Stereoselectivity in Organometallic Reactions: Intramolecular Oxidative Addition of Aryl−Halogen Bonds to Platinum(II)

Cliff R. Baar, Geoffrey S. Hill, Jagadese J. Vittal, and Richard J. Puddephatt*

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

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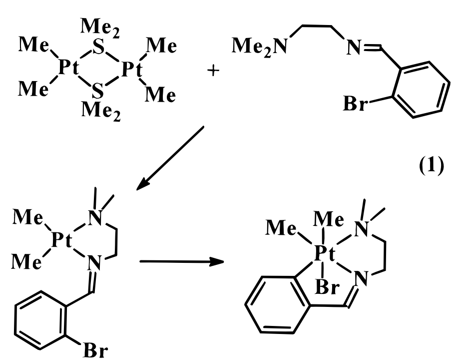
The degree of stereoselectivity in intramolecular oxidative addition of aryl−halogen bonds to platinum(II) has been determined using the following diimine ligands based on *trans*- or *cis*-1,2-diaminocyclohexane, *trans*-1,2-$(N{=}CHC_6H_4X)_2C_6H_{10}$ (X = Br, Cl), and *cis*-1,2-$(N{=}CHC_6H_4Br)_2C_6H_{10}$. Reaction of *trans*-1,2-$(N{=}CHC_6H_4X)_2C_6H_{10}$ (X = Br, Cl) with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ gave the isomerically pure binuclear complexes $[Pt_2Me_4X_2(\mu\text{-}SMe_2)\{$*trans*-1,2-$(N{=}CHC_6H_4)_2C_6H_{10}\}]$, which on further reaction gave the complexes $[Pt_2Me_4(\mu\text{-}X)_2\{$*trans*-1,2-$(N{=}CHC_6H_4)_2C_6H_{10}\}]$ by loss of Me_2S. The products are formed by oxidative addition of both aryl−halogen bonds of the diimine, yielding a novel chiral tetradentate N_2C_2-donor ligand. The ligand *cis*-1,2-$(N{=}CHC_6H_4Br)_2C_6H_{10}$ reacted with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give mononuclear platinum(IV) products of the type $[PtBrMe_2\{$*cis*-1,2-$(N{=}CHC_6H_4)(N{=}CHC_6H_4Br)C_6H_{10}\}]$ with approximately 90% stereoselectivity and $[PtBrMe_2(SMe_2)\{$*cis*-1,2-$(N{=}CHC_6H_4)(N{=}CHC_6H_4Br)C_6H_{10}\}]$, and these reactions involve oxidative addition of only one of the aryl−halogen bonds. ^1H NMR spectroscopy was used to characterize the new complexes and to establish diastereomeric ratios. The structures of complexes $[Pt_2Me_4Br_2(\mu\text{-}SMe_2)\{$*trans*-1,2-$(N{=}CHC_6H_4)_2C_6H_{10}\}]$ **(3a)**, $[Pt_2Me_4(\mu\text{-}Br)_2\{$*trans*-1,2-$(N{=}CHC_6H_4)_2C_6H_{10}\}]$ **(4a)**, and $[PtBrMe_2\{$*cis*-1,2-$(N{=}CHC_6H_4)(N{=}CHC_6H_4Br)C_6H_{10}\}]$ **(6a′)** have been established by X-ray structure determinations.

Introduction

The stereoselectivity of organometallic reactions of complexes containing chiral ligands is fundamental to chiral catalysis, and the tailoring of chiral catalysts requires a deeper understanding of this topic. This paper is concerned with the stereoselectivity of intramolecular aryl−halogen oxidative addition to platinum(II) complexes containing diimine ligands, and the factors considered in the choice of ligands for this study are discussed below.

Schiff-base ligands are useful in chiral catalysis and in the formation of cyclometalated complexes, which themselves have many applications in synthesis.[1−4] The particular ligands used were chosen to contain a pendant aryl−halogen bond in such a position that oxidative addition would yield a favorable five-membered metallacycle.[5−7] Platinum(II) diimine complexes such as $[PtMe_2(NN)]$ (NN = 2,2′-bipyridine or 1,10-phenanthroline) are known to be extremely reactive toward the oxidative addition of alkyl halides but not aryl halides.[8−11] However, aryl halides will react if the diimine ligand contains a pendant aryl−halogen bond which can undergo intramolecular oxidative addition (eq 1).[12] Many



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such reactions occur with *cis*-stereochemistry, and it has been suggested that a concerted mechanism is most probable.[12,13] The regioselectivity and the relative reactivities of different C−X bonds in such reactions have

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been studied[12,13] but not the stereoselectivity. It should, however, be noted that the oxidative addition of alkyl halides to cyclometalated platinum(II) complexes has shown stereoselectivity during both photochemical and thermal oxidative addition to achiral and chiral platinum(II) substrates, respectively.[14] The stereoselective oxidative addition of dihalogens and copper(II) halides to a cyclometalated square-planar platinum(II) center has also been achieved.[15] In order to study the stereoselectivity of aryl−halogen bond oxidative addition, the Schiff-base ligands based on *cis*- and *trans*-diaminocyclohexane were chosen since it was expected that they might have similar reactivity to those based on 1,2-diaminoethane used earlier (eq 1).[12,13]

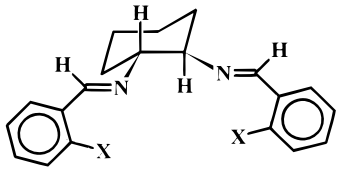
If the ligand used for a cycloplatination reaction is achiral, then two stereoisomers are possible, resulting from either *cis* or *trans* oxidative addition,[12,13] but the use of a chiral ligand necessarily generates two possible diastereomers when oxidative addition occurs at a prochiral metal center. Thus, four isomers are possible: two diastereomers resulting from *cis* oxidative addition and two from *trans* oxidative addition. This work shows that the intramolecular aryl−halogen bond oxidative additions to platinum(II) are highly stereoselective and that the products may arise from *trans* oxidative addition.

Results

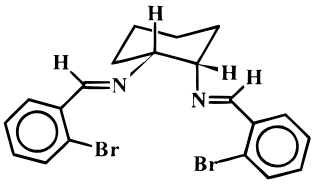
Synthesis and Characterization of Ligands. The optically pure (*R*,*R*) or racemic (*R*,*R*; *S*,*S*) ligands **1a** and **1b** were easily prepared by the condensation of *R*,*R*-*trans*-1,2-diaminocyclohexane or racemic *trans*-1,2-diaminocyclohexane with the appropriate 2-halogenobenzaldehyde derivative. The direct addition of $MgSO_4$ served as a convenient way to ensure continuous removal of water and reaction completion. For comparison, the *cis*-1,2-diaminocyclohexane derivative **1c** was prepared similarly, Chart 1. Efforts were made to prepare the products of condensation with a single benzaldehyde molecule, but the pure compounds could not be isolated. The ligands were formed as single isomers that are assumed to have *anti* stereochemistry about each imine, N═CH bond. Characterization of the ligands **1** by ^{1}H NMR spectroscopy and either microanalysis or high-resolution mass spectrometry was straightforward.

Reactions of the Ligands *trans*-1,2-(N═CHC$_6$H$_4$X)$_2$C$_6$H$_{10}$ (X = Br, Cl). The chemistry of the ligands

Chart 1

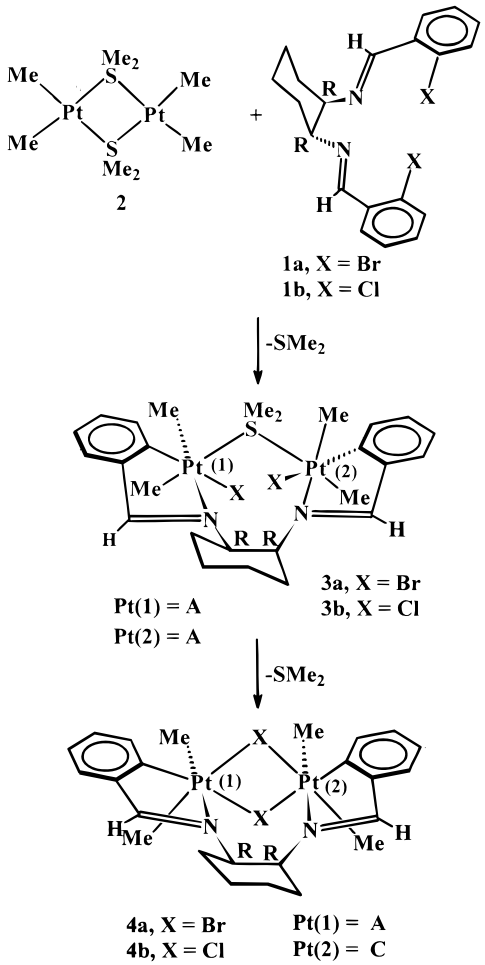


R,R-1a, X = Br
R,R-1b, X = Cl



R,S-1c

Scheme 1



trans-1,2-(N═CHC$_6$H$_4$X)$_2$C$_6$H$_{10}$ (X = Br, Cl) with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$], **2**, using THF as the solvent, yielded a mixture of two diplatinum complexes [Pt$_2$Me$_4$X$_2$(μ-SMe$_2$){*trans*-1,2-(N═CHC$_6$H$_4$)$_2$C$_6$H$_{10}$}] (X = Br (**3a**), Cl (**3b**)) and [Pt$_2$Me$_4$(μ-X)$_2${*trans*-1,2-(N═CHC$_6$H$_4$)$_2$C$_6$H$_{10}$}] (X = Br (**4a**), Cl, (**4b**)), even when excess ligand was used.

By monitoring the above reactions by ^{1}H NMR in CD_2Cl_2 solution, it was shown that **3** formed first and was

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Table 1. 300 MHz ^{1}H NMR Data for Complexes 3a−6a′

	N−Pt−Me		X−Pt−Me		S−Me		N=CH	
complex	δ (ppm)	^2J(PtH) (Hz)	δ (ppm)	^2J(PtH) (Hz)	δ (ppm)	^3J(PtH) (Hz)	δ (ppm)	^3J(PtH) (Hz)
3a[a]	1.06	66.9	1.30	75.3	1.76	7.4 11.8 19.6	8.98	47.6
3b[b]	0.97	67.2	1.20	75.1	1.66	7.4 12.0 19.4	8.91	48.1
4a[a]	1.65 1.91	67.6 71.5	0.99 1.18	77.5 76.0			8.38 8.68	38.2 45.6
4b[b]	1.50 1.75	66.2 71.0	0.87 1.07	77.1 76.8			8.38 8.69	38.0 45.4
5a′[a]	0.72 0.77	69.9 69.0					8.81 8.95	45.0 45.0
5a″[a]	0.48	66.0	0.60	76.5			8.52 8.92	48.0 36.0
6a′[a]	0.54	65.4	0.68	73.4			8.55 8.84	48.2 34.7

[a] In CD_2Cl_2. [b] In $CDCl_3$.

Chart 2

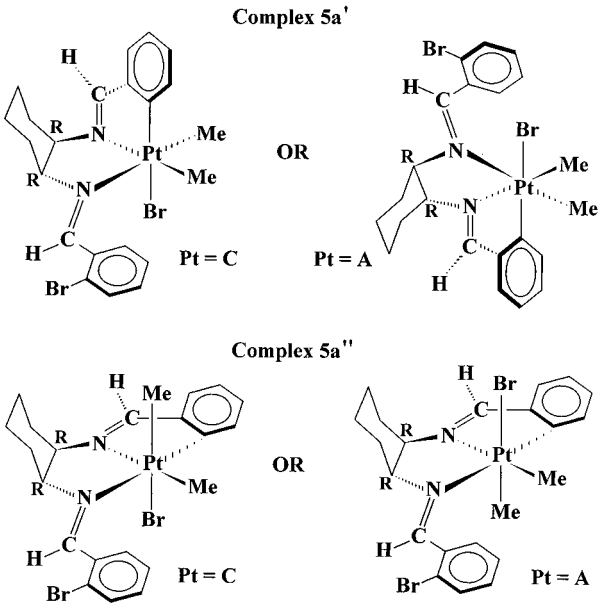
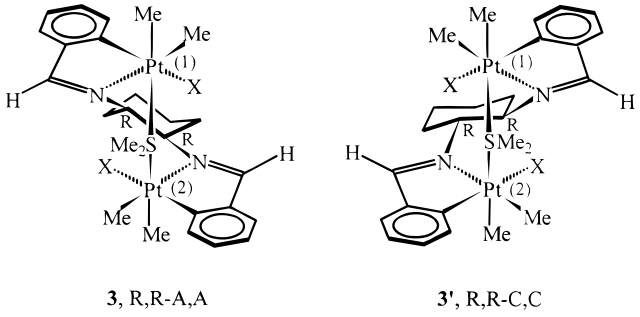


Chart 3



then slowly converted to **4** by loss of Me_2S and formation of the bridging bromide linkages. The formation of these diplatinum complexes **3** and **4** involves oxidative addition of both Ar−X bonds to platinum(II) to give a novel tetradentate ligand having *N*,*C* coordination at each of the two platinum(IV) centers; this was unexpected since analogous reactions (e.g., eq 1) led only to mononuclear platinum(IV) complexes formed by oxidative addition of just one Ar−X bond to give a tridentate, chelating *N*,*N*,*C* ligand, even in ligands where two Ar−X bonds are present.[12bc,13,16] Actually, the ^{1}H NMR spectra of reaction mixtures in CD_2Cl_2 solution did indicate that mononuclear platinum(IV) complexes tentatively identified as [PtBrMe$_2${*trans*-1,2-(N=CHC$_6$H$_4$)-(N=CHC$_6$H$_4$Br)C$_6$H$_{10}$}] (**5a′** and **5a″** formed by *trans* and *cis* oxidative addition, respectively, Chart 2) were also formed, but only as minor products (ca. 5% of each). Only the complexes **4** could be isolated in pure form from the above reactions. However, the intermediate complexes **3a** and **3b** are sparingly soluble in diethyl ether, and they could be isolated as precipitates when the reactions were carried out in this solvent.

The complexes were characterized by ^{1}H NMR spectroscopy in the first instance (Table 1). Each complex **3** gave only two methylplatinum resonances, one methylsulfur resonance, and one imine (N=CH) resonance, indicating a structure **3** or **3′** (Chart 3 shows a view roughly down the 2-fold axis, emphasizing the helical nature of the tetradentate ligand) having a 2-fold axis passing through the sulfur atom and the midpoint of the NC−CN bond of the cyclohexyl ring (C_2 symmetry). For example, **3b** gave methylplatinum resonances at δ = 0.97 (^2J(PtH) = 67.2 Hz) and 1.20 (^2J(PtH) = 75.1 Hz), assigned to the methylplatinum group *trans* to the imine group and the μ-SMe$_2$ ligand, respectively. The coupling constants are typical of methylplatinum(IV) groups and significantly lower than for methylplatinum(II) groups.[8−9,11−13,17] As expected, the three carbon donors are in *facial* geometry. The methylsulfur resonance (Figure 1) was particularly informative; for **3b**, this was observed at δ = 1.66, with platinum satellites

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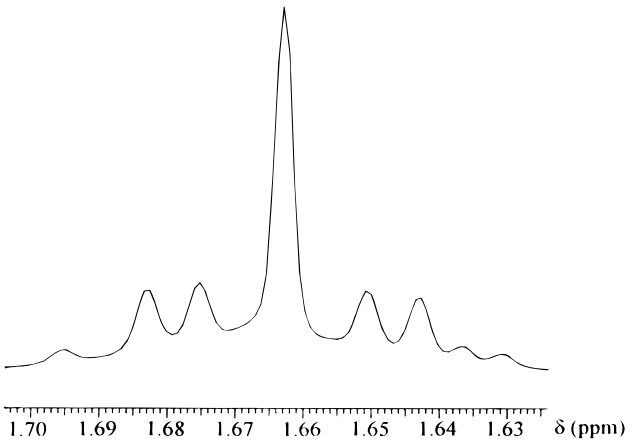

Figure 1. The Me_2S resonance in the ^1H NMR spectrum (300 MHz) of complex **3b**.

having $^3J(PtH) = 7.4$, 12.0, and, at lower intensity, 19.4 Hz, clearly indicating a structure in which the MeS groups of the μ-Me_2S ligand are in chemically equivalent but magnetically inequivalent environments. Hence, the $^3J(PtH)$ couplings of 7.4 and 12.0 Hz are due to molecules containing a single ^{195}Pt atom Pt(1) or Pt(2), while the satellites with $J_{obs} = 19.4$ Hz are due to molecules containing two ^{195}Pt atoms and $J_{obs} = {}^3J(Pt^1H) + {}^3J(Pt^2H)$. The imine protons of **3b** gave a single resonance at $\delta = 8.91$ with $^3J(PtH) = 48.1$ Hz. An X-ray structure determination (see below) subsequently showed that the structure was **3** rather than **3′** (Chart 3, Scheme 1).

The above reactions are remarkably selective. Thus, because the ligands **1a** and **1b** are chiral (*R*,*R* or *S*,*S*) and react with a prochiral metal center, two diastereomers are possible for each *cis* or *trans* oxidative addition; if we take the *R*,*R* isomer of the ligand, the product of an oxidative addition at a single metal center could be *R*,*R*-C or *R*,*R*-A, where C and A represent the absolute stereochemistry (clockwise or anticlockwise) at platinum(IV).[18] This will be the case for complexes **5a**, for which the stereochemistry at platinum is not established, though it appears that only one of the above isomers is present for each of **5a′** and **5a″**. Instead, if a diplatinum complex is formed, the use of a chiral ligand can give four stereoisomers for each *cis* or *trans* oxidative addition, namely those with *R*,*R*-C,A, *R*,*R*-A,C, *R*,*R*-A,A, and *R*,*R*-C,C configurations. For the present system leading to formation of **3**, if we assume that the *fac*-PtC_3 configuration will always be preferred, it is readily shown that there are a total of six stereoisomers possible, but only the isomer **3** arising from *trans* oxidative addition and having the *R*,*R*-A,A stereochemistry is observed (Scheme 1). Naturally, if the racemic ligand **1a** or **1b** is used, the racemic product **3** is obtained with configurations *R*,*R*-A,A and *S*,*S*-C,C.

The ^1H NMR spectra of complexes $[Pt_2Me_4(\mu\text{-}X)_2\{trans\text{-}1,2\text{-}(N{=}CHC_6H_4)_2C_6H_{10}\}]$, (X = Br (**4a**), Cl (**4b**)) also indicated the presence of a single isomer (Table 1) but in this case having C_1 symmetry. Thus, **4a** gave four methylplatinum resonances, two for MePt groups *trans* to halogen at $\delta = 0.99$ ($^2J(PtH) = 77.5$ Hz) and 1.18 ($^2J(PtH) = 76.0$ Hz) and two due to MePt groups *trans* to imine at $\delta = 1.65$ ($^2J(PtH) = 67.6$ Hz) and 1.91 ($^2J(PtH) = 71.5$ Hz). In addition, two imine N=CH resonances were observed at $\delta = 8.38$ ($^3J(PtH) = 38.2$ Hz) and 8.68 ($^3J(PtH) = 45.6$ Hz). The stereochemistry of **4a** was confirmed by an X-ray structure determination, which showed that each platinum center carries an opposing chirality (Pt(1) = A and Pt(2) = C) so that the stereochemistry is *R*,*R*-A,C (Scheme 1). The change in chirality at one of the platinum centers is needed to accommodate the two μ-Br ligands, and perhaps the requirement for this rearrangement may be responsible in part for the slow rearrangement of **3** to **4**.

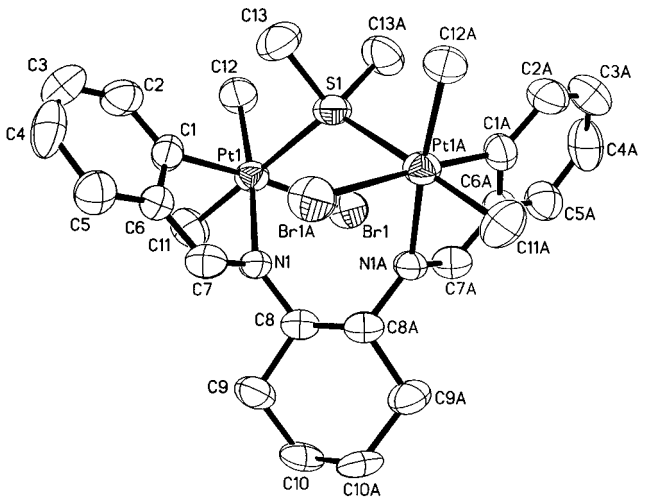

Figure 2. A view of the structure of complex **3a**.

The minor products **5** were not isolated in pure form and, because many of their ^1H NMR resonances were obscured by more intense resonances of **3** and/or **4** in the reaction mixtures, their characterization is uncertain. Complex **5a′** gave two MePt resonances at $\delta = 0.72$ ($^2J(PtH) = 69.9$ Hz) and 0.77 ($^2J(PtH) = 69.0$ Hz); the similarity of both the chemical shifts and coupling constants indicates that both MePt groups are *trans* to imine, hence defining structure **5a′**, but it is not known if the stereochemistry is *R*,*R*-A or *R*,*R*-C. Complex **5a″** also gave two MePt resonances at $\delta = 0.48$ ($^2J(PtH) = 66.0$ Hz) and 0.60 ($^2J(PtH) = 76.5$ Hz), suggesting MePt groups *trans* to imine and halogen, respectively, and hence structure **5a″**, and again the stereochemistry could be *R*,*R*-C or *R*,*R*-A (Chart 2).

Structures of Complexes 3a and 4a. Single crystals of optically pure **3a** $\{[Pt_2Me_4Br_2(\mu\text{-}SMe_2)\{trans\text{-}R,R\text{-}1,2\text{-}(N{=}CHC_6H_4)_2C_6H_{10}\}]\}$, prepared from the optically pure ligand *R*,*R*-**1a**, were grown from a mixture of CH_2Cl_2/pentane. A view of the structure is given in Figure 2, and selected bond lengths and angles are shown in Table 2. Complex **3a** is chiral and was solved in the chiral space group $C222_1$; there was a crystallographic 2-fold rotation axis bisecting the cyclohexyl ring and the sulfur atom of the μ-SMe_2 ligand of each molecule. The absolute stereochemistry was established by the X-ray structure determination as *R*,*R*-A,A, consistent with the known *R*,*R* configuration of the ligand. Each platinum atom is octahedrally coordinated by three carbon donors in a *facial* arrangement, a bromine atom, a nitrogen atom, and a shared μ-SMe_2 group. Each cyclometalated ligand fragment ($C_6H_4CH{=}NPt$) adopts a nearly planar arrangement, while the cyclohexane ring was shown to

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Table 2. Selected Bond Distances and Angles for Complex 3a[a]

Bond Distances (Å)			
Pt(1)−C(1)	2.006 (12)	Pt(1)−C(11)	2.032 (14)
Pt(1)−C(12)	2.082 (13)	Pt(1)−N(1)	2.156 (9)
Pt(1)−S(1)	2.520 (2)	Pt(1)−Br(1)	2.5616 (14)
S(1)−C(13)	1.820 (16)	N(1)−C(7)	1.30 (2)
N(1)−C(8)	1.456 (14)	C(1)−C(6)	1.44 (2)
C(6)−C(7)	1.42 (2)	C(8)−C(8A)	1.52 (2)

Bond Angles (deg)			
C(1)−Pt(1)−C(11)	87.1 (6)	C(1)−Pt(1)−C(12)	92.7 (6)
C(11)−Pt(1)−C(12)	90.7 (7)	C(1)−Pt(1)−N(1)	81.4 (4)
C(11)−Pt(1)−N(1)	87.5 (6)	C(12)−Pt(1)−N(1)	173.9 (5)
C(1)−Pt(1)−S(1)	90.6 (4)	C(11)−Pt(1)−S(1)	176.5 (5)
C(12)−Pt(1)−S(1)	91.9 (5)	N(1)−Pt(1)−S(1)	89.7 (3)
C(1)−Pt(1)−Br(1)	176.9 (4)	C(11)−Pt(1)−Br(1)	91.1 (5)
C(12)−Pt(1)−Br(1)	89.7 (5)	N(1)−Pt(1)−Br(1)	96.1 (3)
S(1)−Pt(1)−Br(1)	91.20 (5)	C(13A)−S(1)−C(13)	100.4 (13)
C(13A)−S(1)−Pt(1)	107.4 (6)	C(13)−S(1)−Pt(1)	107.9 (5)
C(13)−S(1)−Pt(1A)	107.4 (6)	Pt(1)−S(1)−Pt(1A)	123.6 (2)
C(7)−N(1)−Pt(1)	110.6 (8)	C(8)−N(1)−Pt(1)	129.5 (8)
C(6)−C(1)−Pt(1)	111.3 (9)	C(7)−C(6)−C(1)	117.1 (11)
N(1)−C(7)−C(6)	119.2 (12)	N(1)−C(8)−C(8A)	113.3 (8)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1, -z$; #2 $-x, y, -z + {}^1/_2$.

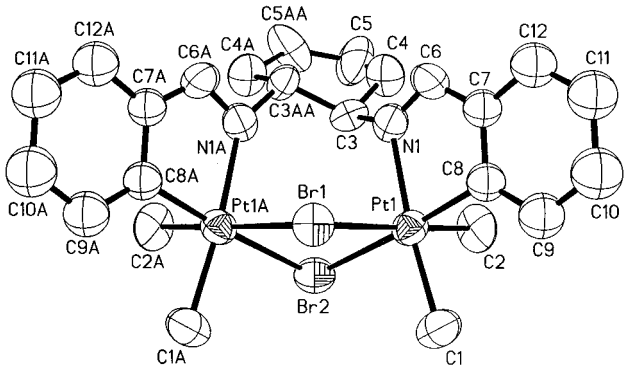


Figure 3. A view of the structure of complex **4a**.

be in the favored chair conformation, with equatorial imine substituents. Most of the angles surrounding each platinum center are close to the ideal 90°, except for C(1)−Pt(1)−N(1) = 81.4(4)° and N(1)−Pt(1)−Br(1) = 96.1(3)° associated with the chelate ring. All bond distances are in their typical ranges, when bond lengthening due to the strong *trans* influence of the carbon donors is taken into consideration.[19]

Crystals were grown of complex **4a** prepared both from optically pure (*R*,*R*) and racemic (*R*,*R*; *S*,*S*) ligand **1a**. There were problems in the refinement of the structure of the optically pure complex **4a**, but a successful structure determination was carried out using single crystals obtained from the racemic ligand. A view of the structure is given in Figure 3, and selected molecular dimensions are provided in Table 3. The structure was solved successfully in space group *Pnma*, but there were some complications. Thus, a crystallographic mirror plane containing the two bromine atoms and perpendicular to the PtPt axis is imposed on the diplatinum complex, although this is clearly impossible for the chiral complex. The situation is rationalized by disorder of the cyclohexyl ring, and the

(19) For example, see: (a) Clegg, D. E.; Hall, J. R.; Swile, G. A. *J. Organomet. Chem.* **1972**, *38*, 403. (b) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209. (c) Levy, C. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 2108.

Table 3. Selected Bond Distances and Angles for Complex 4a[a]

Bond Distances (Å)			
Pt(1)−Br(1)	2.621 (1)	Pt(1)−Br(2)	2.623 (1)
Pt(1)−N(1)	2.184 (9)	Pt(1)−C(1)	2.065 (12)
Pt(1)−C(2)	2.055 (10)	Pt(1)−C(8)	2.010 (6)
N(1)−C(6)	1.297 (15)	N(1)−C(3A)	1.511 (16)
N(1)−C(3)	1.512 (16)	C(6)−C(7)	1.438 (15)
C(3)−C(3AA)	1.548 (28)		

Bond Angles (deg)			
Br(1)−Pt(1)−Br(2)	85.99 (5)	C(8)−Pt(1)−Br(1)	91.8 (2)
C(2)−Pt(1)−Br(1)	178.9 (4)	C(1)−Pt(1)−Br(1)	90.9 (4)
N(1)−Pt(1)−Br(1)	90.8 (2)	C(8)−Pt(1)−Br(2)	176.0 (2)
C(2)−Pt(1)−Br(2)	94.0 (4)	C(1)−Pt(1)−Br(2)	88.8 (4)
N(1)−Pt(1)−Br(2)	96.7 (3)	C(8)−Pt(1)−N(1)	80.0 (4)
C(2)−Pt(1)−N(1)	88.1 (5)	C(1)−Pt(1)−N(1)	174.3 (4)
C(8)−Pt(1)−C(2)	88.2 (4)	C(8)−Pt(1)−C(1)	94.5 (4)
C(2)−Pt(1)−C(1)	90.2 (6)	Pt(1A)−Br(1)−Pt(1)	89.99 (6)
Pt(1)−Br(2)−Pt(1A)	89.94 (6)	C(6)−N(1)−Pt(1)	110.8 (8)
N(1)−C(3)−C(3AA)	109.3 (12)	N(1)−C(3A)−C(3B)	111.1 (12)
N(1)−C(6)−C(7)	118.1 (11)	C(8)−C(7)−C(6)	117.8 (7)
C(7)−C(8)−Pt(1)	113.1 (4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $x, -y + {}^1/_2, z$; #2 $x, -y + {}^3/_2, z$.

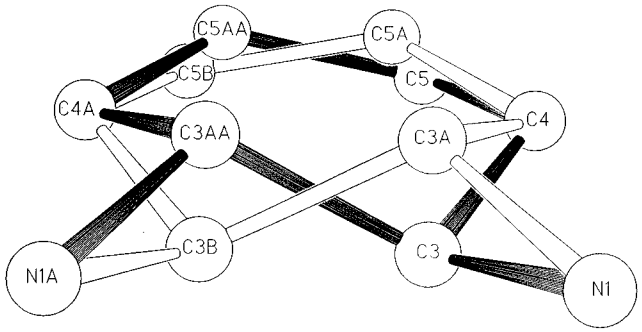


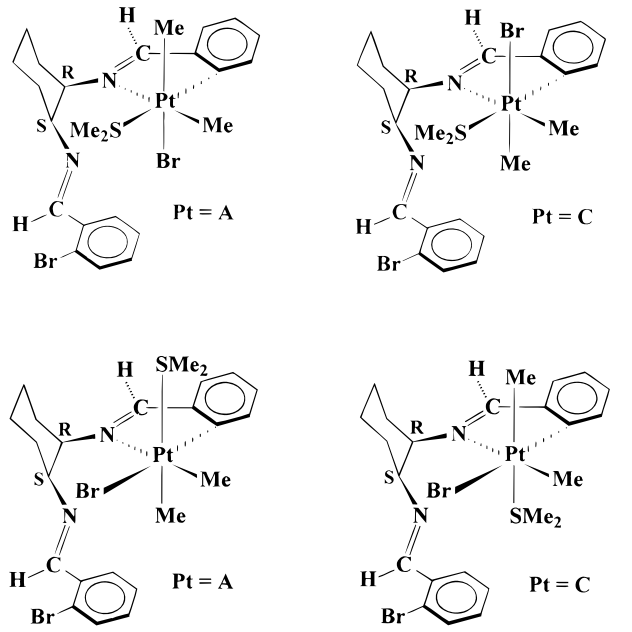
Figure 4. The disorder model for the cyclohexyl ring in **4a**.

successful 50:50 disorder model is shown in Figure 4. Thus, there are equal amounts of stereoisomers *R*,*R*-A,C and *S*,*S*-A,C present. Each platinum atom is octahedrally coordinated by three carbon donors in a *facial* arrangement, one nitrogen donor, and two shared bridging bromine atoms. Most angles surrounding the platinum center are close to the ideal 90°, with the greatest deviation being the chelate bite angle N(1)−Pt(1)−C(8) = 80.0(4)°. The Pt−N and Pt−Br bond lengths are in the expected range when one allows for the strong *trans* influence of the carbon donors.[19] The bond distances Br(1)−Pt(1) and Br(2)−Pt(1) are very similar, illustrating the similar *trans* influences of the aryl and methyl carbon donors C(2) and C(8).

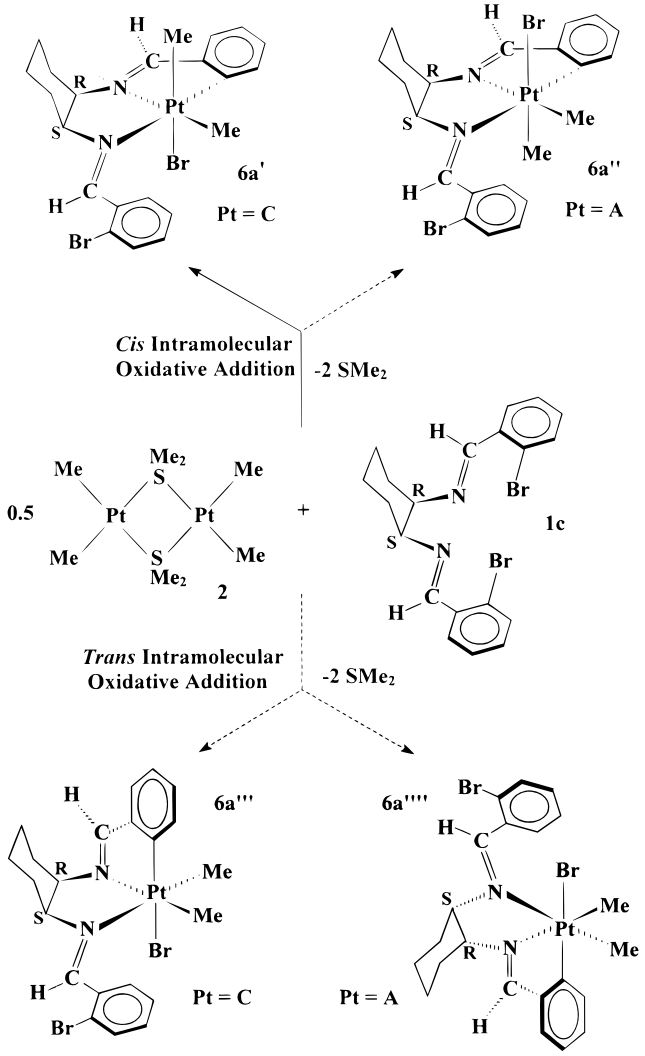
Reactions of the Ligand *cis*-1,2-(N=CHC$_6$H$_4$Br)$_2$-C$_6$H$_{10}$, 1c. The reaction of *cis*-1,2-(N=CHC$_6$H$_4$Br)$_2$C$_6$H$_{10}$, **1c**, with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] in diethyl ether gave, as the major product, the mononuclear platinum(IV) complex [PtBrMe$_2$\{*cis*-1,2-(N=CHC$_6$H$_4$)(N=CHC$_6$H$_4$Br)-C$_6$H$_{10}$\}], **6a′**, with complete displacement of both μ-SMe$_2$ ligands from platinum. In addition, when the reaction was monitored by ^{1}H NMR, a minor isomer of **6a** was tentatively identified. If the reaction is carried out in THF/CH$_3$CN, two other complexes could be identified and were characterized by their ^{1}H NMR spectra as isomers of [PtBrMe$_2$(SMe$_2$)\{*cis*-1,2-(N=CHC$_6$H$_4$)(N=CH-C$_6$H$_4$Br)C$_6$H$_{10}$\}], **7a′** and **7a″** (Chart 4). It was not possible to isolate these complexes **7a** in pure form. There was no evidence for formation of binuclear

Chart 4

Possible Stereochemistries for Complexes 7a' and 7a''



Scheme 2



complexes analogous to **3** or **4**, even when excess [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] was used, and all products are formed by oxidative addition of only one of the two C−Br bonds of the ligand **1c**.

Given this background, it is again useful to consider the possible isomers that could be formed. The ligand **1c**, although not optically active itself, still has the potential to yield four isomers of **6a** with the favored *fac*-PtC_3 grouping as a result of the intramolecular oxidative addition of the C−Br bond to platinum(II). Thus, two diastereomers with configurations *R*,*S*-C, and *R*,*S*-A can be formed for each *cis* or *trans* oxidative addition, as shown in Scheme 2. Isomer **6a′** is dominant although a second isomer, present in about 5% yield, was also tentatively identified.

The complexes were characterized by their ^{1}H NMR spectra and for **6a′**, the only complex which could be isolated in pure form, by an X-ray structure determination. For **6a′**, two methylplatinum resonances were observed at δ = 0.54 (^2J(PtH) = 65.4 Hz) and 0.68 (^2J(PtH) = 73.4 Hz), assigned as the methylplatinum groups *trans* to imine and bromide, respectively. Resonances at δ = 8.55 (^3J(PtH) = 48.2 Hz) and 8.84 (^3J(PtH) = 34.7 Hz) were assigned to the imine proton of the five-membered cycloplatinated ring and the imine proton of the nonmetalated 2-bromophenylimine fragment, respectively. Evidence for a second minor isomer was obtained only by observation of two very low intensity imine resonances at δ = 8.52 and 8.92, and the assignment is very tentative since the ^{195}Pt satellites were not resolved. The data are reported since the experiment gives an upper limit of *ca.* 5% for the yield of a minor isomer and, thus, shows that the reaction is again highly stereoselective; it is not known which of the possible structures **6a″**−**6a‴′** is present.

The isomers **7a′** and **7a″** each gave two MePt resonances, one MeS resonance, and two imine resonances, only one of which had resolved satellites due to coupling to ^{195}Pt; two of the MePt resonances and the MeS resonances of **7a′** and **7a″** had accidentally degenerate chemical shifts. The data define the stoichiometry but not the stereochemistry, and so it is not possible to distinguish between the possible structures shown in Chart 4.

Structure of Complex 6a′. Single crystals were grown by slow diffusion from a CH_2Cl_2/pentane mixture. A view of the structure is given in Figure 5, and selected bond lengths and angles are given in Table 4. The structure shows a stereochemistry consistent with *cis* oxidative addition at the platinum center. The platinum atom is octahedrally coordinated by two nitrogen donors, a bromide ligand, and three carbon donors in a *facial* arrangement. The nitrogen donor of one imine fragment was shown to be part of a metallacycle, and the resulting tridentate ligand adopts the *meridional* coordination geometry. There are no unusual features in the structure, the chief angle distortions C(3)−Pt(1)−N(1) = 81.4(4)° and N(1)−Pt(1)−N(2) = 79.3(3)° being associated with the chelate rings. There may be some angle strain involved in forming the second chelate ring, and this may account for the presence of **7a** in equilibrium with **6a** and Me_2S in the reaction mixtures.

The structure **6a′** is likely to be the thermodynamically preferred product. Thus, if the tridentate ligand

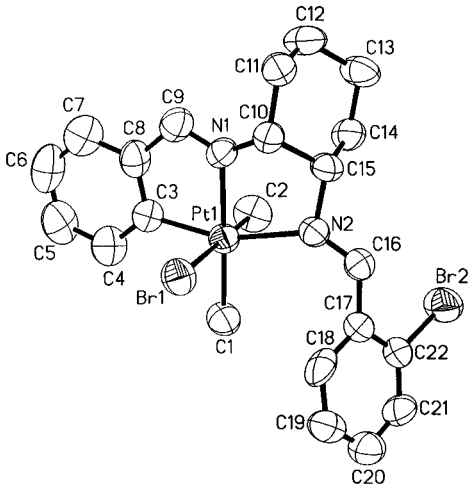


Figure 5. A view of the structure of complex **6a′**.

Table 4. Selected Bond Distances and Angles for Complex 6a′

Bond Distances (Å)			
Pt(1)−Br(1)	2.6217 (13)	Pt(1)−N(1)	2.100 (8)
Pt(1)−N(2)	2.223 (9)	Pt(1)−C(2)	2.073 (12)
Pt(1)−C(1)	2.092 (11)	Pt(1)−C(3)	2.009 (11)
N(1)−C(9)	1.279 (14)	N(1)−C(10)	1.467 (13)
N(2)−C(15)	1.526 (12)	N(2)−C(16)	1.268 (13)
C(3)−C(8)	1.404 (14)	C(8)−C(9)	1.496 (17)
C(10)−C(15)	1.558 (13)	C(16)−C(17)	1.473 (14)
C(22)−Br(2)	1.902 (10)		

Bond Angles (deg)			
N(1)−Pt(1)−Br(1)	87.7 (2)	N(2)−Pt(1)−Br(1)	92.3 (2)
C(1)−Pt(1)−Br(1)	91.6 (4)	C(2)−Pt(1)−Br(1)	177.5 (4)
C(3)−Pt(1)−Br(1)	91.6 (3)	C(3)−Pt(1)−N(1)	81.4 (4)
C(2)−Pt(1)−N(1)	93.7 (4)	C(1)−Pt(1)−N(1)	178.3 (4)
C(3)−Pt(1)−N(2)	160.1 (3)	C(2)−Pt(1)−N(2)	90.0 (5)
C(1)−Pt(1)−N(2)	102.2 (4)	N(1)−Pt(1)−N(2)	79.3 (3)
C(3)−Pt(1)−C(1)	97.1 (5)	C(3)−Pt(1)−C(2)	86.5 (5)
C(2)−Pt(1)−C(1)	87.0 (5)	C(9)−N(1)−C(10)	128.7 (10)
C(9)−N(1)−Pt(1)	115.0 (8)	C(10)−N(1)−Pt(1)	115.1 (6)
C(16)−N(2)−C(15)	113.6 (9)	C(16)−N(2)−Pt(1)	136.8 (7)
C(15)−N(2)−Pt(1)	109.1 (6)	C(4)−C(3)−Pt(1)	130.8 (9)
C(8)−C(3)−Pt(1)	111.2 (7)	C(3)−C(8)−C(9)	117.8 (10)
N(1)−C(9)−C(8)	114.4 (11)	N(1)−C(10)−C(11)	116.8 (9)
N(1)−C(10)−C(15)	106.7 (8)	N(2)−C(15)−C(14)	111.0 (8)
N(2)−C(15)−C(10)	109.9 (8)	N(2)−C(16)−C(17)	125.2 (10)

has a strong preference for the *mer* geometry and there is also a strong preference for the *fac*-PtC_3 geometry, the two most favored structures will be **6a′** and **6a″** (Scheme 2). In structure **6a′**, the bulkier bromide ligand is *anti* to the cyclohexyl group while the smaller methyl group is *syn*, this is likely to be preferred over **6a″**. It is not possible to determine if **6a′** is also the kinetic product.

Discussion

There have been several reports of the intramolecular oxidative addition of aryl−halogen bonds to a platinum(II) substrate, and this work contributes by giving the first results on the stereoselectivity of such reactions.[20] The use of the ligands *trans*- and *cis*-1,2-$(N{=}CHC_6H_4X)_2C_6H_{10}$ (X = Br, Cl), in systems where chiral and prochiral behavior is exhibited, has provided examples of intramolecular oxidative addition of C(aryl)-halogen bonds to a platinum(II) substrate with unprecedented stereoselectivity.

The stereochemistry of the intramolecular aryl-halide oxidative-addition reaction to platinum(II) has always been *cis* in previous studies.[12,13] This observation has provided an important argument in favor of a concerted mechanism of oxidative addition, though it has not been confirmed that the observed products are formed as a result of kinetic rather than thermodynamic control. In the present work, the *cis* oxidative addition was observed in the formation of the complex $[PtBrMe_2\{$*cis*-1,2-$(N{=}CHC_6H_4)(N{=}CHC_6H_4Br)C_6H_{10}\}]$, **6a′**, from the *cis* ligand **1c**, as expected from the above precedents. However, the formation of the complexes $[Pt_2Me_4X_2(\mu\text{-}SMe_2)\{$*trans*-1,2-$(N{=}CHC_6H_4)_2C_6H_{10}\}]$, **3a** and **3b**, from reaction of the *trans* ligands **1a** and **1b** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ occurs with *trans* stereochemistry. Furthermore, since the complexes **3** are not thermodynamically stable and slowly transform to **4** by loss of Me_2S, it is arguable, though by no means certain, that complexes **3** are the products of kinetic control. If this is the case, the mechanism cannot be concerted and a stepwise mechanism, perhaps involving a nucleophilic aromatic substitution, should be invoked instead.

The formation of the binuclear complexes **3** and **4** from the ligands **1a** and **1b** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ is interesting. One likely explanation is that the reaction occurs without fragmentation of the binuclear platinum(II) reagent and that the $Pt_2Me_4(\mu\text{-}SMe_2)$ fragment present in the initial product **3** (Scheme 1) remains throughout the reaction sequence. In any event, it seems unlikely that the two nitrogen donors of **1a** or **1b** chelate to a single platinum center, since this would surely lead to mononuclear products.

Experimental Section

^{1}H NMR spectra were recorded by using a Varian Gemini 300 MHz spectrometer and were referenced to the residual protons of the deuterated solvents. Chemical shifts are reported relative to TMS. The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, **2**, was prepared as described previously.[21] All operations were carried out under standard Schlenk conditions unless otherwise stated.

Ligand Synthesis. To a solution of racemic *trans*-1,2-diaminocyclohexane (4 mmol) in diethyl ether (20 mL) was added 2 equiv of 2-bromobenzaldehyde (8 mmol). Excess $MgSO_4$ was then added directly to the reaction mixture to ensure the continuous removal of water. The solution was stirred for 2 h at ambient temperature and then filtered to remove the $MgSO_4$. The solvent was removed under vacuum, leaving an off-white residue which was recrystallized from CH_2Cl_2/pentane to give racemic *trans*-1,2-$(N{=}CHC_6H_4Br)_2C_6H_{10}$, **1a**. Yield 89%. Anal. Calcd for $C_{20}H_{20}Br_2N_2$: C, 53.60; H, 4.50; N, 6.25. Found: C, 53.94; H, 4.36; N, 6.27%. ^{1}H NMR (acetone-d_6): δ 1.53 (br m, 2H, Cy(H)), 1.82 (br m, 6H, Cy(H)), 3.46 (br m, 2H, Cy(H)), 7.31 (m, 4H), 7.53 (dd, 2H), 7.96 (dd, 2H), 8.52 (s, 2H, N=CH).

The following ligands were similarly prepared. *R,R-trans*-1,2-$(N{=}CHC_6H_4Br)_2C_6H_{10}$, **1a***. ^{1}H NMR (acetone-d_6) as given above. Racemic *trans*-1,2-$(N{=}CHC_6H_4Cl)_2C_6H_{10}$, **1b**. Yield = 75%. Anal. Calcd for $C_{20}H_{20}Cl_2N_2$: C, 66.86; H, 5.61; N, 7.80. Found: C, 66.34; H, 5.61; N, 7.37. ^{1}H NMR ($CDCl_3$): δ 1.49 (br m, 2H, Cy(H)), 1.84 (br m, 6H, Cy(H)), 3.48 (br m, 2H, Cy(H)), 7.22 (m, 6H), 7.88 (dd, 2H), 8.62 (s, 2H, N=CH). *cis*-1,2-$(N{=}CHC_6H_4Br)_2C_6H_{10}$, **1c.** Anal. Calcd for $C_{20}H_{20}Br_2N_2$: C, 53.60; H, 4.50; N, 6.25. Found: C, 53.63; H, 4.46; N, 6.28. ^{1}H

(20) Keyes, M. C.; Young, V. G.; Tolman, W. B. *Organometallics* **1996**, *15*, 4133.

(21) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.

NMR (acetone-d_6): δ 1.60 (br m, 2H, Cy(H)), 1.73 (br m, 2H, Cy(H)), 2.05 (br m, 4H, Cy(H)), 3.71 (br m, 2H, Cy(H)), 7.36 (m, 4H), 7.61 (dd, 2H), 8.04 (dd, 2H), 8.62 (s, 2H, N=CH).

Racemic [$Pt_2Me_4Br_2(\mu$-SMe_2){*trans*-1,2-(N=$CHC_6H_4)_2C_6H_{10}$}], 3a. To a solution of ligand **1a** (0.11 mmol) in diethyl ether (15 mL) was added [$Pt_2Me_4(\mu$-$SMe_2)_2$] (0.11 mmol). The solution immediately turned yellow. Within minutes, a pale yellow precipitate began to form in the reaction mixture. The mixture was stirred overnight, and the precipitate of **3a** was isolated by filtration. It was then washed with diethyl ether (10 mL) and pentane (10 mL). Yield: 58%. Because the μ-SMe_2 ligands in complex **3a** were so readily lost, reliable microanalysis could not be obtained. ^{1}H NMR (CD_2Cl_2): δ 1.06 (s, 3H, ^2J(PtH) = 66.9 Hz, Pt−Me), 1.30 (s, 3H, ^2J(PtH) = 75.3 Hz, Pt−Me), 1.55 (br m, 4H, Cy(H)), 1.76 (s, 6H, ^3J(PtH) = 7.4, 11.8, 19.6 Hz, S−Me), 1.90 (br m, 2H, Cy(H)), 2.06 (br m, 2H, Cy(H)), 5.15 (br m, 2H, Cy(H)), 7.21 (m, 6H), 7.58 (m, 2H), 8.98 (s, 2H, ^3J(PtH) = 47.6 Hz, CH=N).

The optically pure complex was prepared similarly from the chiral ligand **1a***.

Racemic [$Pt_2Me_4Cl_2(\mu$-SMe_2){*trans*-1,2-(N=$CHC_6H_4)_2C_6H_{10}$}], 3b. This chloride analogue was similarly prepared from racemic *trans*-1,2-(N=$CHC_6H_4Cl)_2C_6H_{10}$, **1b**. Yield: 36%. As with the Br analog, the instability of complex **3b** with respect to loss of μ-SMe_2 ligands prevented acquisition of reliable microanalysis. ^{1}H NMR ($CDCl_3$): δ 0.97 (s, 3H, ^2J(PtH) = 67.2 Hz, Pt−Me), 1.20 (s, 3H, ^2J(PtH) = 75.1 Hz, Pt−Me), 1.54 (br m, 4H, Cy(H)), 1.66 (s, 6H, ^{3} J(PtH) = 7.4, 12.0, 19.4 Hz, S−Me), 1.90 (br m, 2H, Cy(H)), 2.04 (br m, 2H, Cy(H)), 4.93 (br m, 2H, Cy(H)), 7.20 (m, 6H), 7.56 (m, 2H), 8.91 (s, 1H, ^3J(PtH) = 48.1 Hz , N=CH).

Racemic [$Pt_2Me_4(\mu$-$Br)_2$){*trans*-1,2-(N=$CHC_6H_4)_2C_6H_{10}$}], 4a. A glass tube was charged with a solution of **3a** in CH_2Cl_2 and was layered with pentane. Crystals of **3a** and **4a** were formed over several days by slow diffusion. Crystals of **4a**, which formed in a large excess, were separated under microscope and washed with pentane (3 × 5 mL). Anal. Calcd for $C_{24}H_{32}Br_2N_2Pt_2$: C, 32.08; H, 3.59; N, 3.12. Found: C, 32.39; H, 3.58; N, 3.09. ^{1}H NMR (CD_2Cl_2): δ 0.99 (s, 3H, ^2J(PtH) = 77.5 Hz, Pt−Me), 1.18 (s, 3H, ^2J(PtH) = 76.0 Hz, Pt−Me), 1.57 (br m, 4H, Cy(H)), 1.65 (s, 3H, ^2J(PtH) = 67.6 Hz, Pt−Me), 1.90 (br m, 2H, Cy(H)), 1.91 (s, 3H, ^2J(PtH) = 71.5 Hz, Pt−Me), 2.06 (br m, 2H, Cy(H)), 4.10 (br m, 1H, Cy(H)), 6.10 (br m, 1H, Cy(H)), 7.11 (m, 2H), 7.21 (m, 2H), 7.34 (m, 2H), 7.43 (m, 2H), 8.38 (s, 1H, ^3J(PtH) = 38.2 Hz, N=CH), 8.68 (s, 1H, ^3J(PtH) = 45.6 Hz, N=CH). The optically pure complex was prepared similarly from ligand **1a***.

Racemic [$Pt_2Me_4(\mu$-$Cl)_2$){*trans*-1,2-(N=$CHC_6H_4)_2C_6H_{10}$}], 4b. A 5 mm NMR tube was charged with a solution of **3b** in CH_2Cl_2 and layered with pentane. Crystals of **4b** which formed over several days by slow diffusion were separated from the supernatant under a microscope and washed with pentane (3 × 5 mL). Due to the inseparable presence of trace amounts of complex **3b**, consistent microanalysis of species **4b** could not be obtained. ^{1}H NMR (CD_2Cl_2): δ 0.87 (s, 3H, ^2J(PtH) = 77.1 Hz, Pt−Me), 1.07 (s, 3H, ^2J(PtH) = 76.5 Hz, Pt−Me), 1.50 (s, 3H, ^2J(PtH) = 66.2 Hz, Pt−Me), 1.56 (br m, 4H, Cy(H)), 1.75 (s, 3H, ^2J(PtH) = 71.0 Hz, Pt−Me), 1.96 (br m, 4H, Cy(H)), 4.12 (br m, 1H, Cy(H)), 5.78 (br m, 1H, Cy(H)), 7.14 (m, 4H), 7.33 (m, 2H), 7.43 (m, 2H), 8.38 (s, 1H, ^3J(PtH) = 38.0 Hz, N=CH), 8.69 (s, 1H, ^3J(PtH) = 45.4 Hz, N=CH).

[$PtBrMe_2$){*trans*-1,2-(N=CHC_6H_4)(N=CHC_6H_4Br)-C_6H_{10}}], 5a′. ^{1}H NMR (CD_2Cl_2): δ 0.72 (s, 3H, ^2J(PtH) = 69.9 Hz, Pt−Me), 0.77 (s, 3H, ^2J(PtH) = 69.0 Hz, Pt−Me), 8.81 (s, 1H, ^3J(PtH) = 45.0 Hz, CH=N), 8.95 (s, 1H, ^3J(PtH) = 45.0 Hz, CH=N).

[$PtBrMe_2$){*trans*-1,2-(N=CHC_6H_4)(N=CHC_6H_4Br)-C_6H_{10}}], 5a″. ^{1}H NMR (CD_2Cl_2): δ 0.48 (s, 3H, ^2J(PtH) = 66.0 Hz, Pt−Me), 0.60 (s, 3H, ^2J(PtH) = 76.5 Hz, Pt−Me), 8.52 (s, 1H, ^3J(PtH) = 48.0 Hz, CH=N), 8.92 (s, 1H, ^3J(PtH) = 36.0 Hz, CH=N).

Racemic [$Pt_2Me_4Br_2(\mu$-SMe_2){*trans*-1,2-(N=$CHC_6H_4)_2$-C_6H_{10}}], 3a, and [$Pt_2Me_4(\mu$-$Br)_2$){*trans*-1,2-(N=$CHC_6H_4)_2$-C_6H_{10}}], 4a. To a solution of ligand **1a** (0.044 mmol) in THF (10 mL) was added [$Pt_2Me_4(\mu$-$SMe_2)_2$], **2** (0.044 mmol). The solution gradually turned pale yellow. The mixture was stirred overnight (*ca*. 15 h), and then the solvent was evaporated under vacuum. The resulting pale yellow residue was washed with pentane (10 mL) and was shown to be a mixture of complexes **3a** and **4a**, which were not easily separated.

The chloride analogues were similarly prepared from racemic *trans*-1,2-(N=$CHC_6H_4Cl)_2C_6H_{10}$, **1b**.

Racemic [$PtBrMe_2$){*cis*-1,2-(N=CHC_6H_4)(N=CHC_6H_4Br)-C_6H_6}], 6a. To a solution of ligand **1c** (0.11 mmol) in diethyl ether (5 mL) was added [$Pt_2Me_4(\mu$-$SMe_2)_2$], **2** (0.056 mmol). The solution color immediately turned yellow, and within minutes an off-white precipitate began to form. After the reaction was stirred overnight (*ca*. 15 h), the precipitate was filtered off, washed with diethyl ether (10 mL) and pentane (10 mL), and dried under vacuum. The product was recrystallized from CH_2Cl_2/pentane. Yield: 55%. Anal. Calcd for $C_{22}H_{26}Br_2N_2Pt$: C, 39.24; H, 3.89; N, 4.16. Found: C, 39.08; H, 3.80; N, 4.04. ^{1}H NMR (CD_2Cl_2): δ 0.54 (s, 3H, ^2J(PtH) = 65.4 Hz, Pt−Me), 0.68 (s, 3H, ^2J(PtH) = 73.4 Hz, Pt−Me), 1.27 (br m, 2H, Cy(H)), 1.55 (br m, 2H, Cy(H)), 1.90 (br m, 4H, Cy-(H)), 2.51 (m, 1H, Cy(H)), 4.50 (m, 1H, Cy(H)), 7.09 (m, 1H), 7.20 (m, 2H), 7.42 (m, 2H), 7.5 (m, 1H), 7.63 (dd, 1H), 8.24 (dd, 1H), 8.55 (s, 1H, ^3J(PtH) = 48.2 Hz, N=CH), 8.84 (s, 1H, ^3J(PtH) = 34.7 Hz, N=CH).

Racemic [$PtBrMe_2$){*cis*-1,2-(N=CHC_6H_4)(N=CHC_6H_4Br)-C_6H_{10}}], 6a, and [$PtBrMe_2(SMe_2)$){*cis*-1,2-(N=CHC_6H_4)-(N=$CHC_6H_4Br)C_6H_{10}$}], 7a. To a solution of ligand **1c** (0.087 mmol) in a 1:1 THF/CH_3CN mixture (10 mL) was added 0.5 equiv of complex [$Pt_2Me_4(\mu$-$SMe_2)_2$], **2** (0.044 mmol). After the reaction was stirred overnight, the solvent was evaporated under reduced pressure to give a bright yellow solid mixture of complexes **6a** and **7a**, which were not easily separated.

Racemic [$PtBrMe_2(SMe_2)$){*cis*-1,2-(N=CHC_6H_4)(N=CH-$C_6H_4Br)C_6H_{10}$}], 7a′. ^{1}H NMR (CD_2Cl_2): δ 1.04 (s, 3H, ^2J(PtH) = 70.5 Hz, Pt−Me), 1.27 (s, 3H, ^2J(PtH) = 68.1 Hz, Pt−Me), 1.45−2.20 (br m, 8H, Cy(H)), 2.01 (s, 6H, ^3J(PtH) = 14.0 Hz, MeS), 3.65 (m, 1H, Cy(H)), 5.10 (m, 1H, Cy(H)), 7.00−7.68 (br m, 6H), 7.86−8.08 (br m, 2H), 8.29 (s, 1H, ^3J(PtH) = 48.2 Hz, N=CH), 8.61 (s, 1H, N=CH).

Racemic [$PtBrMe_2(SMe_2)$){*cis*-1,2-(N=CHC_6H_4)(N=CH-$C_6H_4Br)C_6H_{10}$}], 7a″. ^{1}H NMR (CD_2Cl_2): δ 1.04 (s, 3H, $^2J_{PtH}$ = 70.5 Hz, Pt−Me), 1.25 (s, 3H, ^2J(PtH) = 67.5 Hz, Pt−Me), 2.01 (s, 6H, ^3J(PtH) = 14.0 Hz, MeS), 8.21 (s, 1H, ^3J(PtH) = 48.0 Hz, N=CH), 8.69 (s, 1H, N=CH).

X-ray Structure Determination of 3a. Light yellow blocklike crystals of optically pure [$Pt_2Me_4Br_2(\mu$-$SMe_2)$){*trans*-*R*,*R*-1,2-(N=$CHC_6H_4)_2C_6H_{10}$}] were grown by slow diffusion from a mixture of CH_2Cl_2/pentane. A crystal 0.40 × 0.39 × 0.37 mm in size was mounted on a glass fiber and used for diffraction experiments. The diffraction experiments were carried out using a Siemens P4 diffractometer with XSCANS software package using graphite-monochromated Mo Kα radiation at 25 °C.[22] The cell constants were obtained by centering 27 high-angle reflections (24.52° ≤ 2θ ≤ 24.99°). A total of 3207 reflections were collected in the θ range 1.88−30.0° (−1 ≤ h ≤ 16, −1 ≤ k ≤ 18, −1 ≤ l ≤ 30) in ω−2θ scan mode at variable scan speeds (1−60 deg/min). Background measurements were made at the ends of the scan range. Three standard reflections were monitored at the end of every 297 reflections. An empirical absorption was applied to the data based on the ψ-scan method. The *SHELXTL* programs were used for data processing and the least-squares refinements on F^2.[23] The chiral space group $C222_1$ (No. 20) was uniquely determined from the systematic absences. For Z = 4, the

(22) *XSCANS* version 2.1; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

Table 5. Crystallographic Details[a]

complex	**3a**	**4a**	**6a′**
empirical formula	$C_{26.5}H_{39}Br_2ClN_2Pt_2S$	$C_{25}H_{33}Br_2Cl_3N_2Pt_2$	$C_{22}H_{26}Br_2N_2Pt$
fw	1003.11	1017.88	673.36
temp	25 °C	25 °C	25 °C
wavelength	0.710 73 Å	0.710 73 Å	0.710 73 Å
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$C222_1$ (No. 20)	*Pnma* (No. 62)	$P2_1/n$
unit cell dimens	a = 11.486(1) Å b = 13.046(1) Å c = 21.704(3) Å	a = 11.022(1) Å b = 16.180(1) Å c = 17.062(2) Å	a = 15.575(2) Å b = 13.633(2) Å c = 15.972(4) Å β = 106.11(1)°
volume	3252.3(6) Å^3	3042.8(5) Å^3	2213.5(8) Å^3
Z	4	4	4
density, calcd	2.049 g cm^{-3}	2.222 g cm^{-3}	2.021 g cm^{-3}
abs coeff	11.214 mm^{-1}	12.094 mm^{-1}	9.959 mm^{-1}
no. of indep reflns	3207 (R(int) = 0.0533)	2771 (R(int) = 0.0230)	3866 (R(int) = 0.0392)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	2500/1/176	1754/86/133	2768/21/246
goodness-of-fit (GooF) on F^2	1.027	1.047	1.054
final R indices ($I > 2\sigma(I)$)	R1 = 0.0493, wR2 = 0.1188	R1 = 0.0432, wR2 = 0.1108	R1 = 0.0496, wR2 = 0.1134
R indices (all data)	R1 = 0.0594, wR2 = 0.1227	R1 = 0.0786, wR2 = 0.1317	R1 = 0.0799, wR2 = 0.1287

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $GooF = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

molecule has a crystallographic 2-fold symmetry. The 2-fold axis cut across the cyclohexyl ring and the sulfur atom. Half a molecule of CH_2Cl_2 was found near the 2-fold axis. All the non-hydrogen atoms except the solvent carbon atom were refined anisotropically. No attempt was made to locate the hydrogen atoms. However all the hydrogen atoms were placed in calculated ideal positions for the purpose of structure factor calculations only. In the final least-squares refinement cycles on F^2, the model converged at R1 = 0.0493, wR2 = 0.1188, and Goof = 1.027 for 2500 observations with $F_o \geq 4\sigma(F_o)$ and 176 parameters and R1 = 0.0594, wR2 = 0.1227 for all 3077 data. The Flack parameter, x refined to 0.00(3). An extinction coefficient was refined to 0.00031(7). Crystallographic details are shown in Table 5. The positional and thermal parameters, complete bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and selected torsion angles have been included in the Supporting Information.

X-ray Structure Determination of 4a. Light yellow rodlike single crystals were grown by diffusion method from a mixture of $CHCl_3$/pentane. A long rod was cut to the size 0.38 × 0.19 × 0.19 mm, mounted on a glass fiber and used for diffraction experiments. The cell constants were obtained by centering 26 high-angle reflections (24.47° ≤ 2θ ≤ 25.10°). A total of 3521 reflections were collected in the θ range 2.20−25.0° (−1 ≤ h ≤ 13, −1 ≤ k ≤ 19, −1 ≤ l ≤ 20) in ω−2θ scan mode at variable scan speeds (2−30 deg/min). Background measurements were made at the ends of the scan range. Three standard reflections were monitored at the end of every 297 reflections. An empirical absorption was applied to the data based on the ψ-scan techniques. The space group *Pnma* (No. 62) was determined from the systematic absences. The correctness of the choice of the space group was confirmed by the successful solution and refinement of the structure. For Z = 4, a crystallographic mirror plane is imposed on the diplatinum complex, in which the bromine atoms are on the mirror plane. The cyclohexyl ring is disordered due to the mirror symmetry. This disorder was satisfactorily and successfully resolved. A chloroform solvate was located in the crystal lattice, and again the crystallographic mirror plane passes through a chlorine and a carbon atom. Left-over electron-density peaks around the solvent region indicated the possibility of disorder. Two orientations of $CHCl_3$ fragments were located in the difference Fourier with the occupancy ratio 0.4/0.6. Isotropic thermal parameters were refined for each model. All the non-hydrogen atoms were refined anisotropically. No attempt was made to locate the hydrogen atoms. However, all the hydrogen atoms except those in the cyclohexyl ring were placed in the calculated ideal positions for the purpose of structure factor calculations only. Soft constraints were applied to C−C distances in the cyclohexyl ring carbons. In the final least-squares refinement cycles on F^2, the model converged at R1 = 0.0432, wR2 = 0.1108, and Goof = 1.047 for 1754 observations with $F_o \geq 4\sigma(F_o)$ and 133 parameters and R1 = 0.0786, wR2 = 0.1317 for all 2771 data. Crystal data are given in Table 5; positional and thermal parameters, complete bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates and selected torsion angles have been included in the Supporting Information.

X-ray Structure Determination of 6a′. Yellow blocklike crystals were grown by slow diffusion method from a mixture of CH_2Cl_2/pentane. A crystal with dimensions of 0.29 × 0.21 × 0.17 mm was mounted on a glass fiber and used for the diffraction experiments. The cell constants were obtained by centering 25 high-angle reflections (23.61° ≤ 2θ ≤ 25.13°). A total of 4704 reflections were collected in the θ range of 2.00−25.0° (−1 ≤ h ≤ 12, −1 ≤ k ≤16, −18 ≤ l ≤ 18) in ω−2θ scan mode at variable scan speeds (2−30 deg/min). Background measurements were made at the ends of the scan range. Three standard reflections were monitored at the end of every 297 reflections. An empirical absorption was applied to the data based on the ψ-scan method. The space group $P2_1/n$ was determined from the systematic absences. All the non-hydrogen atoms were refined anisotropically. No attempt was made to locate the hydrogen atoms. However, all the hydrogen atoms were placed in calculated ideal positions for the purpose of structure factor calculations only. In the final least-squares refinement cycles on F^2, the model converged at R1 = 0.0496, wR2 = 0.1134, and Goof = 1.054 for 2768 observations with $F_o \geq 4\sigma(F_o)$ and 246 parameters and R1 = 0.0799, wR2 = 0.1287 for all 3865 data. Crystallographic details are given in Table 5. Positional and thermal parameters, bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and selected torsion angles have been included in the Supporting Information.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond distances and angles for complexes **3a**, **4a**, and **6a′** (19 pages). Ordering information is given on any masthead page.

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(23) *SHELXTL Software* version 5.0; Siemens Analytical X-ray Instruments Inc.: Madison, WI 1994.