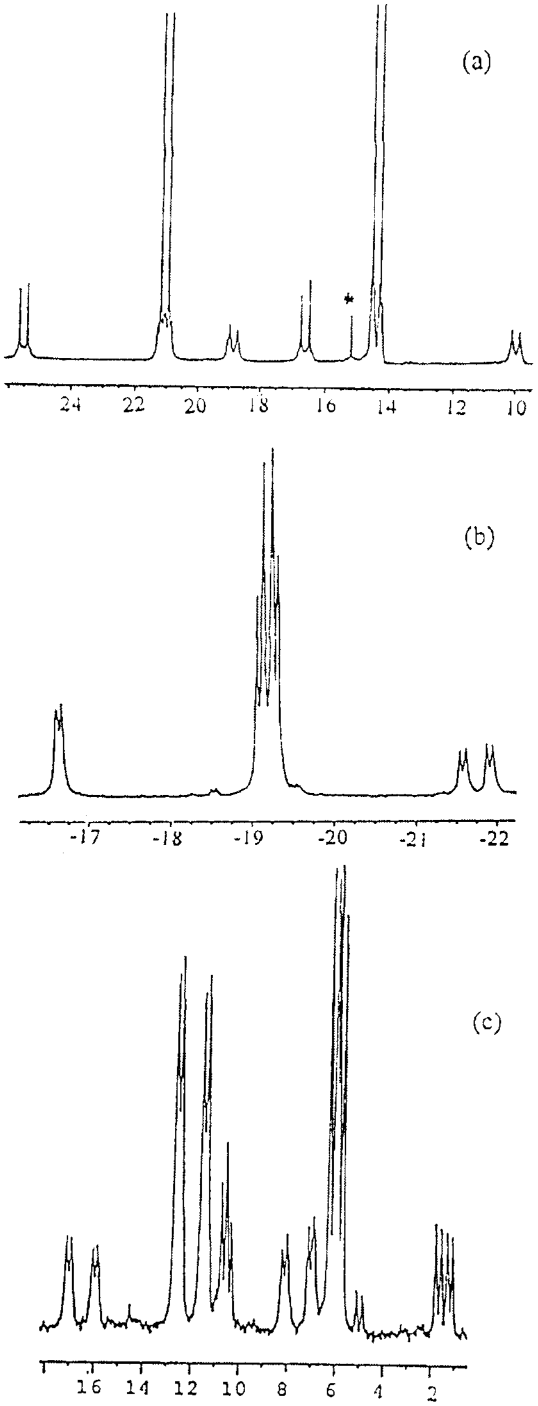
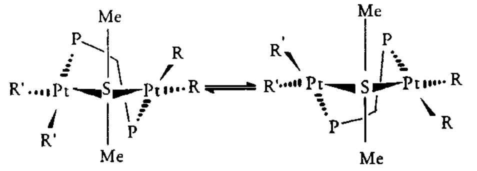


Fig. 1. $^{31}P\{^1H\}$-NMR spectra (202.5 MHz) of: (a) *cis,cis*-[(p-$MeC_6H_4)_2Pt(\mu$-$SMe_2)(\mu$-dppm)$Pt\{(CH_2)_4\}$] (**2b**); (b) [$Me_3Pt(\mu$-$I)_2(\mu$-dppm)$Pt\{(CH_2)_4\}Me$] (**3b**); and (c) [$Me_2Pt(\mu$-dppm$)_2Pt\{(CH_2)_4\}$] (**6b**) at −60 °C.

cle complexes **1b**–**3b**, the ring protons appeared as broad multiplets around $\delta = 1$–1.8. For complexes **2**, the Me substituted aryl ligands attached to the same platinum center, gave two Me resonances which further confirmed the inequivalency of the aryl ligands.

Based on the above results, as originally described for diaryl–diaryl complexes $[Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2]$ [7], structure and fluxionality mechanism given in Eq. (1) is suggested for complexes **1**–**3**. This leads to equivalence of the two Me groups on sulfur atom and also the two CH_2 protons of dppm, while the two organic ligands attached to the same platinum center remain inequivalent.



(1)

2.3.2. Organodiplatinum(IV) complexes **4b** and **5**

In the $^{31}P\{^1H\}$-NMR spectra of the unsymmetrical complexes **4b** and **5** (Fig. 1b) in each case, the two phosphorus atoms are inequivalent, appeared as an AB pattern around δ ca. -20, and showed short-range coupling platinum satellites ($^1J_{PtP}$) while the long-range coupling satellites ($^3J_{PtP}$) were not resolved. The $^1J_{PtP}$ values are in the expected range of 990–1100 Hz and are in agreement with the *trans* influence series $p\text{-}MeC_6H_4 > CH_2$ of metallacycle ring > Me.

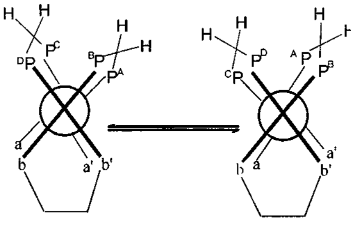
The $^{195}Pt\{^1H\}$-NMR spectra of complexes **4b** and **5** each contained two doublet signals with $^1J_{PtP}$ values exactly as could be predicted from the $^{31}P\{^1H\}$-NMR data described above. However, in contrast to the corresponding diplatinum(II) precursors **2** and **3b**, no platinum–platinum coupling was observed.

The $^{13}C\{^1H\}$-NMR spectrum of **4b** was more useful for structure determination. The methyl group *trans* to phosphorus atom occurred as a doublet at $\delta = 10.6$ with *trans* coupling $^2J_{PC} = 123$ Hz and with $^1J_{PtC} = 519$ Hz. The other methyl resonances *trans* to I (having a lower *trans* influence than phosphorus) occurred around the same region as singlets with $^1J_{PtC}$ values about 140 Hz more than the $^1J_{PtC}$ value for the Me group *trans* to phosphorus atom and with no resolvable *cis* coupling to phosphorus atom. The resonances for α-CH_2 and β-CH_2 groups of the metallacycle ring were appeared in the expected region of $\delta = 35$–45 [12,13]. The α-CH_2 group *trans* to phosphorus atom appeared as a doublet with $^2J_{PC} = 108$ Hz and $^1J_{PtC} = 533$ Hz, while the α-CH_2 group *trans* to I had no observable *cis* coupling to phosphorus atom and a higher $^1J_{PtC}$ value of 662 Hz. Also, the data for the β-CH_2 resonances similarly confirmed the stereochemistry of the metallacycle ring.

The ^1H-NMR spectra of the unsymmetrical diplatinum(IV) complexes **4b** and **5** each gave two broad multiplets around $\delta = 5$ for the two nonequivalent CH_2 groups of bridging dppm. For **4b**, the three Me groups *trans* to I were appeared around $\delta = 1$ with $^2J_{PtH}$ ca. 75 Hz, while the Me group *trans* to the phosphorus atom appeared around $\delta = 2$ with a lower $^2J_{PtH}$ value of 60.1 Hz. One characteristic broad signal at high chemical shift of $\delta = 3.83$ with $^2J_{PtH} = 97$ Hz was observed for one proton of one of the α-CH_2 groups of metallacycle ring, and the other ring protons appeared as broad peaks around $\delta = 1$–2.6. The data for complex **5a** indicated three resonances for Me groups *trans* to I and one resonance for the Me group *trans* to phosphorus atom, and the inequivalency of the aryl ligands was confirmed by the observation of two singlets for the methyl substituents. Similarly, the ^1H-NMR data for complex **5b** confirmed the isomeric form shown as the sole product. The 2/1 ratio of (Me *trans* to I)/(Me *trans* to P) in the ^1H-NMR spectrum of **4a** was also observed in the ^1H-NMR spectrum of the corresponding complex formed from CD_3I and this confirms that the methyl groups on the *fac*-Me_3Pt unit scramble. The changes observed for complexes **4b** and **5a** upon using CD_3I are indicated in the footnote of Table 1.

2.3.3. Bis(dppm-bridged)diplatinum(II) complex **6b**

Based on the multinuclear NMR data (see below), as originally described for complex **6a** [10] and then for $[\{Pt\{(CH_2)_4\}(\mu\text{-}dppm)\}_2]$ [11], the structure and fluxionality shown in Eq. (2) (Newman projection down PtPt axis, a and a′ represent non-equivalent Me groups while b and b′ indicate non-equivalent CH_2 groups of platinacycle) was suggested for the unsymmetrical dimer **6b**. Thus, the eight-membered $Pt_2P_4C_2$ dimetallacycle in the static solution structure (at low temperatures) has the twist–boat conformation which in contrast to the symmetrical dimers, e.g. **6a** [10], does not possess the C_2 symmetry. Therefore, in the low temperature $^{31}P\{^1H\}$-NMR spectrum (Fig. 1c), the four phosphorus atoms are different and in fact four signals with the corresponding platinum satellites were observed with the expected [10,11] parameters. The fine structure of each signal was lost at room temperature, however, due to the fluxionality of the $Pt_2P_4C_2$ skeleton which occurs via a simple twisting motion going through a boat–boat (saddle) intermediate [10].



(2)

The data has a good connectivity with the data obtained from the $^{195}Pt\{^1H\}$-NMR spectrum in which two apparent triplet signals were observed for the two inequivalent Pt atoms.

In the ^1H-NMR spectrum at -60 °C, the two nonequivalent Me groups were appeared at $\delta = -0.28$ ($^2J_{PtH} = 70.2$ Hz and $^3J_{PH} = 8.9$ Hz) and $\delta = 0.67$ ($^3J_{PtH} = 68.7$ Hz and $^3J_{PH} = 8.1$ Hz) (these were collapsed to a broad hump at $\delta = 0.14$ at room temperature). Also, the ring protons appeared as separated signals around $\delta = 0.5$–2 and two broad multiplets were observed for the CH_2P_2 protons.

In the $^{13}C\{^1H\}$-NMR spectrum at room temperature, the Pt–$^{\alpha}CH_2$ groups of the ring appeared as a doublet at $\delta = 28.5$ ($^2J_{(PC(trans))} = 89$ Hz, $^1J_{(PtC)} = 657$ Hz). Also, a broad signal at $\delta = 10.4$ was assigned to the Me groups (which was split into two doublets at $\delta = 8.5$ ($^2J_{P^AC} = 100$ Hz), and $\delta = 11.8$ ($^2J_{P^AC} = 100$ Hz) at -60 °C, although the platinum satellites were not resolved).

3. Experimental

The $^{31}P\{^1H\}$- and $^{195}Pt\{^1H\}$-NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer. Unless otherwise stated, the ^1H- and $^{13}C\{^1H\}$-NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer. References were TMS (^1H- and $^{13}C\{^1H\}$-NMR), 85% H_3PO_4 ($^{31}P\{^1H\}$-NMR), and aqueous $K_2[PtCl_4]$ ($^{195}Pt\{^1H\}$-NMR), and $CDCl_3$ was used as solvent in all cases. All the chemical shifts and coupling constants are in ppm and Hz, respectively. The complexes $[PtR_2(dppm)]$ and *cis*-$[PtR_2(SMe_2)_2]$ in which R = Ph or *p*-MeC_6H_4, are prepared as previously described [7]. The complexes $[Pt\{(CH_2)_4\}(dppm)]$ [14], $[PtMe_2(dppm)]$ [15] and $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ [16], were prepared by literature methods.

3.1. *cis,cis*-$[Ph_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtMe_2]$ (**1a**)

A mixture of *cis*-$[PtPh_2(SMe_2)_2]$ (78 mg, 0.16 mmol) and $[PtMe_2(dppm)]$ (100 mg, 0.16 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature (r.t.) for 8 h. The solvent was removed, and the white residue was washed twice with MeOH (2 ml) and dried in vacuo.

A similar procedure using $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (150 mg, 0.26 mmol) and $[PtPh_2(dppm)]$ (317 mg, 0.52 mmol) in C_6H_6 (15 ml) gave the same product.

The following compounds were made similarly using the appropriate precursors: **2a**, using either an equimolar mixture of *cis*-$[Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2]$ and $[PtMe_2(dppm)]$ or $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and $[Pt\,(p\text{-}MeC_6H_4)_2(dppm)]$ (two equivalents); **1b** and **2b**, using an equimolar mixture of *cis*-$[PtR_2(SMe_2)_2]$ and $[Pt\{(CH_2)_4\}(dppm)]$; **3a**, using $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with either dppm (one equivalent) or $[PtMe_2(dppm)]$ (two equivalents) and stirring for 3 h; **3b**, using $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with $[Pt\{(CH_2)_4\}(dppm)]$ (two equivalents) and stirring for 3 h.

3.2. $[Me_3Pt(\mu\text{-}I)_2(\mu\text{-}dppm)Pt\{(CH_2)_4\}Me]$ (**4b**)

To a solution of **3b** (100 mg, 0.11 mmol), in CH_2Cl_2 (20 ml) at 0 °C, was added excess MeI (2 ml) and the reaction mixture was stirred for 3 h. The solvent and excess of MeI was removed and residue was washed twice with MeOH (2 ml).The white solid was dried in vacuo.

The compound **4a** was prepared similarly using **3a**.

3.3. $[Me_3Pt(\mu\text{-}I)_2(\mu\text{-}dppm)PtMe(p\text{-}MeC_6H_4)_2]$ (**5a**)

Compound **2a** (200 mg) was dissolved in neat MeI (5 ml) at 0 °C and was stirred at this condition for 1.5 h. The solvent was removed and the residue was washed twice with MeOH (2 ml) and Et_2O (2 ml). The white solid was dried in vacuo.

A similar procedure was followed to prepare compound **5b** from **2b**.

The deuterated complexes $[Me_2CD_3Pt(\mu\text{-}I)_2(\mu\text{-}dppm)PtMe_2CD_3]$, $[Me_2CD_3Pt(\mu\text{-}I)_2(\mu\text{-}dppm)Pt\{(CH_2)_4\}CD_3]$ and $[Me_2CD_3Pt(\mu\text{-}I)_2(\mu\text{-}dppm)PtCD_3(p\text{-}MeC_6H_4)_2]$ were made similarly in about 10 mg scale using CD_3I.

3.4. $[Me_2Pt(\mu\text{-}dppm)_2Pt\{(CH_2)_4\}]$ (**6b**)

Compound **3b** (200 mg, 0.22 mmol) and dppm (84.5 mg, 0.22 mmol) were dissolved in C_6H_6 (15 ml). After 2 h at r.t., the volume of the solution was reduced and pentane was added to precipitate the product as a white solid, which was recrystallized from CH_2Cl_2–pentane.

The compound **6a** was made similarly using an equimolar mixture of $[Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtMe_2]$ (**3a**) and dppm.

4. Conclusions

Diplatinum(II) complexes *cis,cis*-$[R_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtR'_2]$ are prepared generally by the reaction of diorgano monomer *cis*-$[PtR_2(SMe_2)_2]$ with diorgano monomer $[PtR'_2(dppm)]$. The reaction of the diplatinum(II) complexes with MeI or dppm is accompanied by the displacement of the labile ligand SMe_2 and formation of diplatinum(IV) complexes *fac*, *fac*-$[MeR_2Pt(\mu\text{-}I)_2(\mu\text{-}dppm)PtMeR'_2]$ or diplatinum(II) complexes *cis,cis*-$[R_2Pt(\mu\text{-}dppm)_2PtR'_2]$, respectively.

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