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

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A versatile and yet simple approach to synthesize a series of uncommon symmetrical and unsymmetrical diplatinum(II) complexes cis, cis-[Ar₂Pt(μ -SMe₂)(μ -dppm)PtAr'₂], **3**, in which Ar or Ar' = Ph, *p*-MeC₆H₄, *m*-MeC₆H₄, or *p*-MeOC₆H₄, has been developed by the reaction of either cis-[PtAr₂(SMe₂)₂], **1**, with [PtAr'₂(dppm)], **2**, or cis-[PtAr'₂(SMe₂)₂] with [PtAr₂(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 $M_2(\mu$ -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 [NBu₄][$(C_6F_5)_2$ Pt(μ -X)(μ -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 AgClO₄ 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 $[Pt_2Me_4(\mu-R_2PCH_2PR_2)_2]$ 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 [PtMe₂(R₂PCH₂PR₂)] vs dinuclear [Pt₂Me₄(µ-R₂PCH₂- $PR_2_2_1$, 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-(CH₂CH₂CH₂CH₂)(dppm)] and dinuclear [{Pt(CH₂CH₂- $CH_2CH_2)(\mu$ -dppm) $_2$] have been synthesized.^{7,8} A versatile approach to bis (dppm-bridged) platinum(II) species uses the η^1 -dppm intermediates, [PtR₂(η^1 $dppm)_2$].⁹ Thus, the dimeric complex *cis,cis*-[(*o*-MeC₆H₄)₂- $Pt(\mu$ -dppm)₂ $PtMe_2$] 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-[Ar₂Pt(μ -SMe₂)(μ -dppm)PtAr'₂], **3**, in which Ar and Ar' are identical or different aryl ligands. The lower steric requirements and the ability of SMe₂ 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-[Ph₂Pt(µ-SMe₂)(µdppm)PtPh₂], **3a**, as well as some of its reactions, is depicted in Scheme 1. Reaction of cis-[PtPh₂(SMe₂)₂], 1a, with 0.5 equiv of dppm in CH₂Cl₂ or CHCl₃ gave after 8 h the dimeric complex 3a in good yield. This reaction was monitored by ¹H NMR spectroscopy in CDCl₃, and it was found that [PtPh₂(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 SMe₂ in C_6D_6 at 50 °C and was converted to the monomeric complex 2a, as monitored by ³¹P NMR spectroscopy. An equivalent amount of cis-[PtPh2-

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 $(SMe_2)_2$], **1a**, was also present in the solution, and on evaporation of the solvent and excess SMe₂, the dimer 3a was re-formed along with trace amounts of 1a and 2a, as confirmed by ¹H and ³¹P NMR spectra. Hence the reaction of **1a** and **2a** to give **3a** and SMe₂ is shown to be reversible. Reaction of **3a** with 1 equiv of dppm in CDCl₃ and at room temperature gave, after 30 h, [PtPh₂-(dppm)], 2a, and free SMe2 in a 2:1 mol ratio as checked by ³¹P and ¹H NMR spectroscopy. It was not possible to convert **2a** to the dimer **3a** by reaction with SMe₂. The reaction of the dimeric complex $[Pt_2Ph_4(\mu-SMe_2)_2]$ with 1 equiv of dppm in CDCl₃ similarly gave the dinuclear complex **3a**. Similarly the complex cis-[Pt(p-MeC₆H₄)₂- $(SMe_2)_2$, **1b**, was reacted with 0.5 equiv of dppm and

Table 1. Characterization Data for Complexes cis,cis-[Ar₂Pt(µ-SMe₂)(µ-dppm)PtAr'₂], 3

			elemental analysis ^c (%)		
complex ^a	yield (%)	mp^b (°C)	С	Н	
$3a \cdot CH_2Cl_2$	96	141	50.5	4.0	
			(50.8)	(4.1)	
$3b \cdot 0.2 CH_2 Cl_2$	79	147	54.4	4.9	
			(54.4)	(4.6)	
$3c \cdot 0.5 CH_2 Cl_2$	86	132	53.7	4.7	
			(53.6)	(4.6)	
3d	69	132	51.5	4.5	
			(52.2)	(4.3)	
$3e \cdot 3/4CH_2Cl_2$	91	136	52.2	4.6	
			(52.2)	(4.3)	
3f-0.2CH ₂ Cl ₂	81	134	53.7	4.5	
			(53.7)	(4.4)	
3g·CH₂Cl₂	73	132	49.8	4.2	
			(50.3)	(4.2)	
3h •0.5CH ₂ Cl ₂	82	126	53.4	4.8	
			(53.6)	(4.6)	
3i.0.1CH ₂ Cl ₂	90	137	53.0	4.5	
			(53.3)	(4.5)	
3j.0.5CH ₂ Cl ₂	86	135	52.4	4.6	
•			(52.2)	(4.5)	

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

gave the dimeric complex *cis,cis*-[(*p*-MeC₆H₄)₂Pt(*u*-SMe₂)- $(\mu$ -dppm)Pt(*p*-MeC₆H₄)₂], **3b**. Again, **3b** further reacted with 1 equiv of dppm to yield the mononuclear complex $[Pt(p-MeC_6H_4)_2(dppm)], 2b.$

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-[Ar₂Pt(µ-SMe₂)(µdppm)PtAr'₂], **3**. Thus, the reaction of either *cis*-[PtAr₂-(SMe₂)₂], **1**, with [PtAr'₂(dppm)], **2**, or *cis*-[PtAr'₂(SMe₂)₂] with [PtAr₂(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 ³¹P (Table 2), ¹H (Table 3) and ¹³C (Table

Scheme	2
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cis- cis-	$[Pt Ar_{2} (SMe_{2})_{2}] + 0$ or $[PtAr'_{2} (SMe_{2})_{2}] = 0$	· [PtAr' r ⊦ [PtAr	2 (dppm)] 2 (dppm)]	$\frac{-\mathrm{SMe}_2}{\mathrm{r.t., 8 h}}$ in CH ₂ Cl ₂	cis,cis-	-[Ar ₂ Pt(µ-SMe ₂))(µ-dppm)PtAr' ₂]
	Ar or Ar'		Ar or Ai	- 1		Ar	Ar'
1a	Ph	2a	Ph		3a	Ph	Ph
1b	<i>p</i> -MeC ₆ H ₄	2b	p-MeC ₆ H	[₄	3b	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄
1c	m-MeC ₆ H ₄	2c	<i>m</i> -MeC ₆ H	ł ₄	3c	<i>m</i> -MeC ₆ H ₄	<i>m</i> -MeC ₆ H ₄

1 <i>d</i>	n-MeOC.H.	2d	p-MeOC ₆ H ₄
Id	p -meOC ₆ π_4	2u	p 1010006114

3d	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -MeOC ₆ H ₄
3e	Ph	<i>p</i> -MeC ₆ H ₄
3f	Ph	<i>m</i> -MeC ₆ H ₄
3g	Ph	<i>p</i> -MeOC ₆ H ₄

p-MeC₆H₄ m-MeC₆H₄ 3h

Table 2. ³¹P NMR Data for Complexes *cis,cis*-[Ar₂Pt(µ-SMe₂)(µ-dppm)PtAr'₂], 3, in CDCl₃

	•	•				
complex	$\delta(\mathbf{P}_{\mathbf{A}})$	$^{1}J_{\mathrm{PtPA}}$	$\delta(P_B)$	$^{1}J_{\mathrm{PtPB}}$	$^{3}J_{\mathrm{PtP}}$	$^{2}J_{\mathrm{PP}}$
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
3ĥ	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. ¹H NMR Data for Complexes *cis,cis*-[Ar₂Pt(µ-SMe₂)(µ-dppm)PtAr'₂], 3, in CDCl₃

	$\mathrm{SMe}_2{}^a$	dppm	$CH_3 \ on \ Ar$	CH ₃ on Ar'	
complex	$\overline{\delta(\text{Me})} (^{3}J_{\text{PtH}})$	$\overline{\delta(\mathrm{CH}_2)} (^2 J_{\mathrm{PH}})$	δ (CH ₃)	δ(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	
0	(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	
3	(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 ¹⁹⁵Pt NMR spectroscopy (see below).

In the ³¹P 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 ¹⁹⁵Pt, 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 ¹⁹⁵Pt atom (¹*J*_{PtP} around 1800 Hz) and the other set due to the phosphorus atom further away from ¹⁹⁵Pt (³*J*_{PtP} around 20 Hz). The splitting in the satellites corresponds to a ²*J*_{PP} value of around 40 Hz.

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

In the ³¹P 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 longrange coupling satellites were not resolved.

In the ¹H NMR spectrum of complex **3a**, a quintet with relative intensity 1:8:18:8:1 was observed, which



Figure 1. ³¹P NMR spectra (202.5 MHz) of (a) *cis,cis*-[(*m*-MeC₆H₄)₂Pt(μ -SMe₂)(μ -dppm)Pt(*m*-MeC₆H₄)₂], **3c**, and (b) *cis,cis*-[(*p*-MeC₆H₄)₂Pt(μ -SMe₂)(μ -dppm)Pt(*m*-MeC₆H₄)₂], **3h**.

is characteristic of SMe₂ 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 ¹H 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 ¹³C 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 ${}^{2}J_{PC(trans)}$ around 120 Hz and ${}^{2}J_{PC(cis)}$ around 6 Hz, respectively. Also, the ${}^{1}J_{PtC}$ for the carbon atom *trans* to the phosphorus atom is about 140 Hz lower than the ${}^{1}J_{PtC}$ for the carbon atom *trans* to SMe₂ 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 SMe₂ acting as bridging ligands. This results in two equivalent phosphorus atoms in the ³¹P NMR spectra of symmetrical dimers **3a**-**3d**, while the aryl ligands on each platinum center are inequivalent in the ¹H and

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Table 4. ¹³C NMR Data for Complexes *cis*,*cis*-[Ar₂Pt(µ-SMe₂)(µ-dppm)PtAr'₂], 3, in CDCl₃

	SMe ₂	dppm	substitution of CH3 or	on aryl ligand; r 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)	$\delta(\mathrm{CH_2})~(^1J_{\mathrm{PC}})$	δ (CH ₃)Ar	δ (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 (15.0)			163.8 (116.3, 904.8)	145.3 (4.3, 1040.4)	163.8 (116.3, 904.8)	145.3 (4.3, 1040.4)
3b	24.13	24.23 (14.2)	21.16 21.32	21.16 21.32	159.9 (118.1. 907.4)	141.0 (3.9, 1054.2)	159.9 (118.1. 907.4)	141.0 (3.9, 1054.2)
3c	23.96	23.96 (15.1)	21.90 21.92	21.90 21.92	163.8 (116.3, 901.4)	145.1 (3.8, 1049.7)	163.8 (116.3, 901.4)	145.1 (3.8, 1049.7)
3 d	24.30	24.10 (15.0)	55.24 55.60	55.24 55.60	154.0 (120.4, 919.9)	135.0 (4.0, 1068.0)	154.0 (120.4, 919.9)	135.0 (4.0, 1068.0)
3e	24.17	24.22 (14.8)		21.10 21.27	164.0 (116.4, 904.7)	145.4 (6.2, 1046.8)	159.9 (118.0, 903.7)	140.8 (4.7, 1044.0)
3f	24.16	24.10 (14.1)		22.02 22.02	164.1 (116.6, 903.1)	145.5 (7.9, 1048.0)	163.8 (116.2, 897.6)	145.1 (7.8, 1036.5)
3g	24.26	24.20 (13.8)		$55.25 \\ 55.61$	164.0 (117.0, 905.1)	145.4 (3.8, 1055.5)	153.9 (121.4, 923.4)	134.9 (2.7, 1081.5)
3h	24.10	24.10 (14.6)	21.13 21.31	21.97 21.97	163.8 (117.0, 903.2)	140.9 (8.8, 1045.4)	159.8 (118.2, 909.4)	145.1 (7.5, 1059.2)
3i	24.28	24.20	21.20 21.37	55.32 55.68	159.8 (116.4, 909.5)	141.0 (6.4, 1051.0)	154.1 (120.4, 919.6)	135.1 (8.2, 1061.7)
3j	24.20	24.02 (15.3)	22.01 22.02	55.66 55.28	163.8 (113.2, 903.2)	145.2 (3.0, 1040.0)	154.1 (120.3, 914.0)	135.1 (6.9, 1060.5)

^{*a*} C¹ is the aryl carbon directly connected to Pt.



Figure 2. Suggested structure and proposed mechanism of fluxionality of the complexes cis, cis-[Ar₂Pt(μ -SMe₂)(μ -dppm)PtAr'₂].

¹³C 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 studies⁵ for *cis*, *cis*-[(C₆F₅)₂-Pt(μ -SC₄H₈)(μ -dppm)Pt(C₆F₅)₂]. Note, however, that the static structure shown in Figure 2 should give two *Me*S and *CHP*₂ resonances when Ar \neq Ar'. Since only one was observed, the complexes must be fluxional, as indicated in Figure 2. The Pt₂C₄S(P₂C) atoms are then effectively coplanar.

Experimental Section

General Considerations. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer. ³¹P NMR spectra were recorded on a Bruker Avance DRX 500 MHz NMR spectrometer. The ¹⁹⁵Pt NMR spectrum was obtained using a Varian XL-300 NMR spectrometer. References were TMS (1H and 13C), H3PO4 (31P), and aqueous K₂[PtCl₄] (¹⁹⁵Pt), and CDCl₃ was used as solvent in all cases. All the chemical shifts and coupling constants are in ppm and Hz, respectively. *cis*-[PtPh₂(SMe₂)₂], 1a, and the corresponding dimeric complex [Pt₂Ph₄(SMe₂)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 SMe2 in CH2Cl2 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*-MeC₆H₄)₂(SMe₂)₂]: C, 43.1; H, 5.2. Found: C, 43.2; H, 4.8. ¹H NMR (CDCl₃): δ 2.12 (s, ³J_{PtH} = 23.5 Hz, 12 H, SMe₂), 2.20 (s, 6 H, ArCH₃). cis-[Pt(p-MeOC₆H₄)₂(SMe₂)₂], 1d: yield 58%; mp 143 °C dec. Anal. Calcd for [Pt(p-MeOC₆H₄)₂-(SMe₂)₂]: C, 40.5; H, 4.9. Found: C, 40.5; H, 4.9. ¹H NMR (CDCl₃): δ 2.10 (s, ${}^{3}J_{PtH} = 23.1$ Hz, 12 H, SMe₂), 3.68 (s, 6 H, ArOCH₃). cis-[Pt(p-MeC₆H₄)₂(SMe₂)₂], 1b, was made by the literature method.11

[PtPh₂(dppm)], **2a**, and [Pt(*p*-MeC₆H₄)₂(dppm)], **2b**, were prepared by the literature method.¹² The following complexes were prepared similarly. [Pt(*m*-MeC₆H₄)₂(dppm)], **2c**: yield 79%; mp 222 °C dec. Anal. Calcd for [Pt(*m*-MeC₆H₄)₂(dppm)]: C, 61.5; H, 4.7. Found: C, 61.0; H, 4.8. ¹H NMR (CDCl₃): δ 2.10 (s, 6 H, ArCH₃), 4.42 (t, ¹J_{PH} = 9.3 Hz, ²J_{PtH} = 21.4 Hz, 2 H, CH₂P₂). ³¹P NMR (CDCl₃): δ - 37.01 (s, ¹J_{PtP} = 1385 Hz). [Pt(*p*-MeOC₆H₄)₂(dppm)], **2d**: yield 81%; mp 222 °C dec. Anal. Calcd for [Pt(*p*-MeOC₆H₄)₂(dppm)]: C, 59.0; H, 4.5. Found: C, 59.0; H, 4.7. ¹H NMR (CDCl₃): δ 3.68 (s, 6 H, ArOCH₃), 4.44 (t, ²J_{PH} = 9.3 Hz, 2 H, CH₂P₂). ³¹P NMR (CDCl₃): δ -38.00 (s, ¹J_{PtP} = 1418 Hz).

cis, *cis*-[**Ph**₂**Pt**(μ -**SMe**₂)(μ -**dppm**)**PtPh**₂], **3a.** (i) To a solution of *cis*-[PtPh₂(SMe₂)₂] (200 mg, 0.42 mmol) in CH₂Cl₂ (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 $[Pt_2Ph_4(\mu-SMe_2)_2]$ (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*-MeC₆H₄)₂(SMe₂)₂].

cis, *cis*-[Ph₂Pt(μ -SMe₂)(μ -dppm)Pt(*p*-MeC₆H₄)₂], 3e. A mixture of *cis*-[PtPh₂(SMe₂)₂] (62 mg, 0.13 mmol)] and [Pt(*p*-MeC₆H₄)₂(dppm)] (100 mg, 0.13 mmol) in CH₂Cl₂ 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**₂**Pt**(μ -**SMe**₂)(μ -**dppm**)**PtPh**₂], 3a, with dppm and SMe₂. (i) A small sample (8 mg, 0.0065)

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mmol) of **3a** was dissolved in CDCl₃ (0.3 mL) in a sealed NMR tube, and dppm (2.5 mg, 0.0065 mmol) was added. Quantitative conversion to [PtPh₂(dppm)] and free SMe₂ took place after 30 h at room temperature as checked by ³¹P and ¹H NMR spectroscopy. Evaporation of the solvent (even in the presence of excess SMe₂ in another run) gave [PtPh₂(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 SMe₂ was added. The sample gave an unchanged ³¹P NMR spectrum after 24 h at room temperature. However, after the sample was heated for 48 h at 50 °C, conversion to [PtPh₂-(dppm)] took place according to the ³¹P NMR spectrum. After the solvent and the excess SMe₂ were completely evaporated, **3a** was re-formed along with trace amounts of [PtPh₂(dppm)] and *cis*-[PtPh₂(SMe₂)₂].

Reaction of *cis*-[PtPh₂(SMe₂)₂] **or** [Pt₂Ph₄(μ -SMe₂)₂] with dppm in an NMR Tube. A small sample (10 mg, 0.021

mmol) of *cis*-[PtPh₂(SMe₂)₂], **1a**, was dissolved in CDCl₃ (0.3 mL) in a sealed NMR tube, and dppm (4 mg, 0.011 mmol) was added. An equimolar mixture of [PtPh₂(dppm)] and *cis*-[PtPh₂-(SMe₂)₂] along with 2 equiv of SMe₂ were immediately observed in the ¹H NMR spectrum. This mixture was gradually converted to **3a** in the solution. [Pt₂Ph₄(μ -SMe₂)₂] on reaction with 1 equiv of dppm behaved similarly.

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