Stereoselective Coordination of Prochiral Olefins to Asymmetric Platinum(II) Complexes and a Diplatinum(II) Complex with a Single Unsupported Halide Bridge

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The chiral complexes [PtMe{*cis*-1-(N=CHC$_6$H$_4$)-2-(N=CHPh)C$_6$H$_{10}$}], **1**, and [PtMe{*trans*-1-(N=CHC$_6$H$_4$)-2-(N=CHPh)C$_6$H$_{10}$}], **2**, react with protic acids HBF$_4$ or [H(OEt$_2$)$_2$][BAr$_4$] (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) in the presence of olefin, with loss of methane, to give complexes of the type [Pt(η^2-CH$_2$=CHR){*cis*/*trans*-1-(N=CHC$_6$H$_4$)-2-(N=CHPh)C$_6$H$_{10}$}][BX$_4$] (R = H, Me, Ph, 4-Me-C$_6$H$_4$; X = F, Ar). For prochiral olefins, R = Me, Ph, and 4-Me-C$_6$H$_4$, highly stereoselective (90−95%) olefin coordination was demonstrated by using ^{1}H and ^{13}C NMR spectroscopy, and for the complex [Pt(η^2-CH$_2$=CHPh){*cis*-1-(N=CHC$_6$H$_4$)-2-(N=CHPh)-C$_6$H$_{10}$}][BF$_4$] by an X-ray structure determination. Olefin dissociation from [Pt(η^2-CH$_2$=CHPh){*trans*-1-(N=CHC$_6$H$_4$)-2-(N=CHPh)C$_6$H$_{10}$}][BAr$_4$] occurred in CD$_2$Cl$_2$ to give the dinuclear complex [Pt$_2$(μ-Cl){*trans*-1-(N=CHC$_6$H$_4$)-2-(N=CHPh)C$_6$H$_{10}$}$_2$][BAr$_4$], and hydrolysis of [Pt(h^2-CH$_2$=CH−C$_6$H$_4$-4-Me){*trans*-1-(N=CHC$_6$H$_4$)-2-(N=CHPh)C$_6$H$_{10}$}][BF$_4$] gave PhCH=O and [Pt(η^2-CH$_2$=CH−C$_6$H$_4$-4-Me){*trans*-1-(N=CHC$_6$H$_4$)-2-(NH$_2$)C$_6$H$_{10}$}][BF$_4$]. These are useful model compounds for intermediates in stereoselective alkene polymerization since they contain mutually *cis* alkenes and M−C σ-bonds.

Introduction

The design and synthesis of soluble, well-defined transition-metal catalysts for the polymerization of olefins is a flourishing field. Increasing numbers of late transition-metal-based catalysts are being reported,[1] following the discovery of nickel(II) and palladium(II) polymerization catalysts with bulky diimine ligands.[2] Similarly, late transition-metal complexes have been effective in the copolymerization of α-olefins with carbon monoxide to give high molecular weight copolymers which contain true carbon stereocenters in the polymer backbone.[3] When enantiopure bis(oxazoline) ligands are employed, highly tactic copolymers can be made.[4] For the polymerization of olefins, bulky substituents on the diimine ligands are needed to block associative olefin substitution leading to chain transfer.[1,2] There is good evidence for the insertion mechanism, and in some cases, intermediates in CO/olefin copolymerization have been isolated and characterized.[6]

The active initiator in the homopolymerization of olefins is thought to be a cationic complex [M(N−N)Me(olefin)]$^+$ (M = Ni, Pd; N−N = diimine), with the methyl and olefin ligands mutually *cis*, and several platinum complexes of this type have been characterized recently.[7] One such platinum(II) complex even showed the unprecedented ability to promote polymerization of electron-rich α-olefins.[8] A high degree of stereoselectiv-

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(1) (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65. (c) Meneghetti, S. M.; Lutz, P. J.; Kress, J. *Organometallics* **1999**, *18*, 2734. (d) Tsuji, S.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1999**, *18*, 4758. (e) Mecking, S. M.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (f) Desjardins, S. Y.; Way, A. A.; Murray, M. C.; Adirim, D.; Baird, M. C. *Organometallics* **1998**, *17*, 2382. (g) Deng, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 1094. (h) Musaev, D. G.; Froese, R. D. J.; Svensson, M.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 367. (i) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005. (j) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

(2) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(3) (a) Zuideveld, M. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Klusener, P. A. A.; Stil, H. A.; Roobeek, C. F. *J. Am. Chem. Soc.* **1998**, *120*, 7977. (b) Aeby, A.; Gsponer, A.; Consiglio, G. *J. Am.Chem. Soc.* **1998**, *120*, 11000. (c) Safir, A. L.; Novak, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 643. (d) Nozaki, K.; Sato, N.; Tonomura, Y.; Yasutomi, M.; Takaya, H.; Hiyama, T.; Matsubara, T.; Koga, N. *J. Am. Chem. Soc.* **1997**, *119*, 12779. (e) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (f) Svensson, M.; Matsubara, T.; Morokuma, K. *Organometallics* **1996**, *15*, 5568. (g) Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 7337. (h) Jiang, Z.; Sen, A. *Organometallics* **1995**, *14*, 4455. (i) Kacker, S.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 10591. (j) Markies, B. A.; Kruis, D.; Rietveld, M. H. P.; Verkerk, K. A. N.; Boersma, J.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 5263. (k) van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977. (l) Jiang, Z.; Adams, S. E.; Sen, A. *Macromolecules* **1994**, *27*, 2694. (m) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (n) Brookhart, M.; Rix, F. C.; DeSimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894. (o) Sen, A.; Jiang, Z. *Macromolecules* **1993**, *26*, 911. (p) Jiang, Z.; Dahlen, G. M.; Houseknecht, K.; Sen, A. *Macromolecules* **1992**, *25*, 2999. (q) Batistini, A.; Consiglio, G. *Organometallics* **1992**, *11*, 1766. (r) Batistini, A.; Consiglio, G.; Suter, U. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 303. (s) Barsacchi, M.; Batistini, A.; Consiglio, G.; Suter, U. W. *Macromolecules* **1992**, *25*, 3604. (t) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235. (u) Barsacchi, M.; Consiglio, G.; Medici, L.; Petrucci, G.; Suter, U. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 989. (v) Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866. (w) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 3520.

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ity of α-olefin coordination has been achieved for chiral, platinum(II) complexes with amino acid ligands and was attributed to electronic interactions between the amino acid ligand and olefin group substituents.[9,10] The stereoselectivity of α-olefin coordination has also been examined in five-coordinate platinum(II) and palladium(II) complexes.[11]

This article demonstrates that for model platinum(II) complexes [Pt(η^2-CH_2=CHR){*cis*/*trans*-1-(N=CHC_6H_4)-2-(N=CHPh)C_6H_{10}}][BX_4], which contain ligands based on *cis*- or *trans*-1,2-diaminocyclohexane, chirality induced by the diimine chelates results in stereoselective α-olefin coordination. In addition, low rates of alkene exchange are observed. X-ray crystallography and molecular modeling were used to illustrate the factors thought necessary for enantioface selectivity in α-olefin coordination, factors that are relevant to late transition-metal homopolymerization and copolymerization of prochiral olefins and carbon monoxide. A part of this work has been published as a communication.[12]

Results and Discussion.

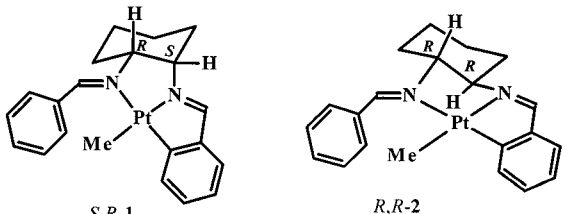
Complexes **1** and **2**, derived from *cis*- and *trans*-1,2-diaminocyclohexane, are chiral and racemic (Chart 1) and were recently used as substrates to study the stereoselectivity of the intermolecular oxidative addition of primary alkyl halides to platinum(II).[13]

The new olefin complexes were prepared by the reaction of racemic complexes **1** or **2** with either HBF_4 or [$H(OEt_2)_2$][BAr_4] (Ar = 3,5-$(CF_3)_2C_6H_3$) in the presence of excess olefin. Protonolysis of the methylplatinum bond, with loss of methane, generates a vacant site and the olefin coordinates to give complexes of the type [Pt(η^2-CH_2=CHR){*cis*/*trans*-1-(N=CHC_6H_4)-2-(N=CHPh)-C_6H_{10}}][BX_4] as outlined in Schemes 1 and 2 for derivatives of the *cis* ligand, **3**−**6**, and Schemes 3−5 for derivatives of the *trans* ligand, **7**−**12**. Several of the products were unstable toward hydrolysis of the free imine group in acid solution, and so the reactions with HBF_4 were carried out at low temperature (−78 °C) to minimize decomposition.

Scheme 1 shows that the stereochemistry about the unmetalated N=C bond changes from *trans* in complex **1** to *cis* in complexes **3**−**6** during the protonolysis reaction, presumably by reversible proton addition to the imine group. This change in stereochemistry was demonstrated by X-ray structure determinations of complexes **3** and **5**. The reaction of **2** with HBF_4 and 4-methylstyrene gave complex **10**, but the free imine group was easily hydrolyzed to give PhCH=O and [Pt(η^2-CH_2=CH-4-Me-C_6H_4){*trans*-1-(N=CHC_6H_4)-2-(NH_2)-C_6H_{10}}][BF_4], **12**, as shown in Scheme 3.

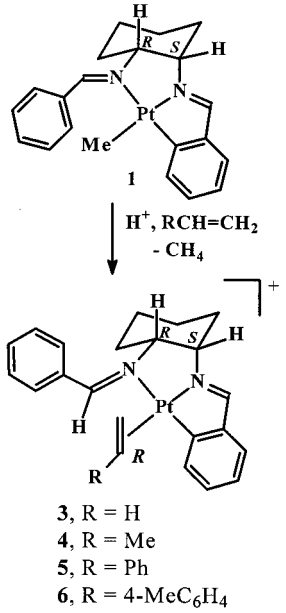
This problem of undesired hydrolysis reactions was minimized by using [$H(OEt_2)_2$][BAr_4] (Ar = 3,5-$(CF_3)_2$-C_6H_3) to cleave the methyl group in complex **2**. The

Chart 1



S,*R*-**1** [PtMe(*S*,*R*-*cis*-L)] *R*,*R*-**2** [PtMe(*R*,*R*-*trans*-L)]

Scheme 1



3, R = H
4, R = Me
5, R = Ph
6, R = 4-MeC_6H_4

(4) (a) Brükner, S.; De Rosa, C.; Corradini, P.; Porzio, W.; Musco, A. *Macromolecules* **1996**, *29*, 1535. (b) Bartolini, S.; Carfagna, C.; Musco, A. *Macromol. Rapid Commun.* **1995**, *16*, 9. (c) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641.

(5) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177.

(6) (a) Reddy, K. R.; Chen, C.-L.; Liu, Y.-H.; Peng, S.-M.; Chen, J.-T.; Liu, S.-T. *Organometallics* **1999**, *18*, 2574. (b) Aeby, A.; Consiglio, G. *J. Chem. Soc., Dalton Trans.* **1999**, 655. (c) Carfagna, C.; Formica, M.; Gatti, G.; Musco, A.; Pierleoni, A. *Chem. Commun.* **1998**, 1113. (d) Green, M. J.; Britovsek, G. J. P.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1996**, 1563. (e) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137. (f) van Leeuwen, P. W. N. M.; Roobeek, C. F.; van der Heijden, H. *J. Am. Chem. Soc.* **1994**, *116*, 12117. (g) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. *Organometallics* **1990**, *9*, 1735.

(7) For platinum(II) complexes containing an olefin unit *cis* to an alkyl ligand see: (a) Yang, K.; Lachicotte, R. J.; Eisenberg, R. *Organometallics* **1998**, *17*, 5102. (b) Ganis, P.; Orabona, I.; Ruffo, F.; Vitagliano, A. *Organometallics* **1998**, *17*, 2646 (c) Fusto, M.; Giordano, F.; Orabona, I.; Ruffo, F. *Organometallics* **1997**, *16*, 5981. (d) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809. (e) Cucciolito, M. E.; De Felice, V.; Panunzi, A.; Vitagliano, A. *Organometallics* **1989**, *8*, 1180. (f) Clark, H. C.; Jablonski, C. R.; von Werner, K. *J. Organomet. Chem.* **1974**, *82*, C51.

(8) Albietz, P. J., Jr.; Yang, K.; Eisenberg, R. *Organometallics* **1999**, *18*, 2747.

(9) (a) Morris, K. F.; Erickson, L. E.; Panajotova, B. V.; Jiang, D. W.; Ding, F. *Inorg. Chem.* **1997**, *36*, 601. (b) Erickson, L. E.; Hayes, P.; Hooper, J. J.; Morris, K. F.; Newbrough, S. A.; Van Os, M.; Slangan, P. *Inorg. Chem.* **1997**, *36*, 284. (c) Erickson, L. E.; Jones, G. S.; Blanchard, J. L.; Ahmed, K. J. *Inorg. Chem.* **1991**, *30*, 3147. (d) Miki, K.; Yamatoya, K.; Kasai, N.; Kurosawa, H.; Urabe, A.; Emoto, M.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1988**, *110*, 3191. (e) Lazzaroni, R.; Uccello-Barretta, G.; Bertozzi, S.; Salvadori, P. *J. Organomet. Chem.* **1985**, *297*, 117.

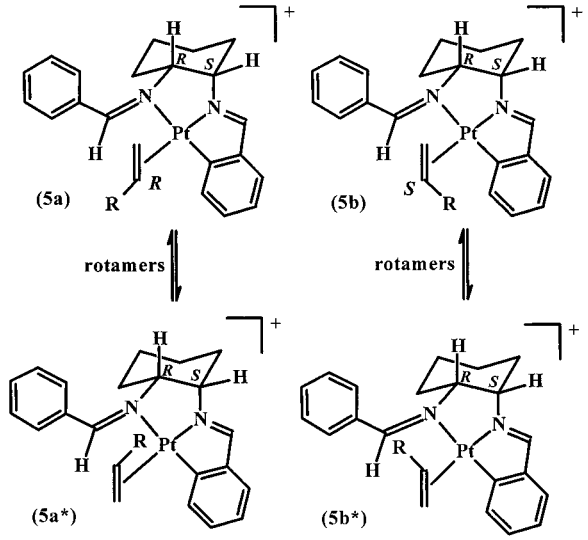
(10) Gladysz, J. A.; Boone, B. J. *Angew Chem., Int. Ed. Engl.* **1997**, *36*, 550.

(11) (a) van der Poel, H.; van Koten, G. *Inorg. Chem.* **1981**, *20*, 2950. (b) Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *8*, 1180. (c) Albano V. G.; Braga, D.; De Felice, V.; Panunzi, A.; Vitagliano, A. *Organometallics* **1987**, *6*, 517.

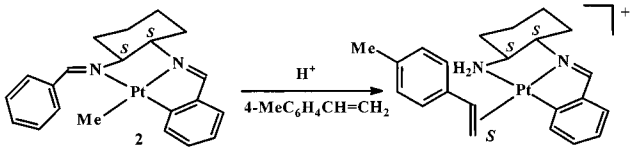
(12) Baar, C. R.; Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 4329.

(13) Baar, C. R.; Jenkins, H. A.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 2805. Because complexes **1** and **2** are used in racemic form (*R*,*S* and *S*,*R* for **1**; *R*,*R* and *S*,*S* for **2**), each diastereomer shown in Schemes 1−5 has a corresponding enantiomer.

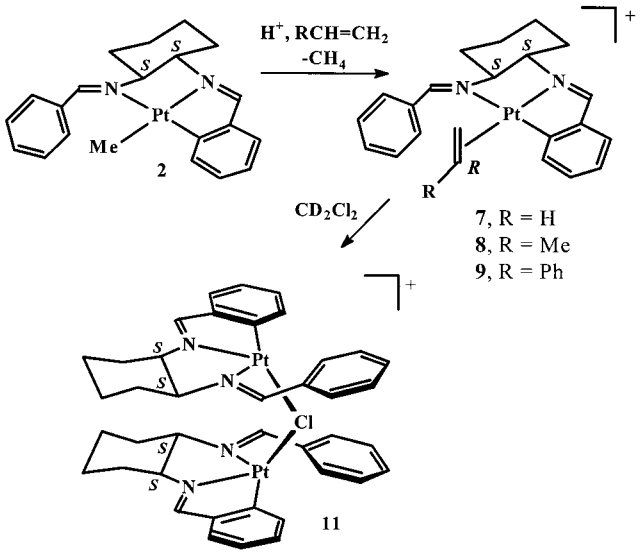
Scheme 2



Scheme 3



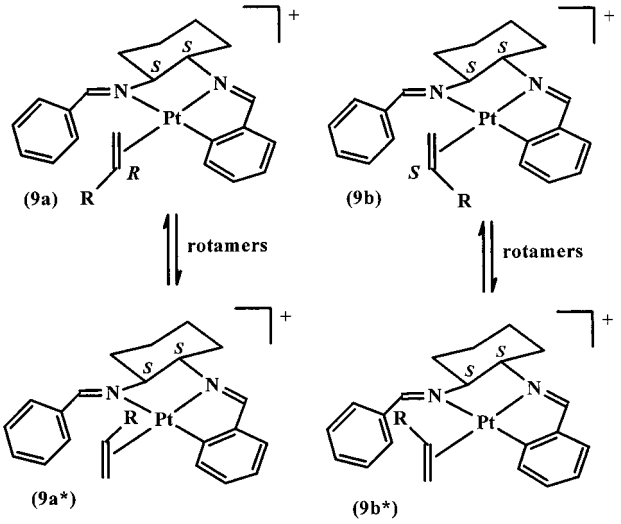
Scheme 4



improved selectivity is attributed to the high crystallinity, large molecular weight, and anhydrous nature of $[H(OEt_2)_2][BAr_4]$, which allowed the precise addition of 1 molar equiv of H^+. In addition, isomerization of the free imine bond did not occur in this case, as was demonstrated by a structure determination of complex **11**. The reactions of **2** with $[H(OEt_2)_2][BAr_4]$ in the presence of excess olefin are outlined in Scheme 4.

The ^{1}H NMR data for the ethylene complexes **3** and **7** show two resonances for the ethylene ligand in an AA′BB′ pattern, with the nonequivalence arising from the chirality of the supporting diimine ligands. For example, the ^{1}H NMR spectrum of **3** shows multiplets at δ 4.03 and 4.29, both with ^2J(PtH) = 61 Hz, corresponding to the protons CH_AH_B═ . The data are

Scheme 5



consistent with rapid rotation of the ethylene ligand about the Pt−C_2H_4 bond, which equilibrates protons that are *trans* to each other in the ethylene unit. The presence of a single resonance for the ethylene ligand in the ^{13}C NMR for complexes **3** and **7** confirms that rapid rotation of the ethylene ligand can occur. If ethylene rotation were slow at room temperature, two carbon signals would be expected in the ^{13}C NMR and an ABCD pattern would be present in the ^{1}H NMR. Well-resolved platinum satellites were observed for the ethylene resonances of **3** and **7** in both the ^{1}H and ^{13}C NMR spectra at room temperature, demonstrating that ethylene exchange was slow on the NMR time scale. The low-temperature (−80 °C) ^{1}H NMR spectrum of complex **3** showed no significant changes from room temperature, suggesting that ethylene rotation is a facile process.

Since complexes **1** and **2** are chiral, the coordination of a prochiral olefin such as propylene, styrene, or 4-methylstyrene can potentially give two diastereomeric forms depending on which face of the olefin coordinates to platinum, *R* or *S* (Schemes 2 and 5).[9,10] For complexes **4**−**6** and **8**−**10** a very high degree of enantioface selectivity (90−95%) was demonstrated by the dominance of a single set of resonances in both the ^{1}H and ^{13}C NMR spectra. For example, the ^{1}H NMR spectrum of complex **5** shows doublets at δ 3.76 and 3.92 with J(PtH) = 51 and 41 Hz, respectively, for the CH_2═ protons of the styrene ligand and a doublet of doublets at δ 6.63, with J(PtH) = 79 Hz, for the CH═ proton (Figure 1a). Corresponding peaks in the ^{13}C NMR spectrum appear at δ 59.8, J(PtC) = 166 Hz, and δ 102.0, J(PtC) = 132 Hz, for the CH_2═ and CH═ carbons, respectively (Figure 1b).

In both the ^{1}H and ^{13}C NMR spectra the alkene resonances for **4**−**6** and **8**−**10** all show well-resolved satellites due to coupling to ^{195}Pt, thus demonstrating that fast olefin exchange does not occur at ambient temperature. Even in the presence of excess styrene, the NMR spectra of complexes **5** and **9** retain these satellites, confirming that the exchange process is slow in these complexes. Low-temperature ^{1}H NMR were carried out for products **4** and **5**. In each case the ^{1}H NMR spectra at −80 °C remained essentially unchanged from that observed at room temperature. This indicates either that the complexes with prochiral olefins are

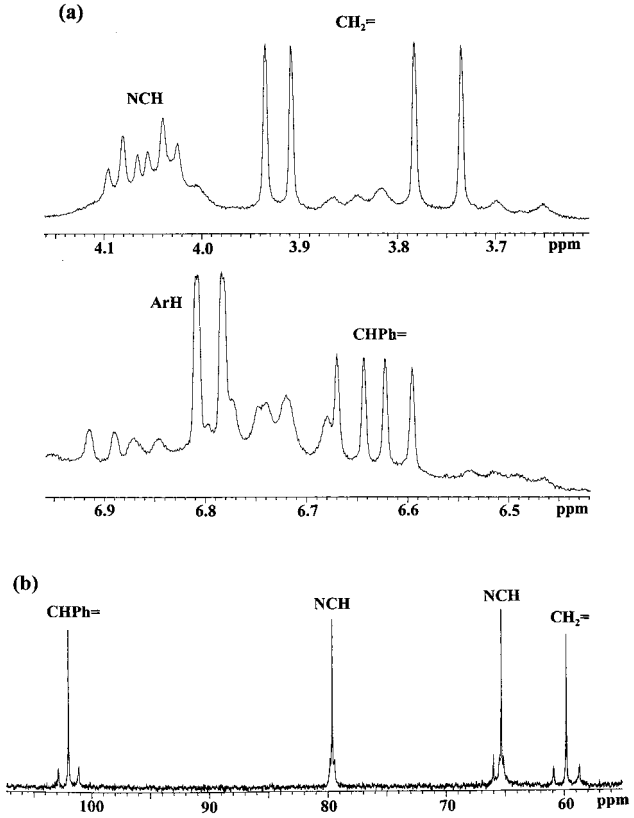


Figure 1. NMR spectrum of complex **5**, showing resonances for the styrene ligand. (a) ^{1}H NMR spectrum showing the resonances for the CH_2= and PhCH= protons. (b) The ^{13}C NMR spectrum. Only isomer **5a** is detected.

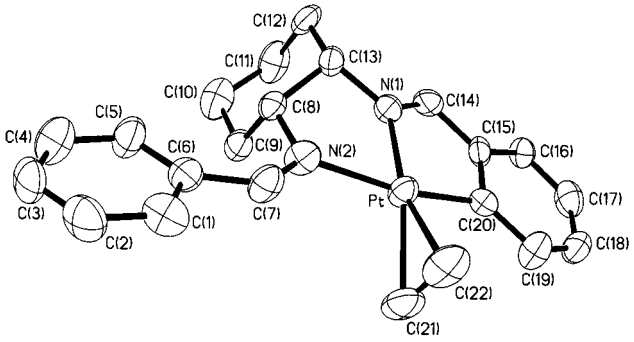


Figure 2. View of the structure of the cation [Pt(η^2-CH_2=CH_2){(*S*,*R*)-*cis*-1-(N=CHC_6H_4)-2-(N=CHPh)C_6H_{10}}]$^+$ in complex **3** (50% thermal ellipsoids).

present as a single rotameric form or that alkene rotation is still rapid at low temperature (Scheme 2).[7c]

The magnitude of the coupling constants ^3J(PtH) for the imine resonances in the ^{1}H NMR spectra of complex **1** are 63 and 45 Hz for imine groups *trans* to methyl and aryl, respectively,[13] but these change on conversion to **5** to 139 and 48 Hz, corresponding to imines *trans* to alkene and aryl, respectively. This change is clearly due to the weaker *trans*-influence of alkene compared to methyl.[14]

The structure of the ethylene complex [Pt(η^2-CH_2=CH_2){*cis*-1-(N=CHC_6H_4)-2-(N=CHPh)C_6H_{10}}][BF_4], **3**, is shown in Figure 2, and selected bond distances and angles are provided in Table 1. The ethylene group is

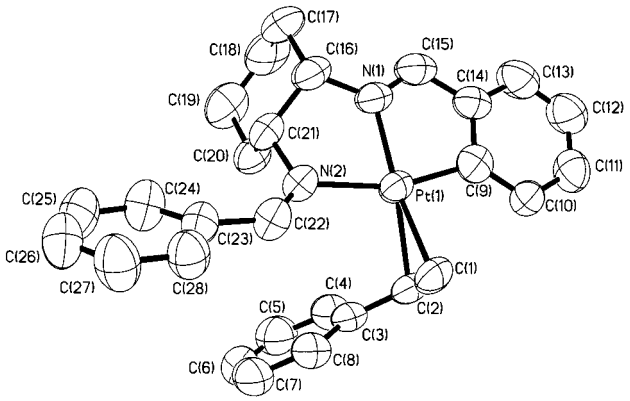


Figure 3. View of the structure of the cation [Pt((*R*)-η^2-CH_2=CHPh){(*S*,*R*)-*cis*-1-(N=CHC_6H_4)-2-(N=CHPh)-C_6H_{10}}]$^+$ in complex **5** (50% thermal ellipsoids).

Table 1. Seleceted Bond Lengths and Angles for Complex 3

(a) Bond Lengths (Å)

Pt−N(1)	1.991(7)	Pt−C(20)	2.000(9)
Pt−N(2)	2.129(8)	Pt−C(21)	2.167(10)
Pt−C(22)	2.169(9)	N(1)−C(14)	1.276(11)
N(2)−C(7)	1.279(11)	C(21)−C(22)	1.38(2)

(b) Bond Angles (deg)

N(1)−Pt−C(20)	82.1(3)	N(1)−Pt−N(2)	81.6(3)
C(20)−Pt−N(2)	163.0(3)	N(1)−Pt−C(21)	161.3(4)
C(20)−Pt−C(21)	95.0(4)	N(2)−Pt−C(21)	98.9(4)
N(1)−Pt−C(22)	161.2(4)	C(20)−Pt−C(22)	95.0(4)
N(2)−Pt−C(22)	101.9(4)	C(21)−Pt−C(22)	37.2(4)
C(14)−N(1)−C(13)	128.1(8)	C(14)−N(1)−Pt	116.1(6)
C(13)−N(1)−Pt	115.8(6)	C(7)−N(2)−C(8)	123.4(8)
C(7)−N(2)−Pt	127.3(6)	C(8)−N(2)−Pt	108.9(5)
N(2)−C(7)−C(6)	134.5(9)	C(22)−C(21)−Pt	71.5(6)
C(21)−C(22)−Pt	71.3(6)		

cis to the aryl ligand. The free imine fragment, N(2)=C(7), has *cis* geometry, whereas the starting material has a *trans* configuration.[13] The *cis* stereochemistry orients the free phenyl group away from the ethylene coordination site and so reduces steric hindrance to olefin coordination. The bulk of the cyclohexyl ligand is below the square plane of the platinum(II) center and appears to force the unmetalated imine unit to lie above the plane to minimize steric interactions. The Pt−N(2) bond *trans* to the aryl group is significantly longer than the Pt−N(1) bond *trans* to the ethylene ligand [2.129(8) vs 1.991(7) Å], due to the stronger *trans*-influence of the aryl group.

A view of the structure of the styrene complex [Pt(η^2-CH_2=CHPh){*cis*-1-(N=CHC_6H_4)-2-(N=CHPh)C_6H_{10}}][BF_4], **5**, is given in Figure 3, and selected bond distances and angles are given in Table 2. As in complex **3**, the bulk of the cyclohexyl ligand lies below the square plane of platinum(II) and, as a result, the free PhCH=N group lies above the plane. The styrene then coordinates with the bulky phenyl substituent below the plane and *syn* to the free PhCH=N group to minimize steric hindrance. Hence, the *Si* face of the styrene is chosen for coordination to platinum(II) to give rotamer **5a** with overall absolute configuration *S*,*R*−*R* (Scheme 2).[15] The structure of **5** thus makes very clear the basis of the high stereoselectivity of olefin coordination in these complexes. It is suggested, on the basis of the similarity

(14) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Sauders: London, 1985; pp 740−705.

(15) The first two descriptors designate the chirality of the cyclohexyl stereocenters in order of priority. The third descibes the chirality of olefin coordination.

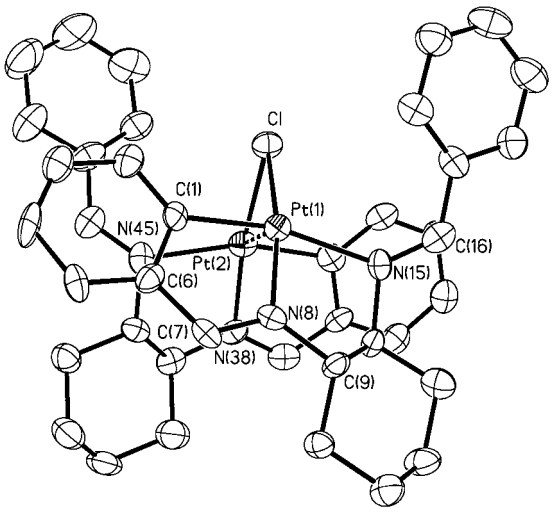


Figure 4. View of the structure of the cation $[Pt_2(\mu\text{-Cl})\{(S,S)\text{-}trans\text{-}1\text{-}(N{=}CHC_6H_4)\text{-}2\text{-}(N{=}CHPh)C_6H_{10}\}_2]^+$ in complex **11** (30% thermal ellipsoids).

Table 2. Selected Bond Lengths and Angles for Complex 5

(a) Bond Lengths (Å)			
Pt(1)−N(1)	2.004(4)	Pt(1)−C(9)	2.008(6)
Pt(1)−N(2)	2.129(4)	Pt(1)−C(1)	2.160(5)
Pt(1)−C(2)	2.218(5)	N(1)−C(15)	1.278(7)
N(2)−C(22)	1.277(7)	C(1)−C(2)	1.380(9)

(a) Bond Angles (deg)			
N(1)−Pt(1)−C(9)	81.6(2)	N(1)−Pt(1)−N(2)	81.0(2)
C(9)−Pt(1)−N(2)	162.7(2)	N(1)−Pt(1)−C(1)	165.7(2)
C(9)−Pt(1)−C(1)	96.3(2)	N(2)−Pt(1)−C(1)	100.6(2)
N(1)−Pt(1)−C(2)	157.2(2)	C(9)−Pt(1)−C(2)	93.7(2)
N(2)−Pt(1)−C(2)	102.0(2)	C(1)−Pt(1)−C(2)	36.7(2)
C(15)−N(1)−C(16)	128.5(5)	C(15)−N(1)−Pt(1)	115.5(4)
C(16)−N(1)−Pt(1)	116.0(4)	C(22)−N(2)−C(21)	123.1(5)
C(22)−N(2)−Pt(1)	129.0(4)	C(21)−N(2)−Pt(1)	107.9(3)
C(2)−C(1)−Pt(1)	73.9(3)	C(1)−C(2)−C(3)	127.1(6)
C(1)−C(2)−Pt(1)	69.4(3)	C(3)−C(2)−Pt(1)	110.4(3)
N(1)−C(15)−C(14)	117.0(5)	N(2)−C(22)−C(23)	132.9(5)

of the ^1H and ^{13}C NMR data between complexes **3**−**6** and molecular mechanics calculations on the platinum(II)−olefin complexes, that all the complexes derived from substrate **1** have the same stereochemistry and that in all cases the olefin coordinates in the manner shown if Figure 3.

Attempted recrystallization of complex **9** from CD_2Cl_2/pentane led to reaction with solvent, and orange needles of complex $[Pt_2(\mu\text{-Cl})\{trans\text{-}1\text{-}(N{=}CHC_6H_4)\text{-}2\text{-}(N{=}CHPh)C_6H_{10}\}_2][BAr_4]$, **11**, were obtained (Scheme 4). The structure of **11** is shown in Figure 4, and selected bond distances and angles are given in Table 3. The styrene ligand has been lost and is replaced by a chloride ligand which bridges two $[Pt\{trans\text{-}1\text{-}(N{=}CHC_6H_4)\text{-}2\text{-}(N{=}CHPh)C_6H_{10}\}]^+$ units. Related homo- and heterodinuclear platinum and palladium complexes with a single unsupported halide bridge are known but are rare (Table 4).[16] In complex **11**, the Pt(1)−Cl−Pt(2) angle of 77.48(9)° is acute and leads to a relatively short distance Pt(1)−Pt(2) = 2.97 Å. In complexes containing a bridging halide and no other bridging ligands, the angle M−X−M bonds can be expected to be near 90°,[17] and significant deviations from this value may be attributed to steric interactions, which will normally give angles > 90°,[18] or to the presence of metal−metal bonding, which will normally give angles < 90°.[16] The structural features for **11** suggest the presence of a weak metal−metal bonding interaction.[19,20] In complex **11** the two square-planar platinum(II) centers are oriented in an approximate face-to-face manner. Because each platinum(II) unit is chiral by virtue of the supporting diimine ligand, the stereochemistry of the binuclear complex is noteworthy. The platinum(II) units are significantly distorted from planarity in each square plane at the chloride coordination site to achieve the bridging motif, but overall the complex is approximately C_2-symmetric, with the chloride atom lying on the C_2 axis. In forming the bridge, the chloride ligand is displaced from each square plane, defined by the NNCPt atoms, to allow the face-to-face conformation. The staggered C_2 conformation in **11** minimizes steric effects between bulky cyclohexyl groups (Figure 4).

The free imine PhCH=N groups in **11** have *trans* geometry, analogous to the starting material **2** but opposite of that observed for the alkene complexes **3** and **5**. The phenyl substituents and chloride ligand are displaced to opposite sides of the square-planar units, and this clearly minimizes steric hindrance between these groups. Much stronger steric hindrance would be present in the precursor styrene complex **9**, since the styrene binds perpendicular to the square plane, and

Table 3. Selected Bond Lengths and Angles for Complex 11[a]

(a) Bond Lengths (Å)			
Pt(1)−N(8)	1.967(9)	Pt(1)−C(1)	2.014(12)
Pt(1)−N(15)	2.114(10)	Pt(1)−Cl	2.366(3)
Pt(1)−Pt(2)	2.9696(6)	Pt(2)−N(38)	1.975(10)
Pt(2)−C(31)	1.984(14)	Pt(2)−N(45)	2.137(10)
Pt(2)−Cl	2.379(3)	C(7)−N(8)	1.306(14)
N(8)−C(9)	1.472(14)	C(14)−N(15)	1.510(13)
N(15)−C(16)	1.264(15)	C(37)−N(38)	1.262(16)
N(38)−C(39)	1.455(15)	C(44)−N(45)	1.485(13)
N(45)−C(46)	1.294(15)		

(b) Bond Angles (deg)			
N(8)−Pt(1)−C(1)	82.2(4)	N(8)−Pt(1)−N(15)	81.4(4)
C(1)−Pt(1)−N(15)	163.5(4)	N(8)−Pt(1)−Cl	165.4(3)
C(1)−Pt(1)−Cl	94.4(3)	N(15)−Pt(1)−Cl	101.8(3)
N(8)−Pt(1)−Pt(2)	114.6(2)	C(1)−Pt(1)−Pt(2)	96.0(3)
N(15)−Pt(1)−Pt(2)	91.9(2)	Cl−Pt(1)−Pt(2)	51.46(7)
N(38)−Pt(2)−C(31)	81.4(5)	N(38)−Pt(2)−N(45)	80.9(4)
C(31)−Pt(2)−N(45)	162.3(5)	N(38)−Pt(2)−Cl	165.3(3)
C(31)−Pt(2)−Cl	95.4(4)	N(45)−Pt(2)−Cl	101.9(3)
N(38)−Pt(2)−Pt(1)	114.9(3)	C(31)−Pt(2)−Pt(1)	96.6(3)
N(45)−Pt(2)−Pt(1)	91.6(2)	Cl−Pt(2)−Pt(1)	51.06(7)
Pt(1)−Cl−Pt(2)	77.48(9)	N(8)−C(7)−C(6)	117.0(11)
C(7)−N(8)−C(9)	126.9(10)	C(7)−N(8)−Pt(1)	115.5(9)
C(9)−N(8)−Pt(1)	117.1(7)	C(16)−N(15)−C(14)	120.1(11)
C(16)−N(15)−Pt(1)	135.7(9)	C(14)−N(15)−Pt(1)	104.0(7)
N(15)−C(16)−C(17)	125.9(13)	N(38)−C(37)−C(36)	117.9(12)
C(37)−N(38)−C(39)	128.7(11)	C(37)−N(38)−Pt(2)	115.7(9)
C(39)−N(38)−Pt(2)	115.2(8)	C(46)−N(45)−C(44)	121.3(11)
C(46)−N(45)−Pt(2)	134.5(10)	C(44)−N(45)−Pt(2)	104.0(8)
N(45)−C(46)−C(47)	127.7(15)		

[a] Symmetry transformations used to generate equivalent atoms: #1 −x+2, −y, −z+2.

(16) (a) Terheijden, J.; van Koten, G.; Grove, D. M.; Vrieze, K.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1987**, 1359. (b) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Spek, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 4285.

(17) Wachter, J.; Jeanneaux, F.; Le Borgne, G.; Riess, J. G. *Organometallics* **1984**, *3*, 1034.

(18) Cotton, F. A.; Frenz, B. A.; White, A. J.*J. Organomet. Chem.* **1973**, *60*, 147.

(19) Olmstead, M. M.; Farr, J. P.; Balch, A. L. *Inorg. Chim. Acta* **1981**, *52*, 47.

(20) (a) Deese, W. C.; Johnson, D. A. *J. Organomet. Chem.* **1982**, *232*, 325. (b) Dai, L.; Zhou, Z.; Zhang, Y.; Ni, C.; Zhang, Z.; Zhou, Y. *J. Chem. Soc., Chem Commun.* **1987**, 1760.

Table 4. Bond Distances and Angles for Selected Complexes with Bridging Halide Ligands M−X−M

complex	*d*(MX)/Å	MXM/deg	*d*(MM)/Å	ref
$[\{Pd\{C_6H_3(CH_2NMe_2)_2\}_2(\mu\text{-Cl})]^+$	2.463(1), 2.458(1)	134.8(1)	4.54	16
$[(CO)_2ClRh(\mu\text{-Cl})Rh(CO)\{PhP(OCMe_2CH_2)_2NH\}]$	2.372(1), 2.454(1)	89.36(3)	3.39	17
$[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-I})]^+$	2.581(2), 2.595(2)	110.8(1)	4.26	18
$[IPd(\mu\text{-I})PdMe(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$	2.740(5), 2.648(5)	67.0(1)	2.98	19
complex **11**	2.366(3), 2.379(3)	77.48(9)	2.97	this work

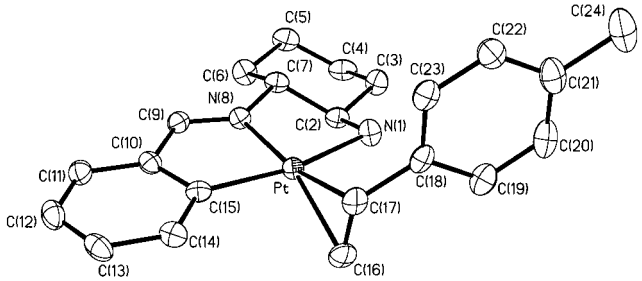


Figure 5. View of the structure of the cation $[Pt((R)\text{-}\eta^2\text{-}CH_2{=}CH\text{-}4\text{-}MePh)\{(R,R)\text{-}trans\text{-}1\text{-}(N{=}CHC_6H_4)\text{-}2\text{-}(NH_2)\text{-}C_6H_{10}\}]^+$ in complex **12** (30% thermal ellipsoids).

Table 5. Selected Bond Lengths and Angles for Complex 12

	(a) Bond Lengths (Å)		
Pt−N(8)	1.999(5)	Pt−C(15)	2.013(7)
Pt−C(16)	2.133(7)	Pt−N(1)	2.155(6)
Pt−C(17)	2.212(6)	N(8)−C(9)	1.280(8)
C(16)−C(17)	1.379(11)		
	(b) Bond Angles (deg)		
N(8)−Pt−C(15)	81.5(2)	N(8)−Pt−C(16)	159.5(3)
C(15)−Pt−C(16)	94.3(3)	N(8)−Pt−N(1)	81.6(2)
C(15)−Pt−N(1)	162.9(2)	C(16)−Pt−N(1)	100.8(3)
N(8)−Pt−C(17)	163.3(3)	C(15)−Pt−C(17)	97.0(2)
C(16)−Pt−C(17)	37.0(3)	N(1)−Pt−C(17)	99.9(2)
C(2)−N(1)−Pt	105.5(4)	C(9)−N(8)−C(7)	127.0(5)
C(9)−N(8)−Pt	116.8(4)	C(7)−N(8)−Pt	116.2(4)
N(8)−C(9)−C(10)	115.3(6)	C(17)−C(16)−Pt	74.6(4)
C(16)−C(17)−C(18)	126.1(7)	C(16)−C(17)−Pt	68.4(4)
C(18)−C(17)−Pt	111.4(4)		

this may account for its high reactivity. It is likely that stereoselective styrene coordination would give rotamer **9a** in Scheme 5 (R = Ph), having absolute configuration *S,S*−*R*, to minimize steric interactions.

Attempts to crystallize complex **10** from THF layered with pentane gave instead crystals of a hydrolysis product, $[Pt(\eta^2\text{-}CH_2{=}CH{-}C_6H_4\text{-}4\text{-}Me)\{trans\text{-}1\text{-}(N{=}CH\text{-}C_6H_4)\text{-}2\text{-}(NH_2)C_6H_{10}\}][BF_4]$, **12**. A view of the structure is shown in Figure 5, and selected bond distances and angles are given in Table 5. The free PhCH=N group of the substrate **2** has been completely hydrolyzed to give an NH_2 group which is coordinated to a square-planar platinum(II) center. The 4-methylstyrene ligand is oriented such that the 4-methyphenyl substituent faces away from the neighboring aryl ligand and is directed toward the smaller NH_2 group. The structure has overall absolute configuration *R,R*−*R*, with enantioface selectivity opposite that assigned for complex **9**. This change clearly arises as a result of the absence of the bulky free imine group.

Molecular Mechanics

Molecular mechanics calculations were carried out for the styrene derivatives **5** and **9**, with structures optimized and energies calculated for each possible diastereomeric pair as well as each rotamer in the pair.[21] Hence, a total of four energy minima were optimized corresponding to placement of the styrene phenyl substituent in each of four possible quadrants; these are **a**, **a***, **b**, and **b*** in Schemes 2 and 5. The results are given in Table 6.

Table 6. Molecular Mechanics Calculations of the Relative Energies of the Possible Diasteoreomers (a, b) and Rotamers (a, A* or b, b*) for Complexes 5 and 9

complex	MMX E (kcal/mol) *cis* imine	MMX E (kcal/mol) *trans* imine
5a	35.5	37.9
5a*	39.1	39
5b	37.2	40.9
5b*	37.9	45.3
9a	40.6	
9a*	43.8	
9b	42	
9b*	46.3	

The lowest energy calculated for the *cis*-ligand complexes corresponded to structure **5a** in Scheme 2, corresponding to the experimental structure of **5** shown in Figure 3. The phenyl substituent is *anti* to the aryl ligand, *syn* to the free phenylimine group, but below the plane with overall absolute configuration *S,R*−*R*, and the free imine has *cis* stereochemistry. The rotamer with the same enantioface selectivity, **5a***, has a significantly higher relative energy, suggesting there would be a significant steric barrier for styrene rotation. The diastereomer with absolute configuration *S,R*−*S* (from opposite enantioface selectivity for the styrene) also shows a significantly higher energy in either rotameric form **5b** or **5b*** compared with **5a**. The complexes with the free imine group having *trans* stereochemistry are calculated to be less stable (Table 6), clearly because the phenyl substituent is directed toward the olefin coordination site. The isomer/rotamer corresponding to **5a** is again most stable.

For complex **9**, which is based on *trans*-1,2-diaminocyclohexane, the orientation with the lowest relative energy once again has the styrene substituent *anti* to the aryl group, *syn* to the free phenyl imine fragment, and below the square plane; compare the relative energies of **9a** to **9a***, **9b**, and **9b*** (Table 6). Hence, the favored diastereomer is predicted to have absolute configuration *S,S*−*R*, with **9a** being the favored rotamer (Scheme 5, R = Ph).

Conclusions

These are the first examples of chiral square-planar platinum(II) complexes with diimine ligands that have steric properties that effect stereoselective α-olefin coordination as well as prohibit easy olefin exchange and rotation processes. Particularly important is the structure of complex **5**, which demonstrates the basis of the high stereoselectivity in these reactions. The complexes are models for the design of new, asymmetric d^8-metal

(21) CACHE Scientific Inc., Version 3.7, 1992.

Table 7. Crystallographic Details for Complexes 3, 5, 11, and 12

	3	5	11	12
formula	$C_{22}H_{25}N_2PtBF_4$	$C_{29}H_{31}N_2Cl_2PtBF_4$	$C_{77}H_{60}BClF_{24}N4Pt_2$	$C_{26}H_{31}N_2OPtBF_4$
fw	599.34	760.36	1933.73	669.43
temp, K	296(2)	293(2)	200(2)	150(2)
wavelength, *l*	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2(1)/n$	$P2_1/n$
a, Å	9.6977(4)	10.64470(10)	15.4727(7)	10.0400(4)
b, Å	8.1380(4)	18.4015(2)	31.767(2)	14.4726(6)
c, Å	26.5986(4)	15.5215(2)	17.187(1)	17.6329(5)
β, deg	93.843(2)	98.166(1)	107.854(4)	91.640(3)
volume, Å^3; *Z*	2094.4(1); 4	3009.50(6), 4	8041.0(8), 4	2561.1(2); 4
d(calcd), Mg/m^3	1.901	1.678	1.597	1.736
abs coeff, mm^{-1}	6.746	4.886	3.608	5.529
F(000)	1160	1488	3776	1312
cryst size, mm^3	0.10 × 0.10 × 0.08	0.30 × 0.30 × 0.20	0.45 × 0.06 × 0.05	0.47 × 0.08 × 0.08
θ range, deg	1.53−22.50	1.73−25.00	2.56−25.03	1.82−26.38
no. rflns collected	9851	15164	31816	15835
no. indep rflns	2742 [*R*(int) = 0.0610]	5249 [*R*(int) = 0.0279]	12 730 [*R*(int) = 0.102]	5188 [*R*(int) = 0.0830]
no. of data/restrnts/params	2741/0/271	5248/0/355	12730/45/842	5188/0/317
goof on F^2	1.029	1.015	1.034	1.044
R (I>2σ(I))	R1 = 0.0411, wR2 = 0.0764	R1 = 0.0319, wR2 = 0.0803	R1 = 0.0643, wR2 = 0.1495	R1 = 0.0575, wR2 = 0.1441
R (all data)	R1 = 0.0668, wR2 = 0.0841	R1 = 0.0443, wR2 = 0.0858	R1 = 0.1527, wR2 = 0.1779	R1 = 0.0650, wR2 = 0.1544
largest diff peak, hole, e Å^{-3}	0.963, −0.755	0.808, −0.629	1.276, −1.300	1.959, −4.681

polymerization catalysts. The structural characterization of complex **11** is an interesting example of a dinuclear platinum(II) complex with a single unsupported halide bridge. The square-planar units have an unexpected face-to-face orientation which may be due to the presence of a weak Pt−Pt attractive interaction.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded by using a Varian Gemini 300 MHz spectrometer. Chemical shifts are reported relative to TMS. The complexes (*R,S/S,R*)-[PtMe{*cis*-1-(N=CHC_6H_4)-2-(N=CHPh)C_6H_{10}}] (**1**) and (*R,R/S,S*)-[PtMe{*trans*-1-(N=CHC_6H_4)-2-(N=CHPh)C_6H_{10}}] (**2**) were prepared as described previously.[13] [$H(OEt_2)_2$][BAr_4] (Ar = 3,5-$(CF_3)_2C_6H_3$) was prepared according to the literature procedure.[22] All operations were performed under standard Schlenk conditions.

[Pt(η^2-CH_2=CH_2){*cis*-1-(N=CHC_6H_4)-2-(N=CHPh)C_6H_{10}}][BF_4] (3). To a solution of **1** (0.025 g, 0.05 mmol) in CH_2Cl_2 at −78 °C, saturated with CH_2=CH_2, was added HBF_4 (0.05 mmol). After stirring for 5 min, the solvent was evaporated under vacuum at low temperature to give an oily residue, which was triturated and then washed with several portions of pentane to yield the desired product as an orange solid. Yield = 0.021 g (70%). Anal. Calcd for $C_{22}H_{25}N_2PtBF_4$·0.5CH_2Cl_2: C, 42.1; H, 4.1; N, 4.4. Found: C, 42.0; H, 4.1; N, 4.8. ^{1}H NMR (CD_2Cl_2): δ 1.23−1.70 [br m, 3H, Cy(H)]; 1.89 [m, 1H, Cy(H)]; 2.08−2.20 [br m, 2H, Cy(H)]; 2.40 [m, 1H, Cy(H)]; 2.54 [br d, 1H, Cy(H)]; 4.03 [m, 2H, ^2J(PtH) = 61 Hz, C_2H_4]; 4.29 [m, 2H, ^2J(PtH) = 61 Hz, C_2H_4]; 4.40−4.53 [br m, 2H, Cy(H)]; 6.57 [d d, 1H, ^3J(PtH) = 38 Hz]; 7.17 [t d, 1H]; 7.26 [t d, 1H]; 7.44−7.76 [m, 6H]; 8.49 [d, 1H, ^3J(PtH) = 142 Hz, CH=N]; 9.34 [s, 1H, ^3J(PtH) = 44 Hz, CH=N]. ^{13}C-APT NMR (CD_2Cl_2): δ 18.3 [CH_2]; 23.8 [CH_2]; 24.0 [CH_2]; 31.0 [CH_2]; 64.8 [^2J(PtC) = 31 Hz, NCH]; 78.0 [^1J(PtC) = 153 Hz, C_2H_4]; 79.6 [^2J(PtC) = 29 Hz, NCH]; 126.8 [CH]; 128.5 [CH]; 129.3 [CH]; 130.4 [CH]; 131.0 [CH]; 132.9 [CH]; 133.3 [CH]; 133.7 [C]; 139.9 [C]; 150.0 [C]; 173.7 [CH=N]; 178.4 [^2J(PtC) = 102 Hz, CH=N].

The following complexes were similarly prepared.

[Pt(η^2-CH_2=CHMe){*cis*-1-(N=CHC_6H_4)-2-(N=CHPh)-C_6H_{10}}][BF_4] (4). Yield = 78%. Anal. Calcd for $C_{23}H_{27}N_2$-$PtBF_4$·0.5CH_2Cl_2: C, 43.0; H, 4.3; N, 4.3. Found: C, 43.0; H, 4.3; N, 4.1. ^{1}H NMR (CD_2Cl_2): δ 1.36−1.68 [br m, 3H, Cy(H)]; 1.62 [d, 3H, *Me*CH=CH_2]; 1.88−2.25 [br m, 3H, Cy(H)]; 2.40−2.62 [br m, 2H, Cy(H)]; 3.12 [d, 1H, ^2J(PtH) = 52 Hz, ^3J(HH) = 14 Hz, =CH_2]; 3.96 [d, 1H, ^2J(PtH) = 61 Hz, ^3J(HH) = 8 Hz, =CH_2]; 4.38−4.50 [br m, 2H, Cy(H)]; 5.75 [m, 1H, ^2J(PtH) = 87 Hz, =C*H*Me]; 6.61 [d d, 1H, ^3J(PtH) = 37 Hz]; 7.19 [t d, 1H]; 7.28 [t d, 1H]; 7.49−7.72 [m, 4H]; 7.95 [d d, 2H]; 8.48 [d, 1H, ^3J(PtH) = 139 Hz, CH=N]; 9.38 [s, 1H, ^3J(PtH) = 48 Hz, CH=N]. ^{13}C-APT NMR (CD_2Cl_2): δ 18.2 [CH_2]; 22.7 [^2J(PtC) = 36.0 Hz, *Me*CH=CH_2]; 23.8 [CH_2]; 24.0 [CH_2]; 31.1 [CH_2]; 65.4 [^2J(PtC) = 27 Hz, NCH]; 70.8 [^1J(PtC) = 155 Hz, = *C*H_2]; 79.8 [^2J(PtC) = 32 Hz, NCH]; 103.8 [^1J(PtC) = 150 Hz, =*C*HMe]; 126.5 [CH]; 129.1 [CH]; 129.6 [CH]; 130.2 [CH]; 130.8 [CH]; 133.1 [CH]; 133.5 [CH]; 134.1 [C]; 139.3 [C]; 150.0 [C]; 172.9 [CH=N]; 177.8 [^2J(PtC) = 100 Hz, CH=N].

[Pt(η^2-CH_2=CHPh){*cis*-1-(N=CHC_6H_4)-2-(N=CHPh)-C_6H_{10}}][BF_4] (5). Yield = 96%. Anal. Calcd for $C_{28}H_{29}N_2$-$PtBF_4$: C, 49.8; H, 4.1; N, 4.3. Found: C, 49.9; H, 4.3; N, 3.7. ^{1}H NMR (CD_2Cl_2): δ 0.77 [br m, 1H, Cy(H)]; 1.10−1.33 [br m, 2H, Cy(H)]; 1.43−1.62 [br m, 3H, Cy(H)]; 2.02 [m, 1H, Cy(H)]; 2.49 [br d, 1H, Cy(H)]; 3.76 [d, 1H, ^2J(PtH) = 51 Hz, ^3J(HH) = 14 Hz, =CH_2]; 3.92 [d, 1H, ^2J(PtH) = 41 Hz, ^3J(HH) = 8 Hz, =CH_2]; 4.06 [m, 1H, Cy(H)]; 4.25 [br m, 1H, Cy(H)]; 6.63 [m, 1H, ^2J(PtH) = 79 Hz, =C*H*Ph]; 6.79 [d d, 1H, ^3J(PtH) = 39 Hz]; 7.03 [d d, 2H]; 7.20−7.37 [m, 4H]; 7.42 [m, 1H]; 7.57 [m, 1H]; 7.68 [m, 2H]; 7.79 [m, 1H]; 8.10 [d d, 2H]; 8.42 [d, 1H, ^3J(PtH) = 143 Hz, CH=N]; 9.10 [s, 1H, ^3J(PtH) = 49 Hz, CH=N]. ^{13}C-APT NMR (CD_2Cl_2): δ 18.1 [CH_2]; 23.5 [CH_2]; 24.1 [CH_2]; 28.9 [CH_2]; 59.8 [^1J(PtC) = 166 Hz, =*C*H_2]; 65.3 [^2J(PtC) = 27 Hz, NCH]; 79.6 [^2J(PtC) = 29 Hz, NCH]; 102.0 [^1J(PtC) = 132 Hz, =*C*HPh]; 126.6 [CH]; 128.5 [CH]; 129.4 [CH]; 129.5 [CH]; 129.7 [CH]; 130.6 [CH]; 130.9 [CH]; 131.8 [CH]; 133.1 [CH]; 133.9 [CH]; 134.0 [C]; 135.6 [C]; 139.3 [C]; 149.9 [C]; 171.6 [CH=N]; 177.6 [^2J(PtC) = 101 Hz, CH=N].

[Pt(η^2-CH_2=CH−C_6H_4-4-Me){*cis*-1-(N=CHC_6H_4)-2-(N=CHPh)C_6H_{10}}][BF_4] (6). Reliable microanalysis could not be obtained due to hydrolysis of product. ^{1}H NMR (CD_2Cl_2): δ 0.79 [br m, 1H, Cy(H)]; 1.12−1.70 [br m, 8H, Cy(H), 4-*Me*-C_6H_4−CH=CH_2]; 2.03 [br m, 1H, Cy(H)]; 2.50 [br m, 1H, Cy-(H)]; 3.72 [d, 1H, ^2J(PtH) = 51 Hz, ^3J(HH) = 14 Hz, =CH_2]; 3.88 [d, 1H,^2J(PtH) = 42 Hz, ^3J(HH) = 7 Hz, =CH_2]; 4.06 [m, 1H, Cy(H)]; 4.24 [br s, 1H, Cy(H)]; 6.63 [m, 1H, ^2J(PtH) = 78 Hz, =C*H*-C_6H_4-4-Me]; 6.79 [d d, 1H, ^3J(PtH) = 39 Hz]; 6.91 [d d, 2H]; 7.08−7.52 [m, 4H]; 7.58 [m, 1H]; 7.68 [m, 2H]; 7.79 [m, 1H]; 8.10 [d d, 2H]; 8.42 [d, 1H, ^3J(PtH) = 138 Hz, CH=N]; 9.10 [s, 1H, ^3J(PtH) = 51 Hz, CH=N]. ^{13}C-APT NMR (CD_2-Cl_2): δ 18.2 [CH_2]; 21.6 [CH_3]; 23.5 [CH_2]; 24.2 [CH_2]; 28.9

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[CH_2]; 59.0 [^1J(PtC) = 169 Hz, =CH_2]; 65.3 [^2J(PtC) = 28 Hz, NCH]; 79.7 [^2J(PtC) = 30 Hz, NCH]; 103.0 [^1J(PtC) = 128 Hz, =CH−C_6H_4-4-Me]; 126.5 [CH]; 128.7 [CH]; 129.4 [CH]; 129.5 [CH]; 130.2 [CH]; 130.6 [CH]; 130.8 [CH]; 133.1 [CH]; 132.9 [C]; 133.9 [CH]; 134.1 [C]; 139.4 [C]; 142.9 [C]; 150.0 [C]; 171.6 [CH=N]; 177.5 [^2J(PtC) = 101 Hz, CH=N].

[Pt(η^2-CH_2=CH_2){*trans*-1-(N=CHC_6H_4)-2-(N=CHPh)-C_6H_{10}}][BAr_4] (7). To a CH_2=CH_2-saturated solution of **1** (0.023 g, 0.046 mmol) in CH_2Cl_2 (6 mL) at −78 °C was added [$H(OEt_2)_2$][BAr_4] (0.046, 0.046 mmol) in CH_2Cl_2 (6 mL) via cannula. The red solution changed to orange. After 15 min the solvent was removed under reduced pressure to give the product as an orange powder. Yield = 0.054 g (83%). Anal. Calcd for $C_{54}H_{37}N_2PtBF_{24}$·0.5CH_2Cl_2: C, 46.2; H, 2.7; N, 2.0. Found: C, 46.0; H, 2.5; N, 2.1. ^{1}H NMR (CD_2Cl_2): δ 1.30−2.20 [br m, 6H, Cy(H)]; 2.43 [m, 1H, Cy(H)]; 2.65 [m, 1H, Cy-(H)]; 3.64 [m, 1H, NCH]; 4.00 [m, ^2J(PtH) = 62 Hz, =CH_2]; 4.04 [m, 1H, NCH]; 4.28 [m, 1H, ^2J(PtH) = 62 Hz, =CH_2]; 6.58 [d, 1H, ^3J(PtH) = 37 Hz]; 7.17 [t d, 1H]; 7.27 [t d, 1H]; 7.46 [d d, 1H]; 7.54−7.85 [m, 5H]; 7.56 [s, 4H, Ar, *p*-H]; 7.73 [m, 8H, Ar, *o*-H]; 8.38 [d, 1H, ^3J(PtH) = 141 Hz, CH=N]; 9.14 [d, 1H, ^3J(PtH) = 45 Hz, CH=N]. ^{13}C NMR (CD_2Cl_2): δ 23.9 [CH_2]; 24.3 [CH_2]; 29.7 [CH_2]; 30.0 [CH_2]; 69.4 [^2J(PtC) = 25 Hz, NCH]; 74.9 [^2J(PtC) = 45 Hz, NCH]; 78.8 [^1J(PtC) = 153 Hz, =CH_2]; 117.9 [d, Ar, *p*-*C*H]; 125.0 [q, ^1J(CF) = 272.5 Hz, CF_3]; 127.0 [CH]; 128.8 [CH]; 129.3 [m, Ar, *m*-C]; 129.6 [CH]; 130.8 [CH]; 131.3 [CH]; 133.7 [CH]; 133.8 [CH]; 135.2 [d, Ar, *o*-*C*H]; 162.2 [q, Ar, *i*-C]; 169.4 [CH=N]; 176.0 [^2J(PtC) = 102 Hz, CH=N].

The following complexes were similarly prepared.

[Pt(η^2-CH_2=CHMe){*trans*-1-(N=CHC_6H_4)-2-(N=CHPh)-C_6H_{10}}][BAr_4] (8). Yield = 70%. Anal. Calcd for $C_{55}H_{39}N_2PtBF_{24}$: C, 47.5; H, 2.8; N, 2.0. Found: C, 47.5; H, 2.7; N, 2.2. ^{1}H NMR (CD_2Cl_2): δ 1.20−1.78 [br m, 3H, Cy(H)]; 1.62 [d, ^3J(PtH) = 61 Hz, ^4J(HH) = 6 Hz, *Me*CH=CH_2]; 2.03 [br m, 3H, Cy(H)]; 2.39 [br d, 1H, Cy(H)]; 2.65 [br t, 1H, Cy(H)]; 2.97 [d, ^2J(PtH) = 51 Hz, ^3J(HH) = 14 Hz, =CH_2]; 3.56 [m, 1H, NCH]; 3.95 [m, 1H, NCH]; 3.96 [d, 1H, ^2J(PtH) = 59 Hz, ^3J(HH) = 8 Hz, =CH_2]; 5.73 [m, ^2J(PtH) = ca. 76 Hz, =C*H*Me]; 6.60 [d, 1H, ^3J(PtH) = 38 Hz]; 7.17 [t d, 1H]; 7.28 [t d, 1H]; 7.47 [d d, 1H]; 7.54−7.85 [m, 9H]; 7.57 [s, 4H, Ar, *p*-H]; 7.75 [m, 8H, Ar, *o*-H]; 8.02 [d, 2H]; 8.38 [d, 1H, ^3J(PtH) = 137 Hz, CH=N]; 9.13 [d, 1H, ^3J(PtH) = 48 Hz, CH=N]. ^{13}C NMR (CD_2Cl_2): *d* = 22.4 [^2J(Pt−C) = 39 Hz, *Me*CH=CH_2]; 23.9 [CH_2]; 24.5 [CH_2]; 29.8 [CH_2]; 30.2 [CH_2]; 69.7 [^2J(PtC) = 25 Hz, NCH]; 70.9 [^1J(PtC) = 152 Hz, =CH_2]; 75.0 [^2J(PtC) = 42 Hz, NCH]; 104.0 [^1J(PtC) = 150 Hz, =*C*HMe]; 117.9 [d, Ar, *p*-*C*H]; 125.0 [q, ^1J(C−F) = 272.5 Hz, Ar, CF_3]; 126.8 [CH]; 129.5 [m, Ar, *m*-C]; 129.7 [CH]; 129.7 [CH]; 130.8 [CH]; 131.0 [CH]; 133.6 [CH]; 134.3 [CH]; 135.2 [d, Ar, *o*-*C*H]; 138.8 [C]; 148.9 [C]; 162.2 [q, Ar, *i*-C]; 168.6 [CH=N]; 175.9 [^2J(PtC) = 102 Hz, CH=N].

[Pt(η^2-CH_2=CHPh){*trans*-1-(N=CHC_6H_4)-2-(N=CHPh)-C_6H_{10}}][BAr_4] (9). Yield = 95%. Anal. Calcd for $C_{60}H_{41}N_2PtBF_{24}$: C, 49.6; H, 2.9; N, 1.9. Found: C, 51.2; H, 2.7; N, 1.9. ^{1}H NMR (CD_2Cl_2): δ 1.10−1.70 [br m, 4H, Cy(H)]; 1.82−2.0 [br m, 3H, Cy(H)]; 2.55 [br d, 1H, Cy(H)]; 3.04 [br t, 1H, NCH]; 3.37 [br t, 1H, NCH]; 3.58 [d, 1H, ^2J(PtH) = 49 Hz, ^3J(HH) = 14 Hz, =CH_2]; 3.92 [d, 1H, ^2J(PtH) = 52 Hz, ^3J(HH) = 8 Hz, =CH_2]; 6.69 [m, 1H, ^2J(PtH) = 80 Hz, =C*H*Ph]; 6.79 [d d, 1H, ^3J(PtH) = 36 Hz]; 7.06 [d, 2H]; 7.18−7.86 [m, 9H]; 7.56 [s, 4H, Ar, *p*-H]; 7.72 [m, 8H, Ar, *o*-H]; 8.08 [d, 2H]; 8.30 [d, 1H, ^3J(PtH) = 137 Hz, CH=N]; 8.66 [s, 1H, ^3J(PtH) = 51 Hz, CH=N]. ^{13}C NMR (CD_2Cl_2): δ 23.8 [CH_2]; 24.3 [CH_2]; 29.4 [CH_2]; 30.0 [CH_2]; 60.7 [^1J(PtC) = 171 Hz, = CH_2]; 69.5 [^2J(PtC) = 30 Hz, NCH]; 74.3 [^2J(PtC) = 37 Hz, NCH]; 101.6 [^1J(PtC) = 134 Hz, =*C*HPh]; 117.9 [d, Ar, *p*-*C*H]; 125.0 [q, ^1J(CF) = 272.5 Hz, CF_3]; 126.8 [CH]; 128.1 [CH]; 129.4 [CH]; 129.7 [CH]; 129.9 [CH]; 131.1 [CH]; 131.2 [CH]; 131.9 [CH]; 133.6 [CH]; 134.6 [CH]; 135.2 [d, Ar, *o*-*C*H]; 139.1 [C]; 148.9 [C]; 162.1 [q, Ar, *i*-C]; 167.0 [CH=N]; 176.4 [^2J(PtC) = 101 Hz, CH=N].

[Pt(η^2-CH_2=CH−C_6H_4-4-Me){*trans*-1-(N=CHC_6H_4)-2-(N=CHPh)C_6H_{10}}][BF_4] (10) was prepared similarly to complexes **3**−**6**. Reliable microanalysis could not be obtained due to hydrolysis of the product to give complex **12**. ^{1}H NMR (CD_2Cl_2): δ 1.15−2.50 [br m, 10H, Cy(H), 4-*Me*-C_6H_4−CH=CH_2]; 2.66 [br m, 1H, Cy(H)]; 3.06 [br t, 1H, NCH]; 3.47 [br m, 1H, NCH]; 3.48 [d, 1H, =CH_2]; 3.83 [d, 1H, ^2J(PtH) = 54 Hz, =CH_2]; 6.64 [m, 1H, =C*H*-C_6H_4-4-Me]; 6.78 [d, 1H, ^3J(PtH) = 37 Hz]; 6.97 [d, 2H]; 7.08−7.48 [m, 5H]; 7.56 [m, 1H]; 7.68 [m, 2H]; 7.79 [m, 1H]; 8.10 [d, 2H]; 8.43 [d, 1H, ^3J(PtH) = 138 Hz, CH=N]; 8.79 [s, 1H, ^3J(PtH) = 54 Hz, CH=N]. ^{13}C NMR (CD_2Cl_2): δ 21.7 [4-*Me*-C_6H_4CH=CH_2]; 24.0 [CH_2]; 24.4 [CH_2]; 29.3 [CH_2]; 30.1 [CH_2]; 59.2 [^1J(PtC) = 172 Hz, = CH_2]; 69.5 [^2J(PtC) = 30 Hz, NCH]; 74.6 [^2J(PtC) = 37 Hz, NCH]; 101.8 [^1J(PtC) = 134 Hz, = *C*H−C_6H_4-4-Me]; 126.6 [CH]; 128.2 [CH]; 129.5 [CH]; 129.6 [C]; 130.0 [CH]; 130.1 [CH]; 131.0 [CH]; 131.2 [CH]; 133.1 [CH]; 134.1 [CH]; 134.5 [C]; 139.3 [C]; 142.7 [C]; 149.5 [C]; 167.0 [CH=N]; 176.3 [^3J(PtC) = 97 Hz, CH=N].

X-ray Crystal Structure Determinations. Data were collected by using either a Siemens or an Enraf-Nonius diffractometer fitted with a CCD detector. Crystallographic details are included in Table 7. Semiempirical absorption corrections were applied using redundant data at several effective azimuthal angles with $I/\sigma > 5$ (SADABS) or by using SCALEPACK. Full-matrix least-squares refinement on F^2 was performed using the solution package SHELXTL 5.03 or 5.1 (Sheldrick, G. M., Madison, WI).

Crystals of complex **3** were grown from a concentrated CH_2Cl_2 solution layered with pentane. An orange needle was mounted inside a capillary tube.

Crystals of **5** were grown from a saturated solution of CH_2Cl_2. A crystal was cut to appropriate size and mounted inside a glass capillary. Anisotropic thermal parameters were used for all non-hydrogen atoms except for a disordered methylene chloride molecule found in the lattice.

Crystals of **11** were grown by slow diffusion of pentane into a CD_2Cl_2 solution. A red needle was cut and mounted on a glass fiber. The cation was well behaved and was refined fully anisotropically. The anion was disordered and was modeled with isotropic phenyl carbons and an anisotropic boron atom. The eight C−CF_3 distances were constrained to be identical and the distance refined to a value of 1.547 Å. The C−F distance was fixed at 1.30 Å. The ordered CF_3 groups were refined anisotropically, but, if disordered, the CF_3 disorder was modeled as two isotropic units. There were two solvent molecules in the asymmetric unit. One pentane (C61−C65) was modeled as an isotropic, half-occupancy solvent. The other pentane (C71−C75) was located on a symmetry element. It was modeled as five isotropic carbon atoms at half-occupancy. Where applicable, the hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms.

Crystals of **12** were grown by slow diffusion of pentane into a THF solution. An orange needle was mounted on a glass fiber. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were either riding or, in the case of methyl groups, riding as rigid groups on their respective carbon atoms. The THF of solvation refined in a satisfactory way.

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Supporting Information Available: Tables of X-ray data for complexes **3**, **5**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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