Electrophilic Binuclear Methylplatinum(II) Complexes

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Received March 29, 1999

The bis(bidentate) ligands *trans*- and *cis*-1,2-$C_6H_{10}(N{=}CH\text{-}2\text{-}C_5H_4N)_2$ (**1** and **2**) yield the diplatinum(II) complexes *trans*- and *cis*-1,2-$[C_6H_{10}\{N{=}CH\text{-}2\text{-}C_5H_4N(PtMe_2)\}_2]$ (**3** and **4**, respectively). Reaction of **3** and **4** with $[H]^+[HOB(C_6F_5)_3]^-$ in MeCN or with HBF_4 in the presence of excess CO gave the corresponding electrophilic binuclear complexes *trans*- and *cis*-1,2-$[C_6H_{10}\{N{=}CH\text{-}2\text{-}C_5H_4N(PtMeL)\}_2][X]_2$ (**5**, *trans*, L = MeCN, X = $[HOB(C_6F_5)_3]$; **6**, *cis*, L = MeCN, X = $[HOB(C_6F_5)_3]$; **7**, *trans*, L = CO, X = BF_4; **8**, *cis*, L = CO, X = BF_4). The electrophilic complexes **5**−**8** are formed by selective methyl group protonolysis, and the stereochemistries were confirmed for complexes **7** and **8** by X-ray structure determinations.

Introduction

Electrophilic, late-transition-metal complexes that are supported by diimine or diamine ligands continue to be of interest due to their catalytic potential in processes such as olefin polymerization and selective C−H or C−C bond activation.[1,2] For example, the active initiator in the polymerization of ethylene and α-olefins into high polymers is thought to be a cationic complex of the type $[(N{-}N)M(Me)L]^+$ (M = Ni, Pd; N−N = diimine; L = MeCN, olefin).[2] Furthermore, when the supporting diimine ligands are asymmetric, a high degree of tacticity in the product polymers can be achieved.[3] This article describes the synthesis and structure of new cationic diplatinum(II) complexes which are stabilized by bis(bidentate) diimine ligands based on *cis*- and *trans*-1,2-diaminocyclohexane, which have asymmetric carbon atoms. The cationic platinum(II) centers are generated by methylplatinum bond protonolysis.[4] Because the complexes share the general formula $[(N{-}N)M(Me)L]_2^+$ (N−N = chiral/achiral diimine; L = CO, MeCN), they represent new model systems for both asymmetric and homobimetallic late-transition-metal catalysts.

Simple diimine ligands based on *cis*- and *trans*-diaminocyclohexane have been shown to promote stereoselective inter- and intramolecular oxidative addition of C−X bonds to platinum(II), as well as promoting very high stereoselectivity of α-olefin coordination in cationic platinum(II) complexes.[5,6] The modification of these ligands to include a second pair of nitrogen donors allows for a bis(bidentate) coordination mode,[7] which can then be exploited in the formation of both chiral and achiral diplatinum(II) complexes. It should be noted that the bis(bidentate) Schiff-base ligands *cis*-1,2-$C_6H_{10}(N{=}CH\text{-}2\text{-}C_5H_4N)_2$ and *cis*-1,2-$C_6H_{10}(N{=}CH\text{-}2\text{-thiophene})_2$ have recently been employed to investigate the structural and dynamic features of Ag(I) and Cu(I) complexes,[8] while the related chiral ligand *trans*-1,2-$C_6H_{10}(N{=}CH\text{-}2\text{-}C_5H_4N)_2$ has been used as the supporting ligand in the formation of homochiral Ag(I) coordination polymers.[9] Finally, because the coordination behavior of polydentate ligands with respect to transition metals can sometimes model or even mimic several of the

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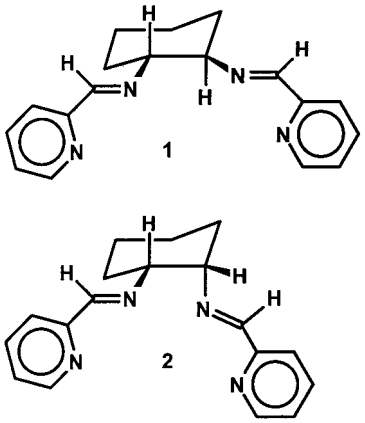
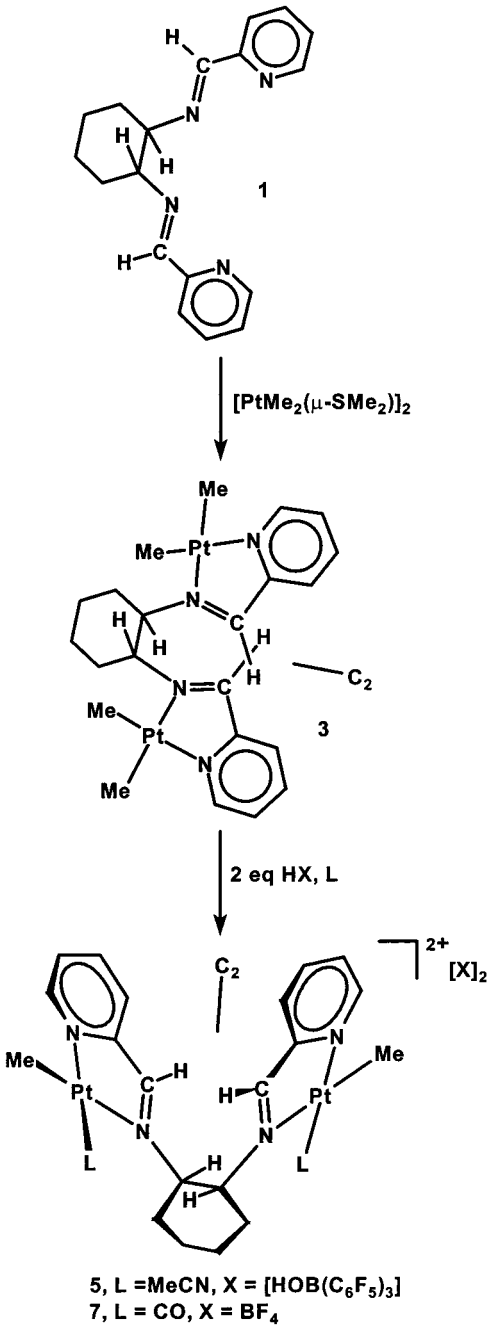
10.1021/om990218y CCC: $18.00
Publication on Web 09/21/1999

Chart 1



Scheme 1



specific physical and chemical properties of important biological molecules, there has been interest in the use of related N_4-donor ligands as quadridentate ligands for forming complexes of Co(III),[10] Ni(II),[11] Cu(II),[12] and Pd(II).[13]

Results and Discussion

Synthesis and Characterization of Ligands. The ligands *rac*(*R*,*R*/*S*,*S*)-*trans*-1,2- $C_6H_{10}(N{=}CH\text{-}2\text{-}C_5H_4N)_2$ (**1**) and *meso*(*R*,*S*)-*cis*-1,2-$C_6H_{10}(N{=}CH\text{-}2\text{-}C_5H_4N)_2$ (**2**) (Chart 1) were easily prepared by condensation of *cis*- or *trans*-1,2-diaminocyclohexane with 2-pyridinecarboxaldehyde in the presence of magnesium sulfate. The ligands were formed as single isomers, and *anti* stereochemistry about each imine N=CH bond was confirmed by the structural characterization of complexes derived from them.

Racemic *trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(Pt-Me$_2$)}$_2$] (3). The chemistry derived from the racemic ligand **1** is shown in Scheme 1. Reaction of **1** with a stoichiometric amount of $[PtMe_2(\mu\text{-}SMe_2)]_2$ gave the chiral bis(dimethylplatinum) complex *trans*-1,2-[C_6H_{10}-{N=CH-2-C_5H_4N(PtMe_2)}$_2$] (**3**), in which each $PtMe_2$ unit is coordinated to one pyridine and one imine nitrogen atom. The complex is C_2 symmetric, as a result of this bis(bidentate) coordination mode, and chiral, due to the cyclohexane motif.

At room temperature, the ^{1}H NMR spectra of complex **3** in CD_2Cl_2 contained broad resonances, indicative of an exchange process (Figure 1). There were broad methylplatinum resonances at δ 1.12 and 1.24, with ^2J(Pt−H) = ca. 85 and 84 Hz, respectively, and two broad imine N=CH resonances at δ 9.32 and 9.56 with unresolved platinum satellites, as well as broad resonances for the aromatic and cyclohexyl protons. At low temperature, the imine signals become sharper and, at −20 °C, gave singlets at δ 9.23 and 9.50, with ^3J(Pt−H) = 33 and 36 Hz, respectively, with relative intensities of approximately 1:2. At −20 °C, three methylplatinum resonances were resolved, at δ 1.01, 1.07, and 1.21 with ^2J(Pt−H) = ca. 85, 84, and 86 Hz, respectively, and the peak at δ 1.07 split further into two resonances at δ 1.06 and 1.08 at −60 °C (Figure 1a). Relative intensities of the methylplatinum peaks at δ 1.01, 1.06, 1.08, and 1.21 were approximately 1:2:2:1. The methylplatinum resonances also exhibit an unusually large temperature dependence of the chemical shifts as seen in Figure 1. At higher temperatures in $CDCl_3$ solution, the nonequivalent imine and methylplatinum resonances coa-

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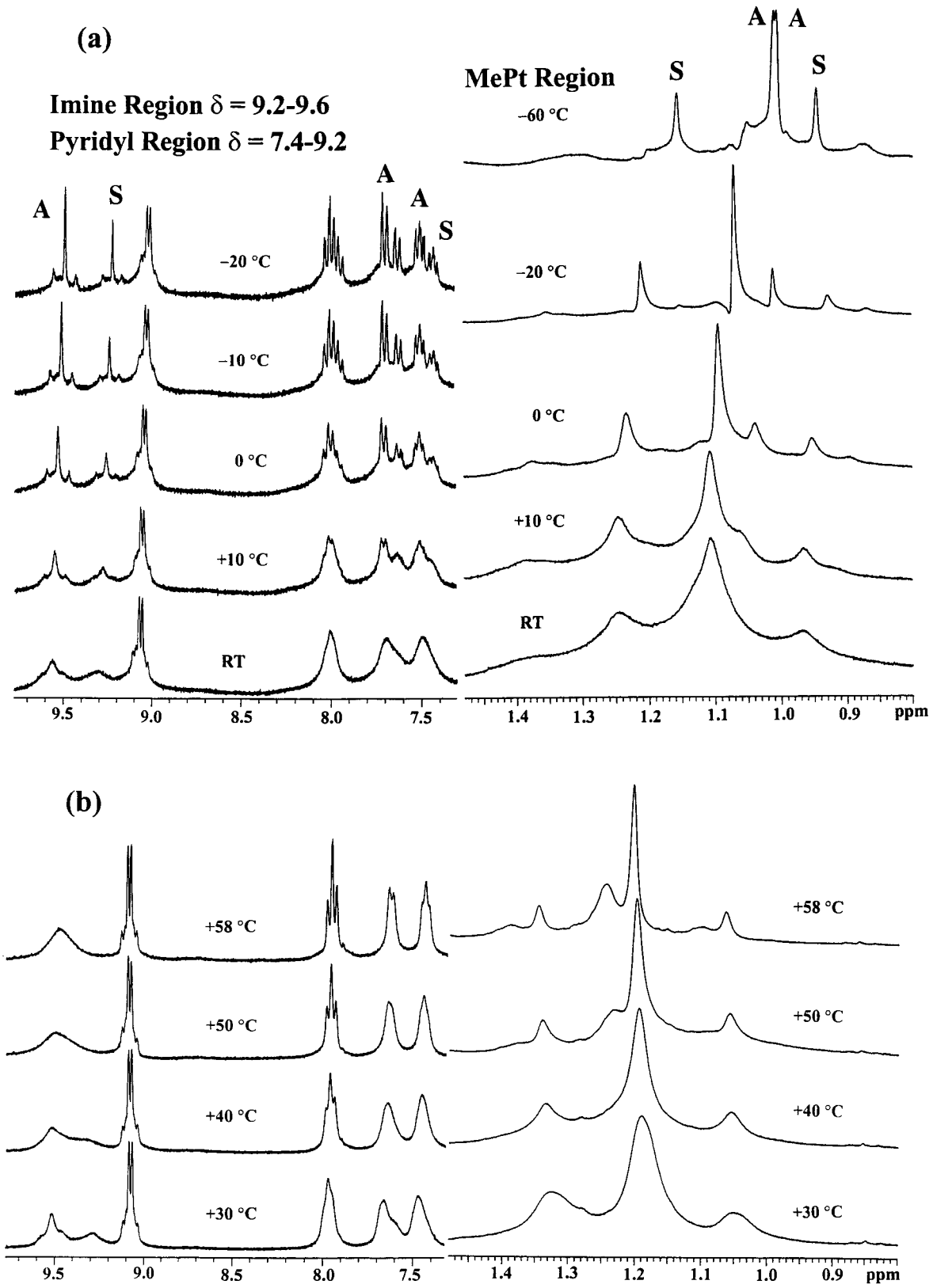
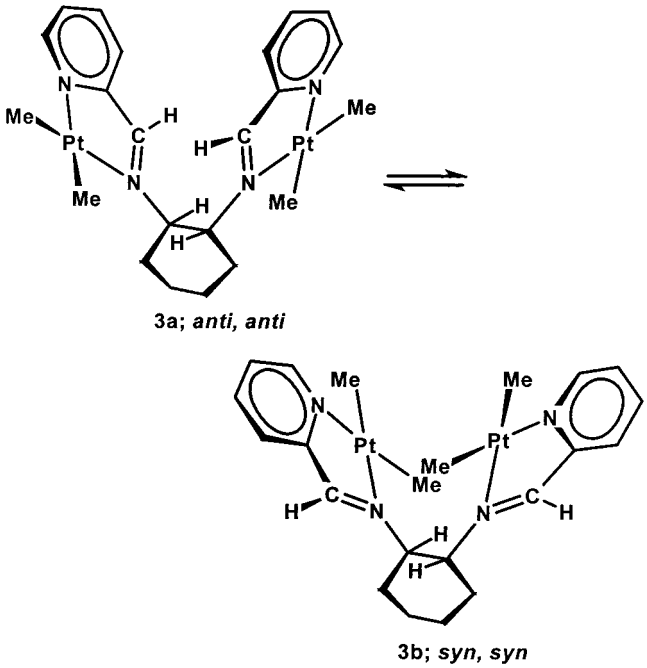


Figure 1. Variable-temperature ^{1}H NMR spectra of complex **3** showing only the imine, bis(pyridyl), and MePt regions: (a) from room temperature to −60 °C in CD_2Cl_2 (A = *anti, anti* conformer; S = *syn,syn* conformer); (b) from room temperature to +58 °C in $CDCl_3$. The fast exchange spectrum is almost reached at +58 °C.

lesced and the spectrum at 58 °C contained one broad imine resonance and two methylplatinum resonances (Figure 1b). These data can be interpreted in terms of restricted rotation about the cyclohexyl C−N bonds, as shown in Scheme 2. Thus, the conformers can be defined according to whether the methylplatinum groups are *anti* or *syn* to the neighboring cyclohexyl CH group. The resolved spectra at low temperature are consistent with freezing out of the *anti,anti* and *syn,syn* conformers **3a** and **3b** in a 2:1 ratio. Each of these conformers has C_2

Scheme 2

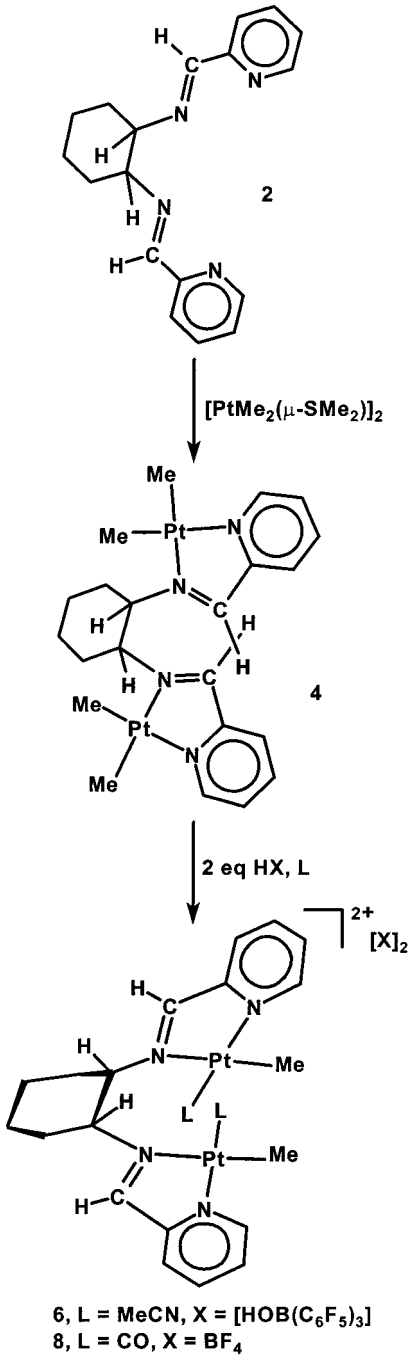


symmetry, and so each should give one N=CH and two MePt resonances in the ^{1}H NMR spectrum as observed. The difficulty with this interpretation is that a third *syn,anti* conformer, having no symmetry and hence giving two N=CH and four MePt resonances, might be expected but was not observed. Perhaps its resonances are too weak and broad at low temperature to be resolved, or perhaps it exchanges more easily with one of the other isomers. The *anti,anti* conformer is found in the solid-state structure of a derivative (see below) and so is assumed to be the dominant conformer in **3**. The restricted rotation is a clear indication of steric congestion in **3**.

***cis*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PtMe$_2$)}$_2$] (4).** The *meso* ligand *cis*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$ (**2**) reacted with [PtMe$_2$(μ-SMe$_2$)]$_2$ to give [*cis*-1,2-C_6H_{10}{N=CH-2-C_5H_4N(PtMe$_2$)}$_2$] (**4**) in which the C_s symmetry is maintained (Scheme 3). The ^{1}H NMR spectrum of **4** contains two methylplatinum resonances at δ 1.03 and 1.08 with ^2J(Pt−H) = 86 and 85 Hz, respectively, and a single imine resonance at δ 9.43 with ^3J(Pt−H) = 36 Hz. The spectra are unchanged down to −70 °C, but line broadening was observed at −90 °C. Hence, in this case, there is no clear evidence for restricted rotation about the cyclohexyl C−N bonds. This is surprising, since the platinum atoms in **4** will be closer together than in **3**.

***trans*- and *cis*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PtMe(MeCN))}$_2$][HOB(C_6F_5)$_3$]$_2$ (5 and 6).** The reaction of **3** with 2 equiv of B(C_6F_5)$_3$ in moist acetonitrile solution at room temperature gave the chiral complex *trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PtMe(MeCN))}$_2$][HOB(C_6F_5)$_3$]$_2$ (**5**) by cleavage of one methylplatinum group from each dimethylplatinum unit (Scheme 1). The cleavage of methylplatinum groups from **3** is selective, in that the methyl group *trans* to the pyridyl nitrogen undergoes protonolysis while the methyl group *trans* to the imine nitrogen atom remains intact. This is shown by the ^{1}H NMR spectrum of **5**, which contains single methylplatinum and imine resonances at δ 1.12 (^2J(Pt−H) = 76 Hz) and δ 9.30 (^3J(Pt−H) = 36 Hz),

Scheme 3



respectively. The stereochemistry is indicated by the similarity of the values of ^3J(PtH) for the imine protons of **3** and **5**, indicating that the imine nitrogen in both complexes is *trans* to methyl. The selective cleavage of two methyl groups maintains the C_2 symmetry of the complex, but there was no evidence of restricted rotation similar to that found in **3**. On the basis of earlier work,[4b] it is suggested that the protonolysis occurs by reaction with [H_2OB(C_6F_5)$_3$], which acts as a strong acid, [H]$^+$[HOB(C_6F_5)$_3$]$^-$, formed by reaction of B(C_6F_5)$_3$ with water. The presence of the counterion [HOB(C_6F_5)$_3$]$^-$ was demonstrated by the ^{11}B NMR spectrum, which contained a characteristic broad singlet at δ −4.49.[4b,14,15]

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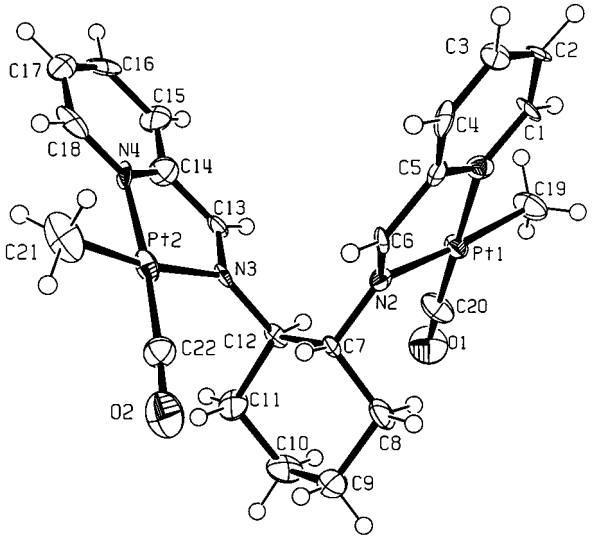

Figure 2. View of the structure of complex **7**.

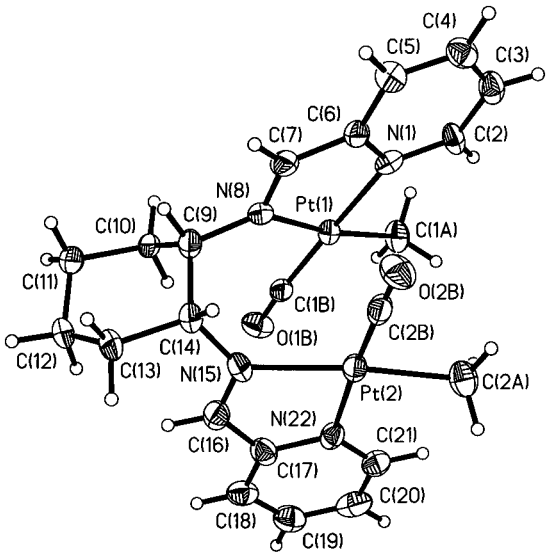

Figure 3. View of the structure of complex **8**.

Attempts to prepare the electrophilic cation present in complex **5** by reaction of **3** with triflic acid or $H[BF_4]$ were unsuccessful, thus confirming that the reagent $B(C_6F_5)_3/H_2O$ is particularly useful for synthesis of electrophilic platinum complexes containing weakly bound ligands such as acetonitrile.[4b]

The complex *cis*-1,2-$[C_6H_{10}\{N{=}CH\text{-}2\text{-}C_5H_4N(PtMe(MeCN))\}_2][HOB(C_6F_5)_3]_2$ (**6**) was prepared in a similar way (Scheme 3). Again the NMR data indicate that the C_s symmetry is maintained in complex **6** and hence that the methylplatinum cleavage is selective, as shown in Scheme 3.

***trans*- and *cis*-1,2-$[C_6H_{10}\{N{=}CH\text{-}2\text{-}C_5H_4N(PtMe(CO))\}_2][BF_4]_2$ (7 and 8).** The reaction of complex **3** or **4** with 2 equiv of HBF_4 in the presence of excess CO gave the corresponding complex *trans*- or *cis*-1,2-$[C_6H_{10}\{N{=}CH\text{-}2\text{-}C_5H_4N(PtMe(CO))\}_2][BF_4]_2$ (**7** or **8**), respectively (Schemes 1 and 3). The protonolysis reactions were carried out at low temperature to prevent side reactions, leading to hydrolysis of the imine groups, from occurring. The ^1H NMR spectra of complexes **7** and **8** were similar to those of **5** and **6**. Complex **7** has effective C_2 symmetry and is chiral, whereas **8** has effective C_s symmetry and is achiral by virtue of the mirror plane. Low-temperature NMR failed to freeze out conformers having lower symmetry, though line broadening did occur at −90 °C. These complexes **7** and **8** are again formed by selective cleavage of the methylplatinum bond, which is *trans* to the pyridyl nitrogen atom in **3** and **4**, respectively, as indicated by the NMR data and confirmed by X-ray crystal structure determinations. The reason for the high selectivity is not obvious but might be due to the higher donor power of the pyridine ligand. Note, however, that the NMR data for the methylplatinum groups of **3** and **4** indicate similar *trans* influences of the pyridine and imine groups.

Structures of Complexes 7 and 8. The structure of complex **7** is shown in Figure 2 , and selected bond distances and angles are listed in Table 1. As expected, compound **1** acts as a bis(bidentate) ligand in **7** by binding to two $PtMe(CO)^+$ units. Each platinum(II) center has approximately square-planar stereochemistry. The cyclohexane ring is in the favored chair conformation, with the bulky substituents equatorial. The dication **7** has no imposed crystallographic symmetry, but it does have an approximate C_2 axis running through the midpoint of the C(9)−C(10) and C(7)−C(12) bonds. The structure is thus consistent with that deduced from the NMR data and has the $PtMe(CO)^+$ groups *anti* to the adjacent cyclohexyl C−H groups. This *anti,anti* conformation keeps the platinum atoms well-separated from each other (Pt(1)···Pt(2) = 5.974(1) Å). The structure confirms that the CO ligands are *trans* to the pyridyl rather than the imine nitrogen atoms.

Table 1. Selected Bond Lengths and Angles for Complex 7

(a) Bond Lengths (Å)			
Pt(1)−C(20)	1.85(1)	O(2)−C(22)	1.19(2)
Pt(1)−C(19)	2.05(1)	N(1)−C(5)	1.35(2)
P(1)−N(1)	2.08(1)	N(2)−C(6)	1.30(1)
Pt(1)−N(2)	2.11(1)	N(2)−C(7)	1.49(2)
Pt(2)−C(22)	1.79(2)	N(3)−C(13)	1.27(1)
Pt(2)−N(4)	2.03(1)	N(3)−C(12)	1.49(2)
Pt(2)−C(21)	2.06(1)	N(4)−C(14)	1.36(2)
Pt(2)−N(3)	2.12(1)	C(5)−C(6)	1.51(2)
O(1)−C(20)	1.12(2)	C(13)−C(14)	1.45(2)
(b) Bond Angles (deg)			
C(20)−Pt(1)−C(19)	84.3(6)	C(22)−Pt(2)−N(3)	104.1(5)
C(20)−Pt(1)−N(1)	176.6(5)	N(4)−Pt(2)−N(3)	78.1(4)
C(19)−Pt(1)−N(1)	92.9(5)	C(21)−Pt(2)−N(3)	171.1(5)
C(20)−Pt(1)−N(2)	104.2(5)	C(5)−N(1)−Pt(1)	114.7(8)
C(19)−Pt(1)−N(2)	171.5(5)	C(6)−N(2)−Pt(1)	115.7(9)
N(1)−Pt(1)−N(2)	78.6(4)	C(13)−N(3)−Pt(2)	114.5(9)
C(22)−Pt(2)−N(4)	175.3(5)	O(1)−C(20)−Pt(1)	178(1)
C(22)−Pt(2)−C(21)	84.4(7)	O(2)−C(22)−Pt(2)	176(1)
N(4)−Pt(2)−C(21)	93.5(6)		

The structure of complex **8**, illustrated in Figure 3 with selected bond parameters in Table 2, also shows the ligand **2** in the bis(bidentate) coordination mode, binding to two square-planar platinum(II) centers. At each platinum center, the CO ligand occupies a site *trans* to the pyridyl nitrogen while the methyl group is *trans* to the imine nitrogen. The cyclohexane ring is in the chair conformation, such that the substituents

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Table 2. Selected Bond Lengths and Angles for Complex 8

(a) Bond Lengths (Å)

Pt(1)−C(1B)	1.85(1)	C(2B)−O(2B)	1.12(1)
Pt(1)−C(1A)	2.070(9)	N(1)−C(6)	1.365(12)
P(1)−N(1)	2.079(8)	C(6)−C(7)	1.453(13)
Pt(1)−N(8)	2.148(7)	C(7)−N(8)	1.30(1)
C(1B)−O(1B)	1.13(1)	N(8)−C(9)	1.46(1)
Pt(2)−C(2B)	1.87(1)	C(14)−N(15)	1.48(1)
Pt(2)−N(22)	2.058(8)	N(15)−C(16)	1.29(1)
Pt(2)−C(2A)	2.07(1)	C(16)−C(17)	1.46(1)
Pt(2)−N(15)	2.147(7)	C(17)−C(22)	1.38(1)

(b) Bond Angles (deg)

C(1B)−Pt(1)−C(1A)	84.6(4)	C(7)−N(8)−Pt(1)	112.4(6)
C(1B)−Pt(1)−N(1)	177.6(4)	O(1B)−C(1B)−Pt(1)	175.4(9)
C(1A)−Pt(1)−N(1)	93.1(3)	C(2B)−Pt(2)−N(22)	173.7(4)
C(1B)−Pt(1)−N(8)	103.8(3)	C(2B)−Pt(2)−C(2A)	85.3(4)
C(1A)−Pt(1)−N(8)	171.3(3)	N(22)−Pt(2)−C(2A)	93.1(4)
N(1)−Pt(1)−N(8)	78.4(3)	C(2B)−Pt(2)−N(15)	103.0(3)
C(6)−N(1)−Pt(1)	114.1(6)	N(22)−Pt(2)−N(15)	78.6(3)
N(1)−C(6)−C(7)	115.5(8)	C(2A)−Pt(2)−N(15)	171.7(4)
N(8)−C(7)−C(6)	119.1(9)	O(2B)−C(2B)−Pt(2)	178.4(8)

containing Pt(1) and Pt(2) are equatorial and axial, respectively. The conformation is such that the equatorial Pt(1)Me(CO)$^+$ substituent and the axial Pt(2)Me(CO)$^+$ substituent are *anti* and *syn*, respectively, to the adjacent cyclohexyl C−H bonds. In this *anti,syn* conformation, there is no mirror plane, whereas the NMR data for **8** show that there is an effective mirror plane in solution. Presumably, therefore, rotation about the cyclohexyl C−N bonds is rapid in **8**, leading to easy equilibration of conformers. The observed spectra are unlikely to be due to the *syn,anti* isomer, since that would require accidental degeneracy of both methylplatinum and imine resonances. The *anti,syn* conformation in **8** also has the platinum centers sufficiently far apart (Pt(1)···Pt(2) = 3.253 Å) to indicate that no Pt−Pt bonding interaction is present but close enough that cooperative effects might be anticipated.

Conclusions

Complexes **5**−**8** model the precatalytic complexes of general formula [(N−N)PdMeL]$^+$ (N−N = diimine; L = MeCN, CO) that have been employed in several late-transition-metal-catalyzed olefin polymerization processes.[2,3] In addition, the complexes contain two electrophilic centers, each of which is indirectly connected to an asymmetric carbon atom of the cyclohexane unit. Although the reactions have been carried out by using the racemic ligand **1**, the chemistry will be the same with the readily available chiral ligand. These may be considered as models for binuclear electrophilic palladium complexes derived from the ligands **1** and **2** for application in α-olefin polymerization or copolymerization with CO, in which cooperative effects in the binuclear complexes might lead to interesting reactivity and selectivity. Research in this area is continuing.

Experimental Section

General Procedures. All reactions were carried out under a N_2 atmosphere using standard Schlenk techniques. NMR spectra were recorded using a Varian Gemini spectrometer (^{1}H at 300.10 MHz, ^{11}B at 64.17 MHz, and ^{19}F at 282.32 MHz). Chemical shifts are given in ppm with respect to TMS (^{1}H), $BF_3{\cdot}Et_2O$ (^{11}B), or $CFCl_3$ (^{19}F). The ^{11}B and ^{19}F chemical shifts are referenced to $BF_3{\cdot}Et_2O$ or $CFCl_3$, respectively, contained in a coaxial insert. IR spectra were recorded as Nujol mulls in the range 4000−400 cm^{-1} using a Perkin-Elmer 2000 FT-IR instrument. The complex $[PtMe_2(\mu\text{-}SMe_2)]_2$ was prepared by the literature method.[16]

Synthesis of Ligands 1 and 2. The procedure used is a modification of that provided in the literature.[8d] To a solution of *rac*(*R*,*R*/*S*,*S*)-*trans*-1,2-diaminocyclohexane (1 mL) in diethyl ether (40 mL) was added 2-pyridinecarboxaldehyde (1.58 mL). Excess $MgSO_4$ was added to the reaction mixture to remove product water. The solution was stirred for 15 h at room temperature and then filtered to remove the $MgSO_4$. The solvent was evaporated under reduced pressure to give a pale yellow solid. This was redissolved in diethyl ether (5 mL) and pentane (20 mL), and then the yellow solution was concentrated at low temperature, under reduced pressure, to give a white precipitate. This was separated by filtration and washed with small amounts of cold diethyl ether (5 mL) to give pure racemic *trans*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$ (**1**), yield 1.25 g (51%). ^{1}H NMR (acetone-d_6): δ 1.54 [br m, 2H]; 1.82 [br m, 6H]; 3.48 [m, 2H, NCH]; 7.29 [m, 2H]; 7.73 [m, 2H]; 7.92 [m, 2H]; 8.24 [s, 2H, N=CH]; 8.49 [m, 2H]. Anal. Calcd for $C_{18}H_{20}N_4$: C, 73.9; H, 6.9; N, 19.2. Found: C, 74.1; H, 7.0; 19.2. The ligand *cis*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$ (**2**) was similarly prepared; yield 50%. ^{1}H NMR ($CDCl_3$): δ 1.60 [br m, 2H]; 1.75 [br m, 2H]; 2.05 [br m, 4H]; 3.68 [m, 2H, NCH]; 7.24 [m, 2H]; 7.65 [m, 2H]; 8.00 [m, 2H], 8.32 [s, 2H, N=CH]; 8.56 [m, 2H]. Anal. Calcd for $C_{18}H_{20}N_4$: C, 73.9; H, 6.9; N, 19.2. Found: C, 73.8; H, 7.1; 19.2.

***rac*(*R*,*R*/*S*,*S*)-*trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(Pt-Me$_2$)}$_2$] (3).** To a suspension of $[PtMe_2(\mu\text{-}SMe_2)]_2$ (0.200 g, 0.348 mmol) in diethyl ether (10 mL) was added *rac-trans*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$ (**1**; 0.101 g, 0.348 mmol) to give an intense red solution from which a dark red precipitate began to separate. The mixture was stirred for 15 h at room temperature, the volume was reduced to 3 mL under reduced pressure, and the red solid was isolated by filtration. The product was washed with several portions of cold diethyl ether (3 × 10 mL) and then pentane (3 × 10 mL) to afford a red powder, yield 0.230 g (89%). ^{1}H NMR at 25 °C (CD_2Cl_2): δ 1.12 [br s, ^2J(PtH) = ca. 85 Hz, Pt−Me]; 1.24 [v br, ^2J(PtH) = ca. 84 Hz, Pt−Me]; 1.62 [br m]; 1.98 [br m]; 2.65 [br m]; 4.94 [m]; 7.49 [br m]; 7.70 [br m]; 8.00 [br m]; 9.05 [br d]; 9.32 [br s, N=CH]; 9.56 [br s, 1H, N=CH]. See text and Figure 1 for VT NMR data. Anal. Calcd for $C_{22}H_{32}N_4Pt_2$: C, 35.6; H, 4.3; N, 7.5. Found: C, 35.8; H, 4.5; N, 7.2.

***cis*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PtMe$_2$)}$_2$] (4).** To a solution of $[PtMe_2(\mu\text{-}SMe_2)]_2$ (0.47 g, 0.82 mmol) in THF (10 mL) was added *cis*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$ (**2**; 0.24 g, 0.82 mmol) to give an intense red solution from which a dark red precipitate began to separate. After it was stirred for 15 h at room temperature, the solution was concentrated (ca. 3 mL), followed by addition of pentane (50 mL). The resulting red precipitate was separated by filtration and washed with pentane (3 × 10 mL). The product was recrystallized from CH_2Cl_2/pentane to afford a deep red powder, yield 0.56 g (92%). ^{1}H NMR (CD_2Cl_2): δ 1.03 [s, 6 H, ^2J(PtH) = 86 Hz, Pt−Me]; 1.08 [s, 6 H, ^2J(PtH) = 85 Hz, Pt−Me]; 1.56 [br m, 2H]; 1.76 [br m, 2H]; 2.20 [br m, 2H]; 2.38 [br m, 2H]; 5.29 [m, 2H, NCH]; 7.52 [m, 2H]; 7.66 [d, 2H]; 8.05 [dt, 2H]; 9.10 [d t, 2H]; 9.43 [s, 2H, ^3J(PtH) = 36 Hz, N=CH]. Anal. Calcd for $C_{22}H_{32}N_4Pt_2$: C, 35.6; H, 4.3; N, 7.5. Found: C, 35.3; H, 4.5; N, 7.3.

***rac*(*R*,*R*/*S*,*S*)-*trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(Pt-Me(MeCN))}$_2$][HOB(C_6F_5)$_3$]$_2$ (5).** To a suspension of complex **3** (0.05 g, 0.067 mmol) in CH_3CN (10 mL) was added $B(C_6F_5)_3$ (0.069 g, 0.134 mmol). Within seconds the color had changed from red to bright orange. After 30 min the solvent was evaporated under reduced pressure to give an orange solid, which was washed with ether and pentane and dried under

(16) Hill, G. S.; Irwin, M. J.; Levy, C. J.; Rendina, L. M.; Puddephatt, R. J. *Inorg. Synth.* **1998**, *32*, 149.

vacuum; yield 0.08 g (64%). ^{1}H NMR (CD_2Cl_2): δ 1.12 [s, 6 H, ^2J(PtH) = 76 Hz, Pt−Me]; 1.32 [br m, 2H]; 1.70−2.14 [br m, 6H]; 2.62 [s, 6H, MeCN]; 4.35 [m, 2H, NCH]; 7.59 [br t, 2H]; 7.79 [br d, 2H]; 8.02 [br t, 2H]; 8.78 [br d, 2H, ^3J(PtH) = 60 Hz, pyr N=CH]; 9.30 [s, 2H, ^3J(PtH) = 36 Hz, N=CH]. ^{11}B NMR (CD_2Cl_2): δ −4.49 [s]. ^{19}F NMR (CD_2Cl_2): δ −136.3 (d); −162.7 (t); −166.5 (m). Anal. Calcd for $C_{60}H_{33}B_2F_{30}N_6O_2Pt_2$: C, 38.9; H, 1.9; N, 4.5. Found: C, 38.6; H, 2.0; N, 4.4.

***cis*-1,2-[C$_6$H$_{10}${N=CH-2-C$_5$H$_4$N(PtMe(MeCN))}$_2$][HOB(C$_6$F$_5$)$_3$]$_2$ (6)** was similarly prepared from complex **4**; yield 80%. ^{1}H NMR (CD_2Cl_2): δ 0.91 [s, 6 H, ^2J(PtH) = 76 Hz, Pt−Me]; 1.60−2.25 [br m, 6H]; 2.52 [s, 6H, MeCN]; 2.52 [br m, 2H]; 4.65 [m, 2H, NCH]; 7.70 [br t, 2H]; 8.08 [br t, 2H]; 8.15 [br d, 2H]; 8.79 [br d, 2H, ^3J(PtH) = 56 Hz, pyr N=CH]; 9.25 [s, 2H, ^3J(PtH) = 40 Hz, N=CH]. ^{11}B NMR (CD_2Cl_2): δ −4.48 (s). ^{19}F NMR (CD_2Cl_2): δ −136.3 (d), −162.4 (t), −166.6 (m). Anal. Calcd for $C_{60}H_{33}B_2F_{30}N_6O_2Pt_2$: C, 38.9; H, 1.9; N, 4.5. Found: C, 38.9; H, 1.8; N, 4.4.

***rac*(*R*,*R*/*S*,*S*)-*trans*-1,2-[C$_6$H$_{10}${N=CH-2-C$_5$H$_4$N(Pt-Me(CO))}$_2$][BF$_4$]$_2$ (7).** To a cold (−78 °C), CO-saturated solution of complex **3** (0.027 g, 0.360 mmol) in CH_2Cl_2 (10 mL) was added HBF_4 (9.9 μL, 0.72 mmol). The red solution turned deep purple. After 5 min at −78 °C, the cold bath was removed and the solution was slowly warmed to room temperature while CO saturation was continued. The purple color gradually lightened to a bright yellow. The solvent was then evaporated under reduced pressure to give an orange-yellow product. Trituration and washing with pentane (3 × 10 mL) gave a yellow powder, which was recrystallized from CH_2Cl_2/pentane; yield 0.016 g (46%). ^{1}H NMR (CD_2Cl_2): δ 1.45 [s, 6 H, ^2J(PtH) = 66 Hz, Pt−Me]; 1.55−1.98 [br m, 4H]; 2.08 [br m, 2H]; 2.35 [br m, 2H]; 4.39 [m, 2H, NCH]; 7.88 [m, 2H]; 8.30 [d t, 2H]; 8.43 [d t, 2H]; 8.79 [d, 2H, ^3J(PtH) = 40 Hz, pyr N=CH]; 9.71 [s, 2H, ^3J(PtH) = 36 Hz, N=CH]. IR (Nujol, cm^{-1}): 2092 [vs, ν(CO)]. Anal. Calcd for $C_{22}H_{26}B_2F_8N_4O_2Pt_2$: C, 28.0; H, 2.8; N, 6.0. Found: C, 27.9; H, 3.2; N, 5.7.

***cis*-1,2-[C$_6$H$_{10}${N=CH-2-C$_5$H$_4$N(PtMe(CO))}$_2$][BF$_4$]$_2$ (8)** was similarly prepared from complex **4**; yield 55%. ^{1}H NMR (CD_2Cl_2): δ 1.33 [s, 6 H, ^2J(PtH) = 67 Hz, Pt−Me]; 1.70−2.30 [br m, 8H]; 4.97 [m, 2H, NCH]; 8.05 [t, 2H]; 8.44 [d t, 2H]; 8.58 [d, 2H]; 8.87 [d, 2H, ^3J(PtH) = 42 Hz, pyr N=CH]; 9.73 [s, 2H, ^3J(PtH) = 42 Hz, N=CH]. IR (Nujol, cm^{-1}): 2108 [vs, ν(CO)]. Anal. Calcd for $C_{22}H_{26}B_2F_8N_4O_2Pt_2$: C, 28.0; H, 2.8; N, 6.0. Found: C, 28.2; H, 3.0; N, 5.8.

X-ray Structure Determinations. Orange block-shaped crystals of complexes **7** and **8** were grown by slow diffusion from CH_2Cl_2/pentane solutions. The crystal data and refinement parameters are given in Table 3. Complete data are available in the Supporting Information.

The diffraction measurements on crystals of **7**, which were small and of poor quality, were made at 150 K with a Bruker SMART CCD diffractometer and synchrotron radiation on station 9.8 at the Daresbury Laboratory, Warrington, U.K. The data set is essentially (96%) complete to θ = 22.6°. It was collected and processed using SAINT and SADABS software (Bruker, 1997). A noisy final difference synthesis (Table 3) and physically unreasonable vibrational parameters for a few of the lighter atoms indicate that the structure is of only moderate quality. Despite this, we consider that it provides a sufficiently reliable basis for the structural discussion presented above.

Table 3. Crystallographic Details for Complexes 7 and 8

	7	8
formula; fw	$C_{22}H_{26}B_2F_8N_4O_2Pt_2$; 942.27	$C_{22}H_{26}B_2F_8N_4O_2Pt_2$; 942.27
temp, K	150(2)	100(2)
wavelength, Å	0.691 50	0.710 73
cryst syst, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a, Å	16.2350(8)	14.345(3)
b, Å	16.2438(7)	10.475(2)
c, Å	10.3115(3)	18.826(4)
β, deg	95.235(2)	104.46(3)
V, Å^3; Z	2708.0(2); 4	2739.4(10); 4
d(calcd), Mg/m^3	2.311	2.285
abs coeff, mm^{-1}	10.404	10.285
F(000)	1760	1760
cryst size, mm^3	0.12 × 0.10 × 0.10	0.30 × 0.12 × 0.10
θ range, deg	1.7−27.3	4.1−25.0
no. of rflns collected	7408	16125
no. of indep rflns	5208 (R(int) = 0.057)	4786 (R(int) = 0.079)
no. of data/ restraints/params	5208/106/361	4786/0/363
goodness of fit on F^2	0.890	1.043
R ($I > 2\sigma(I)$)	R1 = 0.052, wR2 = 0.090	R1 = 0.040, wR2 = 0.091
R (all data)	R1 = 0.113, wR2 = 0.108	R1 = 0.059, wR2 = 0.097
largest diff peak, hole, e Å^{-3}	3.1, −2.2	2.8, −2.2

Data for **8** were collected at 100 K using a Nonius Kappa CCD diffractometer and the COLLECT software (Nonius, Delft, The Netherlands, 1998). Crystal cell refinement and data reduction were carried out using the Nonius DENZO package.

The structures were solved by direct methods and refined using SHELXL97 for **7** and the SHELXTL 5.10 program package for **8** (G. M. Sheldrick, 1997 and 1992). All non-hydrogen atoms were refined with anisotropic thermal parameters. Rigid bond (DELU) restraints were applied in **7.** Hydrogen atoms rode on their respective carbon atoms. For the two methyl groups in **8** an orientation parameter was also refined.

Acknowledgment. We thank the NSERC of Canada for financial support and for a Postgraduate Scholarship to C.R.B. We are grateful to the EPSRC of the U.K. for providing time on the Daresbury Synchrotron and to the Station 9.8 scientists Dr. D. Taylor and Dr. S. Cole for their help.

Supporting Information Available: Tables of X-ray data for complexes **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990218Y