Organometallics **2000,** *19,* 2751−2755

Aryldiplatinum(II) Complexes Containing Dimethyl Sulfide and Bis(diphenylphosphino)methane as Bridging Ligands

Mehdi Rashidi,* Majid Hashemi, and Mozhgan Khorasani-Motlagh

Chemistry Department, College of Sciences, Shiraz University, Shiraz, Iran, 71454

Richard J. Puddephatt

Chemistry Department, The University of Western Ontario,
London, Ontario, N6A 5B7, Canada

Received October 4, 1999

A versatile and yet simple approach to synthesize a series of uncommon symmetrical and unsymmetrical diplatinum(II) complexes *cis,cis*-[$Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2$], **3**, in which Ar or Ar′ = Ph, *p*-MeC_6H_4, *m*-MeC_6H_4, or *p*-$MeOC_6H_4$, has been developed by the reaction of either *cis*-[$PtAr_2(SMe_2)_2$], **1**, with [$PtAr'_2(dppm)$], **2**, or *cis*-[$PtAr'_2(SMe_2)_2$] with [$PtAr_2(dppm)$].

Introduction

Although dinuclear platinum complexes have been known for many years, their number and variety have increased tremendously through the use of bridging bidentate phosphine ligands, notably bis(diphenylphosphino)methane (dppm = $Ph_2PCH_2PPh_2$), with a bite size more suitable for bridging than chelation.[1] 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.[2,3] Recently, anionic dinuclear platinum(II) complexes of general formula [NBu_4][$(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-}dppm)Pt(C_6F_5)_2$] each with two very different bridging ligands, a dppm and a halide ligand (X), have been synthesized and structurally characterized,[4] and the reactivity of this type of complex toward Lewis acids such as $AgClO_4$ has been studied.[5] However, dinuclear complexes with such different ligands bridging the metal centers at the same time are unusual.[2,3]

In the binuclear complexes [$Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2$] in which R = Me, Et, or Ph, steric effects influence the stability and the reactivity to a major extent. Thus, the bulk of the substituents R in the bidentate ligands has a significant effect on the stability of mononuclear [$PtMe_2(R_2PCH_2PR_2)$] vs dinuclear [$Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2$], and for R = Ph (i.e., dppm ligand), both complexes could be isolated, although the mononuclear form was more stable.[6] For the metallacyclic analogues of the above dppm complexes, again both mononuclear [$Pt(CH_2CH_2CH_2CH_2)(dppm)$] and dinuclear [$\{Pt(CH_2CH_2CH_2CH_2)(\mu\text{-}dppm)\}_2$] have been synthesized.[7,8] A versatile approach to bis (dppm-bridged) platinum(II) species uses the η^1-dppm intermediates, [$PtR_2(\eta^1\text{-}dppm)_2$].[9] Thus, the dimeric complex *cis,cis*-[$(o\text{-}MeC_6H_4)_2Pt(\mu\text{-}dppm)_2PtMe_2$] has been synthesized and structurally characterized.[9]

In this study, we observed that the bis (dppm-bridged) diplatinum(II) complexes with aryl ligands on both metal centers were not easily formed, most probably due to steric overcrowding. However, using a general approach, we have synthesized a series of symmetrical and unsymmetrical diplatinum(II) complexes of the type *cis,cis*-[$Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2$], **3**, in which Ar and Ar′ are identical or different aryl ligands. The lower steric requirements and the ability of SMe_2 to act as a bridging ligand appear to be responsible for the formation of this uncommon type of complex.

Results and Discussion

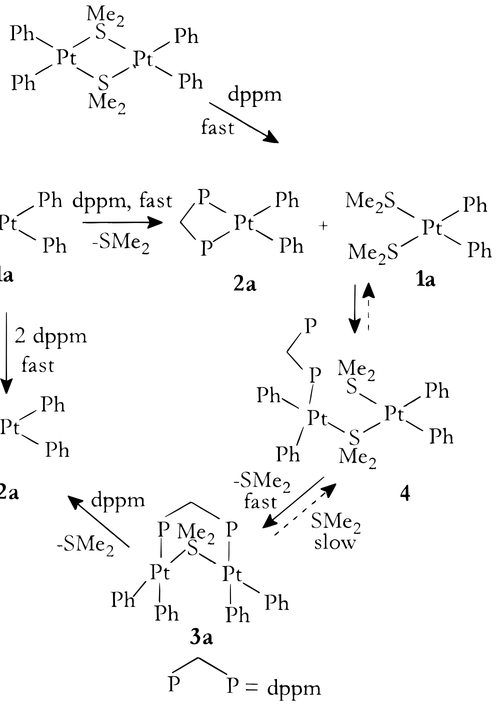
Synthesis of the Complexes. The synthetic route to the diplatinum(II) complex *cis,cis*-[$Ph_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtPh_2$], **3a**, as well as some of its reactions, is depicted in Scheme 1. Reaction of *cis*-[$PtPh_2(SMe_2)_2$], **1a**, with 0.5 equiv of dppm in CH_2Cl_2 or $CHCl_3$ gave after 8 h the dimeric complex **3a** in good yield. This reaction was monitored by ^1H NMR spectroscopy in $CDCl_3$, and it was found that [$PtPh_2(dppm)$], **2a**, was formed first. This then slowly reacted with **1a** to give the diplatinum(II) complex **3a**, probably via a transient intermediate **4**. The complex **3a** reacted slowly (over 48 h) with excess SMe_2 in C_6D_6 at 50 °C and was converted to the monomeric complex **2a**, as monitored by ^{31}P NMR spectroscopy. An equivalent amount of *cis*-[$PtPh_2$-

---

(1) Anderson, G. K. *Adv. Organomet. Chem.* **1993**, *35*, 1.
(2) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.
(3) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.
(4) Casas, J. M.; Falvello, L. R.; Fornies, J.; Martin, A.; Tomas, M. *J. Chem. Soc., Dalton Trans.* **1993**, 1107.
(5) Casas, J. M.; Falvello, L. R.; Fornies, J.; Martin, A. *Inorg. Chem.* **1996**, *35*, 7867.
(6) Muir, L. M.; Muir, K. W.; Frew, A. A.; Ling, S. S. M.; Thompson, M. A.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 1637.
(7) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 849.
(8) Rashidi, M.; Esmaeilbeig, A. R.; Shahabadi, N.; Tangestaninejad, S.; Puddephatt, R. J. *J. Organomet. Chem.* **1998**, *53*, 568.
(9) Hutton, A. T.; Pringle, P. G.; Shaw. B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1677.

10.1021/om990784t CCC: $19.00

Scheme 1



$(SMe_2)_2]$, **1a**, was also present in the solution, and on evaporation of the solvent and excess SMe_2, the dimer **3a** was re-formed along with trace amounts of **1a** and **2a**, as confirmed by ^1H and ^{31}P NMR spectra. Hence the reaction of **1a** and **2a** to give **3a** and SMe_2 is shown to be reversible. Reaction of **3a** with 1 equiv of dppm in $CDCl_3$ and at room temperature gave, after 30 h, $[PtPh_2(dppm)]$, **2a**, and free SMe_2 in a 2:1 mol ratio as checked by ^{31}P and ^1H NMR spectroscopy. It was not possible to convert **2a** to the dimer **3a** by reaction with SMe_2. The reaction of the dimeric complex $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ with 1 equiv of dppm in $CDCl_3$ similarly gave the dinuclear complex **3a**. Similarly the complex *cis*-$[Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2]$, **1b**, was reacted with 0.5 equiv of dppm and gave the dimeric complex *cis,cis*-$[(p\text{-}MeC_6H_4)_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)Pt(p\text{-}MeC_6H_4)_2]$, **3b**. Again, **3b** further reacted with 1 equiv of dppm to yield the mononuclear complex $[Pt(p\text{-}MeC_6H_4)_2(dppm)]$, **2b**.

Table 1. Characterization Data for Complexes *cis,cis*-$[Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2]$, 3

complex[a]	yield (%)	mp[b] (°C)	elemental analysis[c] (%) C	H
3a·CH_2Cl_2	96	141	50.5 (50.8)	4.0 (4.1)
3b·$0.2CH_2Cl_2$	79	147	54.4 (54.4)	4.9 (4.6)
3c·$0.5CH_2Cl_2$	86	132	53.7 (53.6)	4.7 (4.6)
3d	69	132	51.5 (52.2)	4.5 (4.3)
3e·$3/4CH_2Cl_2$	91	136	52.2 (52.2)	4.6 (4.3)
3f·$0.2CH_2Cl_2$	81	134	53.7 (53.7)	4.5 (4.4)
3g·CH_2Cl_2	73	132	49.8 (50.3)	4.2 (4.2)
3h·$0.5CH_2Cl_2$	82	126	53.4 (53.6)	4.8 (4.6)
3i·$0.1CH_2Cl_2$	90	137	53.0 (53.3)	4.5 (4.5)
3j·$0.5CH_2Cl_2$	86	135	52.4 (52.2)	4.6 (4.5)

[a] The solids tenaciously retain fractional amounts of solvent as confirmed by ^1H NMR spectroscopy. [b] Decomposed. [c] Found (calcd).

The above results directed us to develop the general approach shown in Scheme 2 to allow the synthesis of a series of symmetrical and unsymmetrical diplatinum(II) complexes of the type *cis,cis*-$[Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2]$, **3**. Thus, the reaction of either *cis*-$[PtAr_2(SMe_2)_2]$, **1**, with $[PtAr'_2(dppm)]$, **2**, or *cis*-$[PtAr'_2(SMe_2)_2]$ with $[PtAr_2(dppm)]$ at room temperature yielded the corresponding unsymmetrical complexes **3**.

Characterization of the Complexes. The complexes **3** were fully characterized using microanalysis (Table 1) and ^{31}P (Table 2), ^1H (Table 3) and ^{13}C (Table

Scheme 2

$$\left.\begin{array}{c} cis\text{-}[Pt\,Ar_2\,(SMe_2)_2] \;+\; [PtAr'_2\,(dppm)] \\ \text{or} \\ cis\text{-}[PtAr'_2\,(SMe_2)_2] \;+\; [PtAr_2\,(dppm)] \end{array}\right. \xrightarrow[\text{in } CH_2Cl_2]{-\,SMe_2 \atop \text{r.t., 8 h}} cis,cis\text{-}[Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2]$$

	Ar or Ar'		Ar or Ar'		Ar	Ar'
1a	Ph	**2a**	Ph	**3a**	Ph	Ph
1b	*p*-MeC_6H_4	**2b**	*p*-MeC_6H_4	**3b**	*p*-MeC_6H_4	*p*-MeC_6H_4
1c	*m*-MeC_6H_4	**2c**	*m*-MeC_6H_4	**3c**	*m*-MeC_6H_4	*m*-MeC_6H_4
1d	*p*-$MeOC_6H_4$	**2d**	*p*-$MeOC_6H_4$	**3d**	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$
				3e	Ph	*p*-MeC_6H_4
				3f	Ph	*m*-MeC_6H_4
				3g	Ph	*p*-$MeOC_6H_4$
				3h	*p*-MeC_6H_4	*m*-MeC_6H_4
				3i	*p*-MeC_6H_4	*p*-$MeOC_6H_4$
				3j	*m*-MeC_6H_4	*p*-$MeOC_6H_4$

Table 2. ^{31}P NMR Data for Complexes *cis,cis*-[$Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2$], 3, in $CDCl_3$

complex	$\delta(P_A)$	$^1J_{PtPA}$	$\delta(P_B)$	$^1J_{PtPB}$	$^3J_{PtP}$	$^2J_{PP}$
3a	15.16	1808			22	40.5
3b	15.40	1805			22	41.0
3c	16.11	1797			18	41.0
3d	15.66	1822			21	40.5
3e	15.40	1806	15.51	1806[a]	*b*	40.3
3f	15.46	1803	16.34	1801	*b*	42.6
3g	15.58	1814	15.72	1814[a]	*b*	41.3
3h	15.17	1805	16.16	1798	*b*	42.5
3i	15.31	1805	15.55	1805[a]	*b*	41.1
3j	14.52	1821	15.29	1797	*b*	42.0

[a] Short-range satellites for P_A and P_B were overlapped. [b] Not resolved.

Table 3. ^{1}H NMR Data for Complexes *cis,cis*-[$Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2$], 3, in $CDCl_3$

	SMe_2[a]	dppm	CH_3 on Ar	CH_3 on Ar′
complex	δ(Me) ($^3J_{PtH}$)	$\delta(CH_2)$ ($^2J_{PH}$)	$\delta(CH_3)$	$\delta(CH_3)$
3a	1.43	3.29		
	(20.1)	(7.5)		
3b	1.40	3.26	1.99	1.99
	(20.0)	(7.3)	2.02	2.02
3c	1.42	3.34	1.86	1.86
	(19.3)	(7.4)	2.09	2.09
3d	1.43	3.30	3.55	3.55
	(19.3)	(7.5)	3.59	3.59
3e	1.45	3.30		2.02
	(20.0)	(7.3)		2.05
3f	1.41	3.30		1.82
	(19.6)	(7.5)		2.05
3g	1.47	3.34		3.59
	(19.2)	(7.4)		3.61
3h	1.40	3.29	1.99	1.82
	(19.7)	(7.4)	2.03	2.05
3i	1.43	3.29	2.00	3.56
	(19.2)	(7.2)	2.04	3.59
3j	1.41	3.30	1.83	3.56
	(19.2)	(7.4)	2.06	3.60

[a] Appeared as a quintet with relative intensity 1:8:18:8:1.

4) NMR spectroscopy. The complex **3a** was further characterized by ^{195}Pt NMR spectroscopy (see below).

In the ^{31}P NMR spectra of the symmetrical complexes **3a**–**3d** (Figure 1a), the two equivalent phosphorus atoms resonated as a singlet around 15 ppm and showed platinum satellites. When one platinum center is ^{195}Pt, the two phosphorus atoms are no longer equivalent and appeared as two sets of satellites, one set due to the phosphorus atom attached directly to the ^{195}Pt atom ($^1J_{PtP}$ around 1800 Hz) and the other set due to the phosphorus atom further away from ^{195}Pt ($^3J_{PtP}$ around 20 Hz). The splitting in the satellites corresponds to a $^2J_{PP}$ value of around 40 Hz.

As expected in the light of the above data, the ^{195}Pt NMR spectrum of **3a** contained a doublet of doublets at $\delta = -4558$, with $^1J_{PtP}$ and $^3J_{PtP}$ values (1809 and 25 Hz, respectively) close to the $^1J_{PtP}$ and $^3J_{PtP}$ couplings obtained from the ^{31}P spectrum. The ^{195}Pt NMR data are particularly useful since it clearly confirms the presence of only one dppm bridging two platinum atoms.

In the ^{31}P NMR spectra of the unsymmetrical complexes **3e**–**3j** (Figure 1b), the two phosphorus atoms are inequivalent, appeared as an AB pattern, and showed short-range coupling platinum satellites, while the long-range coupling satellites were not resolved.

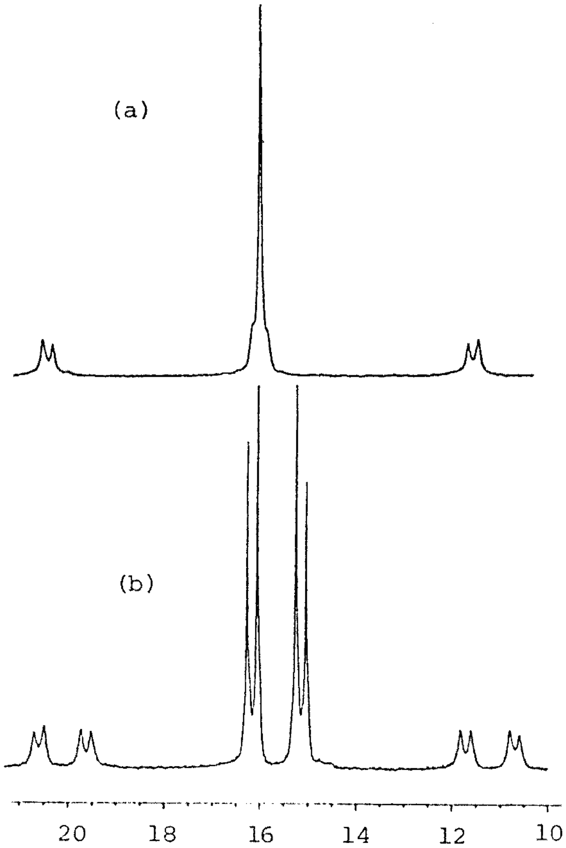


Figure 1. ^{31}P NMR spectra (202.5 MHz) of (a) *cis,cis*-[(m-$MeC_6H_4)_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)Pt(m\text{-}MeC_6H_4)_2$], **3c**, and (b) *cis,cis*-[(p-$MeC_6H_4)_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)Pt(m\text{-}MeC_6H_4)_2$], **3h**.

In the ^{1}H NMR spectrum of complex **3a**, a quintet with relative intensity 1:8:18:8:1 was observed, which is characteristic of SMe_2 acting as a bridging ligand between platinum centers, but with the unusual chemical shift $\delta = 1.42$.[10] A similar characteristic quintet was observed in the ^{1}H NMR spectrum of each of the other symmetrical or unsymmetrical dimers **3**. Also, in the case of methyl-substituted aryl ligands attached to the same platinum center, two Me resonances were observed, which confirmed the inequivalency of the aryl ligands at each platinum center.

The ^{13}C NMR spectra of complexes **3** were also useful for structure determination. In particular, the aryl carbon atoms attached directly to the platinum centers appeared further downfield from the other aromatic carbons and showed that the two aryl groups on each platinum center are inequivalent. Thus, the carbon atoms *trans* or *cis* to phosphorus gave $^2J_{PC(trans)}$ around 120 Hz and $^2J_{PC(cis)}$ around 6 Hz, respectively. Also, the $^1J_{PtC}$ for the carbon atom *trans* to the phosphorus atom is about 140 Hz lower than the $^1J_{PtC}$ for the carbon atom *trans* to SMe_2 due to the higher *trans*-influence of phosphorus over sulfur.

On the basis of the above results, the core given in Figure 2 with a twisted skeleton is suggested for the dimers **3**. As can be seen, each dimer is formed by two *cis*-Pt(aryl)$_2$ fragments joined by a bidentate dppm and a SMe_2 acting as bridging ligands. This results in two equivalent phosphorus atoms in the ^{31}P NMR spectra of symmetrical dimers **3a**–**3d**, while the aryl ligands on each platinum center are inequivalent in the ^{1}H and

---

(10) Rashidi, M.; Fakhroeian, Z.; Puddephatt, R. J. *J. Organomet. Chem.* **1991**, *261*, 406.

Table 4. ^{13}C NMR Data for Complexes *cis,cis*-[$Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2$], 3, in $CDCl_3$

	SMe_2	dppm	substitution on aryl ligand; CH_3 or OCH_3		C^1 of Ar[a] *trans* to P	C^1 of Ar[a] *trans* to SMe_2 (*cis* to P)	C^1 of Ar′[a] *trans* to P	C^1 of Ar′[a] *trans* to SMe_2 (*cis* to P)
complex	δ(Me)	$\delta(CH_2)$ ($^1J_{PC}$)	$\delta(CH_3)$Ar	$\delta(CH_3)$Ar′	$\delta(C^1)$ ($^2J_{PC}$,$^1J_{PtC}$)	$\delta(C^1)$ ($^2J_{PC}$,$^1J_{PtC}$)	$\delta(C^1)$ ($^2J_{PC}$,$^1J_{PtC}$)	$\delta(C^1)$ ($^2J_{PC}$,$^1J_{PtC}$)
3a	24.17	24.17			163.8	145.3	163.8	145.3
		(15.0)			(116.3, 904.8)	(4.3, 1040.4)	(116.3, 904.8)	(4.3, 1040.4)
3b	24.13	24.23	21.16	21.16	159.9	141.0	159.9	141.0
		(14.2)	21.32	21.32	(118.1, 907.4)	(3.9, 1054.2)	(118.1, 907.4)	(3.9, 1054.2)
3c	23.96	23.96	21.90	21.90	163.8	145.1	163.8	145.1
		(15.1)	21.92	21.92	(116.3, 901.4)	(3.8, 1049.7)	(116.3, 901.4)	(3.8, 1049.7)
3d	24.30	24.10	55.24	55.24	154.0	135.0	154.0	135.0
		(15.0)	55.60	55.60	(120.4, 919.9)	(4.0, 1068.0)	(120.4, 919.9)	(4.0, 1068.0)
3e	24.17	24.22		21.10	164.0	145.4	159.9	140.8
		(14.8)		21.27	(116.4, 904.7)	(6.2, 1046.8)	(118.0, 903.7)	(4.7, 1044.0)
3f	24.16	24.10		22.02	164.1	145.5	163.8	145.1
		(14.1)		22.02	(116.6, 903.1)	(7.9, 1048.0)	(116.2, 897.6)	(7.8, 1036.5)
3g	24.26	24.20		55.25	164.0	145.4	153.9	134.9
		(13.8)		55.61	(117.0, 905.1)	(3.8, 1055.5)	(121.4, 923.4)	(2.7, 1081.5)
3h	24.10	24.10	21.13	21.97	163.8	140.9	159.8	145.1
		(14.6)	21.31	21.97	(117.0, 903.2)	(8.8, 1045.4)	(118.2, 909.4)	(7.5, 1059.2)
3i	24.28	24.20	21.20	55.32	159.8	141.0	154.1	135.1
		(14.3)	21.37	55.68	(116.4, 909.5)	(6.4, 1051.0)	(120.4, 919.6)	(8.2, 1061.7)
3j	24.20	24.02	22.01	55.66	163.8	145.2	154.1	135.1
		(15.3)	22.02	55.28	(113.2, 903.2)	(3.0, 1040.0)	(120.3, 914.0)	(6.9, 1060.5)

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

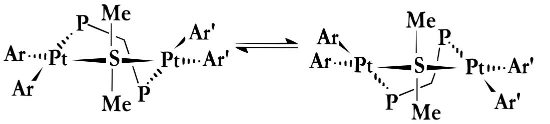


Figure 2. Suggested structure and proposed mechanism of fluxionality of the complexes *cis,cis*-[$Ar_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtAr'_2$].

^{13}C NMR spectra. The phosphorus atoms of dppm are inequivalent in the unsymmetrical dimers **3e**−**3j** since the metal centers are attached to different aryl ligands. This structural type was originally determined by single-crystal X-ray diffraction studies[5] for *cis,cis*-[$(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-}dppm)Pt(C_6F_5)_2$]. Note, however, that the static structure shown in Figure 2 should give two *Me*S and C*H*P_2 resonances when Ar ≠ Ar′. Since only one was observed, the complexes must be fluxional, as indicated in Figure 2. The $Pt_2C_4S(P_2C)$ atoms are then effectively coplanar.

Experimental Section

General Considerations. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer. ^{31}P NMR spectra were recorded on a Bruker Avance DRX 500 MHz NMR spectrometer. The ^{195}Pt NMR spectrum was obtained using a Varian XL-300 NMR spectrometer. References were TMS (^{1}H and ^{13}C), H_3PO_4 (^{31}P), and aqueous $K_2[PtCl_4]$ (^{195}Pt), and $CDCl_3$ was used as solvent in all cases. All the chemical shifts and coupling constants are in ppm and Hz, respectively. *cis*-[$PtPh_2(SMe_2)_2$], **1a**, and the corresponding dimeric complex [$Pt_2Ph_4(SMe_2)_2$] were made by the known method.[10] The following complexes were made similarly, except that in each case the residue, before the final washing with ether, was treated with SMe_2 in CH_2Cl_2 in order to convert the coexisting dimeric species into the monomer. *cis*-[Pt(*m*-$MeC_6H_4)_2(SMe_2)_2$], **1c**: yield 68%; mp 152 °C dec. Anal. Calcd for [Pt(*m*-$MeC_6H_4)_2(SMe_2)_2$]: C, 43.1; H, 5.2. Found: C, 43.2; H, 4.8. ^{1}H NMR ($CDCl_3$): δ 2.12 (s, $^3J_{PtH} = 23.5$ Hz, 12 H, SMe_2), 2.20 (s, 6 H, $ArCH_3$). *cis*-[Pt(*p*-$MeOC_6H_4)_2(SMe_2)_2$], **1d**: yield 58%; mp 143 °C dec. Anal. Calcd for [Pt(*p*-$MeOC_6H_4)_2(SMe_2)_2$]: C, 40.5; H, 4.9. Found: C, 40.5; H, 4.9. ^{1}H NMR ($CDCl_3$): δ 2.10 (s, $^3J_{PtH} = 23.1$ Hz, 12 H, SMe_2), 3.68 (s, 6 H, $ArOCH_3$). *cis*-[Pt(*p*-$MeC_6H_4)_2(SMe_2)_2$], **1b**, was made by the literature method.[11]

[$PtPh_2$(dppm)], **2a**, and [Pt(*p*-$MeC_6H_4)_2$(dppm)], **2b**, were prepared by the literature method.[12] The following complexes were prepared similarly. [Pt(*m*-$MeC_6H_4)_2$(dppm)], **2c**: yield 79%; mp 222 °C dec. Anal. Calcd for [Pt(*m*-$MeC_6H_4)_2$(dppm)]: C, 61.5; H, 4.7. Found: C, 61.0; H, 4.8. ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 6 H, $ArCH_3$), 4.42 (t, $^1J_{PH} = 9.3$ Hz, $^2J_{PtH} = 21.4$ Hz, 2 H, CH_2P_2). ^{31}P NMR ($CDCl_3$): $\delta - 37.01$ (s, $^1J_{PtP} = 1385$ Hz). [Pt(*p*-$MeOC_6H_4)_2$(dppm)], **2d**: yield 81%; mp 222 °C dec. Anal. Calcd for [Pt(*p*-$MeOC_6H_4)_2$(dppm)]: C, 59.0; H, 4.5. Found: C, 59.0; H, 4.7. ^{1}H NMR ($CDCl_3$): δ 3.68 (s, 6 H, $ArOCH_3$), 4.44 (t, $^2J_{PH} = 9.3$ Hz, 2 H, CH_2P_2). ^{31}P NMR ($CDCl_3$): δ −38.00 (s, $^1J_{PtP} = 1418$ Hz).

***cis,cis*-[$Ph_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtPh_2$], 3a.** (i) To a solution of *cis*-[$PtPh_2(SMe_2)_2$] (200 mg, 0.42 mmol) in CH_2Cl_2 (10 mL) was added dppm (81 mg, 0.21 mmol). The reaction mixture was stirred for 8 h at room temperature. The solvent was removed, and residue was washed twice with acetone (2 mL). The white solid was dried in vacuo.

A similar procedure using [$Pt_2Ph_4(\mu\text{-}SMe_2)_2$] (200 mg, 0.24 mmol) and dppm (94 mg, 0.24 mmol) gave the same product.

(ii) A mixture of *cis*-[$PtPh_2(SMe_2)_2$] (65 mg, 0.14 mmol) and [$PtPh_2$(dppm)] (100 mg, 0.14 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 8 h. The solvent was removed, and the residue was washed twice with acetone (2 mL). The white solid was dried in vacuo.

The other symmetrical dimers, **3b**, **3c**, and **3d**, were prepared similarly by method (ii) using the appropriate monomeric precursors. The complex **3b** was also prepared by method (i) using *cis*-[Pt(*p*-$MeC_6H_4)_2(SMe_2)_2$].

***cis,cis*-[$Ph_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)Pt(p\text{-}MeC_6H_4)_2$], 3e.** A mixture of *cis*-[$PtPh_2(SMe_2)_2$] (62 mg, 0.13 mmol)] and [Pt(*p*-$MeC_6H_4)_2$(dppm)] (100 mg, 0.13 mmol) in CH_2Cl_2 was stirred at room temperature for 8 h. The solvent was removed, and the white residue was washed twice with acetone (2 mL) and dried in vacuo.

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

The other unsymmetrical dimers, **3f**−**3j**, were made similarly using the appropriate mononuclear complexes.

Reaction of *cis,cis*-[$Ph_2Pt(\mu\text{-}SMe_2)(\mu\text{-}dppm)PtPh_2$], 3a, with dppm and SMe_2. (i) A small sample (8 mg, 0.0065

---

[11] Puddephatt, R. J.; Thomson, M. A. *J. Organomet. Chem.* **1982**, *238*, 231.

[12] Hassan, F. S.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1501.

mmol) of **3a** was dissolved in $CDCl_3$ (0.3 mL) in a sealed NMR tube, and dppm (2.5 mg, 0.0065 mmol) was added. Quantitative conversion to $[PtPh_2(dppm)]$ and free SMe_2 took place after 30 h at room temperature as checked by ^{31}P and ^1H NMR spectroscopy. Evaporation of the solvent (even in the presence of excess SMe_2 in another run) gave $[PtPh_2(dppm)]$.

(ii) A small sample (ca. 5 mg) of **3a** was dissolved in C_6D_6 (0.3 mL) in a sealed NMR tube, and a relatively large excess of SMe_2 was added. The sample gave an unchanged ^{31}P NMR spectrum after 24 h at room temperature. However, after the sample was heated for 48 h at 50 °C, conversion to $[PtPh_2(dppm)]$ took place according to the ^{31}P NMR spectrum. After the solvent and the excess SMe_2 were completely evaporated, **3a** was re-formed along with trace amounts of $[PtPh_2(dppm)]$ and *cis*-$[PtPh_2(SMe_2)_2]$.

Reaction of *cis*-$[PtPh_2(SMe_2)_2]$ or $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ with dppm in an NMR Tube. A small sample (10 mg, 0.021 mmol) of *cis*-$[PtPh_2(SMe_2)_2]$, **1a**, was dissolved in $CDCl_3$ (0.3 mL) in a sealed NMR tube, and dppm (4 mg, 0.011 mmol) was added. An equimolar mixture of $[PtPh_2(dppm)]$ and *cis*-$[PtPh_2(SMe_2)_2]$ along with 2 equiv of SMe_2 were immediately observed in the ^1H NMR spectrum. This mixture was gradually converted to **3a** in the solution. $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ on reaction with 1 equiv of dppm behaved similarly.

Acknowledgment. We thank the Shiraz University Research Council, Iran (Grant No. 73-SC-847-492) and NSERC (Canada) for financial support and Professors Banihashemi and Firouzabadi for their great help in purchasing the 250 MHz NMR instrument for the Shiraz University.

OM990784T