ORGANOMETALLICS

Volume 17, Number 20, September 28, 1998

Communications

Stereoselective α-Olefin Coordination to Chiral Organoplatinum(II) Complexes

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Received July 6, 1998

Summary: Very high (>95%) stereoselectivity of α-olefin coordination is observed in a new class of chiral platinum(II) complexes of the general formula [Pt(η²-CH₂=CHR){cis-1-(N=CHC₆H₄)-2-(N=CHPh)C₆H₁₀}]BF₄ and [Pt(η²-CH₂=CHR){trans-1-(N=CHC₆H₄)-2-(N=CHPh)-C₆H₁₀}]BF₄ (R = H, Me, Ph, 4-Me-C₆H₄) and is attributed to the steric bulk and asymmetry of the supporting diimine ligands. The first structurally characterized chiral model complex for stereoselective copolymerization of a prochiral olefin by a late-transition-metal complex is described.

The activity of palladium(II) and nickel(II) complex catalysts for polymerization of ethylene and α-olefins is critically dependent on the steric properties of the supporting diimine ligands. In particular, bulky substituents are needed to block associative olefin substitution leading to chain transfer, while asymmetry in the diimine ligands can induce high tacticity in polymers or copolymers of α-olefins based on stereoselectivity of olefin coordination.[1,2] The active initiator in the polymerization is thought to be a cationic complex, [M(N−N)Me(olefin)]$^+$, (NN = diimine), with the methyl and olefin ligands mutually cis, and several complexes of this type have been characterized recently.[3,4] This article reports the model platinum(II) complexes [Pt(η²-CH₂=CHR){*cis*/*trans*-1-(N=CHC₆H₄)-2-(N=CHPh)C₆H₁₀}]-BF₄, which contain diimine ligands based on *cis*- and *trans*-1,2-diaminocyclohexane, in which chirality induced by the diimine chelates leads to very high stereoselectivity of α-olefin coordination, low rates of alkene exchange, and the first structurally characterized *chiral* complex of the type thought to be important in stereoselective copolymerization of prochiral olefins.[4−6]

The new olefin complexes were prepared by reaction of the racemic complexes **1** and **2** (derived from *cis*- and *trans*-diaminocyclohexane, respectively; Chart 1),[7] with H[BF₄] in the presence of the alkene at low temperature

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(1) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (c) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005. (d) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641. (e) Jiang, Z.; Adams, S. E.; Sen, A. *Macromolecules* **1994**, *27*, 2694. (f) Bartolini, S.; Carfagna, C.; Musco, A. *Macromol. Rapid Commun.* **1995**, *16*, 9. (g) Bruckner, S.; De Rosa, C.; Corradini, P.; Porzio, W.; Musco, A. *Macromolecules* **1996**, *29*, 1535.

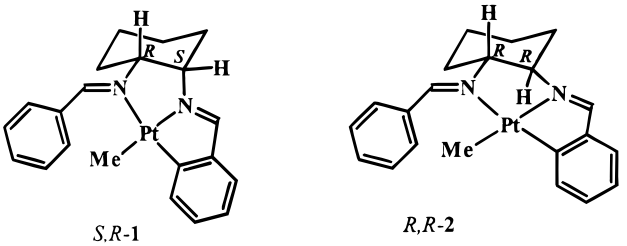
(2) (a) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177. (b) Deng, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 1094. (c) Musaev, D. G.; Froese, R. D. J.; Svensson, M.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 367.

(3) (a) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137. (b) Desjardins, S. Y.; Way, A. A.; Murray, M. C.; Adirim, D.; Baird, M. C. *Organometallics* **1998**, *17*, 2382.

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

S0276-7333(98)00566-4 CCC: $15.00
Publication on Web 09/04/1998

Chart 1

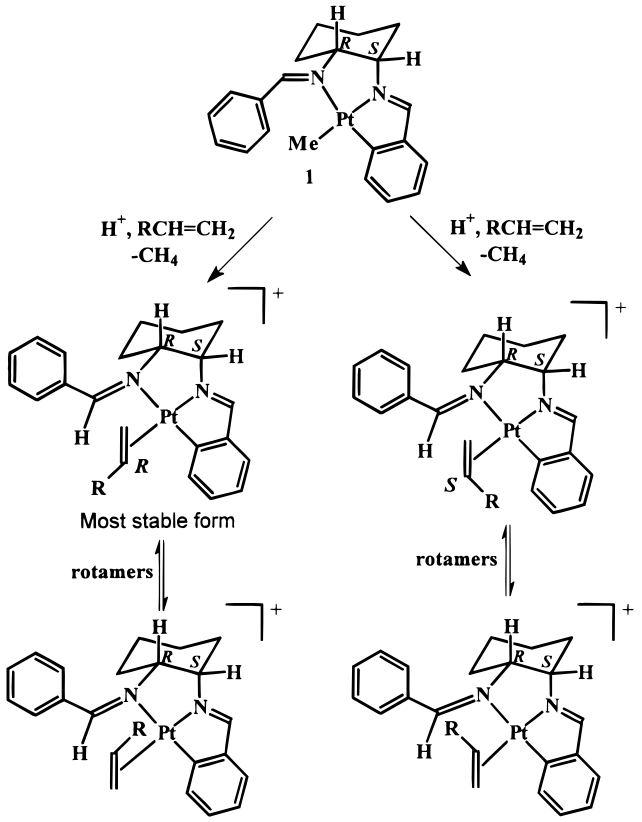


S,R-**1**
[PtMe(*S,R-cis*-L)]

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

(−78 °C). Methane is eliminated to generate a vacant site for olefin coordination, giving the corresponding complexes [Pt(η^2-CH_2═CHR)(*cis*-/*trans*-L)][BF_4], (L = 1-(N═CHC_6H_4)-2-(N═CHPh)C_6H_{10}) from **1** and **2**, respectively, as illustrated in Scheme 1. Complexes isolated include the complexes from *cis*-L with R = H (**3**), Me (**4**), Ph (**5**), 4-MeC_6H_4 (**6**) and from *trans*-L with R = Ph (**7**), R = 4-MeC_6H_4 (**8**).[8] The alkene complexes are decomposed in the presence of H[BF_4] at room temperature in solution, primarily by hydrolysis of the free imine group,[9] but are more stable when pure and acid-free.

Scheme 1[a]



[a] Products: **3**, R = H; **4**, R = Me; **5**, R = Ph; **6**, R = 4-MeC_6H_4.

The presence of the chiral ligand L can lead to formation of isomers having different NMR spectra when a prochiral olefin is coordinated, as in complexes **4**−**8**, but the ^{1}H and ^{13}C NMR spectra each contained only a single set of resonances,[8] thus showing that the stereoselectivity of the α-olefin coordination is essentially perfect in all cases. The alkene resonances in the ^{1}H and ^{13}C NMR spectra of complexes **3**−**8** all show well-resolved satellites due to coupling to ^{195}Pt, thus demonstrating that fast olefin exchange does not occur.[4−6] In addition, low-temperature NMR spectra for **3**−**5** were unchanged from room-temperature spectra,[8] suggesting that the complexes with prochiral alkenes are present in a single rotameric form.[4d]

The structures of complexes **3** and **5**, each derived from *cis*-L, were determined crystallographically and are shown in Figures 1 and 2.[10] In both structures the platinum atoms are square planar with the alkene cis to the aryl group and the Pt−N(2) bond distances trans to the aryl group are significantly longer than the Pt−N(1) distances trans to the olefin. The structures clearly reveal the basis of the high stereoselectivity observed. In both structures, the stereochemistry about the free imine group (N(2)C(7) in **3**, N(2)C(22) in **5**) is cis, whereas it was trans in the starting material **1**;[7b] this

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

(6) For stereoselectivity of α-olefin coordination in five-coordinate platinum(II) and palladium(II) complexes: (a) Albano, V. G.; Braga, D.; De Felice, V.; Panunzi, A.; Vitagliano, A. *Organometallics* **1987**, *6*, 517. (b) Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1989**, *8*, 1180.

(7) (a) Baar, C. R.; Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 32. (b) 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 Scheme 1 has a corresponding enantiomer.

(8) To a solution of **1** or **2** and excess alkene in CH_2Cl_2 at −78 °C was added HBF_4 in a 1:1 molar ratio. After the mixture was stirred 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 products as orange solids. Selected NMR data are as follows. **3**: δ(^{1}H) 4.03 [m, 2H, J(PtH) = 61 Hz, C_2H_4], 4.29 [m, 2H, J(PtH) = 61 Hz, C_2H_4], 8.49 [d, 1H, J(PtH) = 142 Hz, CH═N], 9.34 [s, 1H, J(PtH) = 44 Hz, CH═N]; δ(^{13}C) 78.0 [J(PtC) = 153 Hz, C_2H_4], 173.7 [CH═N], 178.4 [J(PtC) = 102 Hz, CH═N]. Anal. Calcd for $C_{22}H_{25}BF_4N_2Pt\cdot0.5CH_2Cl_2$: C, 42.1; H, 4.1; N, 4.4. Found: C, 42.0; H, 4.1; N, 4.8. **4**: δ(^{1}H) 3.12 [d, 1H, J(PtH) = 52 Hz, ═CH_2], 3.96 [d, 1H, J(PtH) = 61 Hz, ═CH_2], 5.75 [m, 1H, J(PtH) = 87 Hz, ═CH], 8.48 [d, 1H, J(PtH) = 139 Hz, CH═N], 9.38 [s, 1H, J(PtH) = 48 Hz, CH═N]; δ(^{13}C) 70.8 [J(PtC) = 155 Hz, ═CH_2], 103.8 [J(PtC) = 150 Hz, ═CH], 172.9 [CH═N], 177.8 [J(PtC) = 100 Hz, CH═N]. Anal. Calcd for $C_{23}H_{27}BF_4N_2Pt\cdot0.5CH_2Cl_2$: C, 43.0; H, 4.3; N, 4.3. Found: C, 43.0; H, 4.3; N, 4.1. **5**: δ(^{1}H) 3.76 [d, 1H, J(PtH) = 51 Hz, ═CH_2], 3.92 [d, 1H, J(PtH) = 41 Hz, ═CH_2], 6.63 [m, 1H, J(PtH) = 79 Hz, ═CH], 8.42 [d, 1H, J(PtH) = 143 Hz, CH═N], 9.10 [s, 1H, J(PtH) = 49 Hz, CH═N]; δ(^{13}C) 59.8 [J(PtC) = 166 Hz, ═CH_2], 102.0 [J(PtC) = 132 Hz, ═CH], 171.6 [CH═N], 177.6 [J(PtC) = 101 Hz, CH═N]. Anal. Calcd for $C_{28}H_{29}BF_4N_2Pt$: C, 49.8; H, 4.1; N, 4.3. Found: C, 49.9; H, 4.3; N, 3.7. **6**: δ(^{1}H) 3.72 [d, 1H, J(PtH) = 51 Hz, ═CH_2], 3.88 [d, 1H, J(PtH) = 42 Hz, ═CH_2], 6.63 [m, 1H, J(PtH) = 78 Hz, ═CH], 8.42 [d, 1H, J(PtH) = 138 Hz, CH═N], 9.10 [s, 1H, J(PtH) = 51 Hz, CH═N]; δ(^{13}C) 59.0 [J(PtC) = 169 Hz, ═CH_2], 103.0 [J(PtC) = 128 Hz, ═CH], 171.6 [CH═N], 177.5 [J(PtC) = 101 Hz, CH═N]. **7**: δ(^{1}H) 3.54 [d, 1H, J(PtH) = 50 Hz, ═CH_2], 3.87 [d, 1H, J(PtH) = 52 Hz, ═CH_2], 6.72 [m, 1H, J(PtH) = 80 Hz, ═CH], 8.44 [d, 1H, J(PtH) = 146 Hz, CH═N], 8.78 [s, 1H, J(PtH) = 53 Hz, CH═N]; δ(^{13}C) 60.2 [J(PtC) = 170 Hz, ═CH_2], 100.8 [J(PtC) = 138 Hz, ═CH], 167.0 [CH═N], 176.4 [J(PtC) = 99 Hz, CH═N]. Anal. Calcd for $C_{28}H_{29}BF_4N_2Pt\cdot CH_2Cl_2$: C, 45.8; H, 4.1; N, 3.7. Found: C, 45.8; H, 4.3; N, 4.1. **8**: δ(^{1}H) 3.48 [d, 1H, ═CH_2], 3.83 [d, 1H, J(PtH) = 54 Hz, ═CH_2], 6.64 [m, 1H, ═CH], 8.43 [d, 1H, J(PtH) = 138 Hz, CH═N], 8.79 [s, 1H, J(PtH) = 54 Hz, CH═N]; δ(^{13}C) 59.2 [J(PtC) = 172 Hz, ═CH_2], 101.8 [J(PtC) = 134 Hz, ═CH], 167.0 [CH═N], 176.3 [J(PtC) = 97 Hz, CH═N].

(9) For example, hydrolysis of **1** gave [Pt(η^2-CH_2═CH_2){*cis*-1-(N═CHC_6H_4)-2-(NH_2)C_6H_{10}}]BF_4.

(10) Attempts to grow suitable single crystals of complexes derived from *trans*-L have so far been unsuccessful.

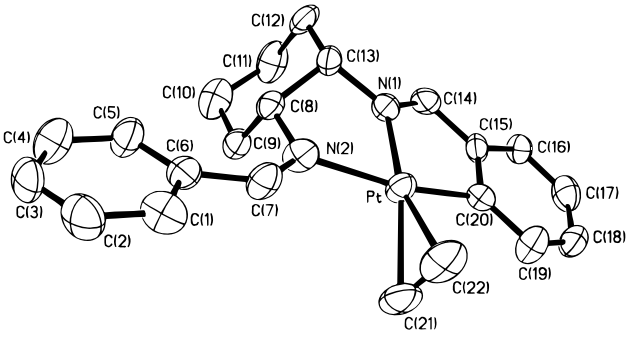


Figure 1. View of the structure of [Pt(η^2-CH_2═CH_2){(*S*,*R*)-*cis*-1-(N═CHC_6H_4)-2-(N═CHC_6H_5)C_6H_{10}}]BF_4 (**3**). Selected bond lengths in Å: Pt−C(21), 2.17(1); Pt−C(22), 2.169(9); Pt−N(1), 1.991(7); Pt−N(2), 2.129(8), Pt−C(20), 2.000(9), C(1)−C(2), 1.38(2).

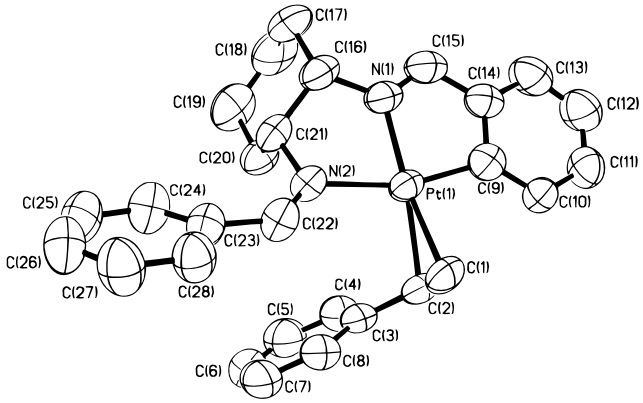


Figure 2. View of the structure of [Pt((*R*)-η^2-CH_2═CHC_6H_5){(*S*,*R*)-*cis*-1-(N═CHC_6H_4)-2-(N═CHC_6H_5)C_6H_{10}}]BF_4 (**5**). Selected bond lengths in Å: Pt−C(1), 2.160(5); Pt−C(2), 2.218(5); Pt−N(1), 2.004(4); Pt−N(2), 2.129(4), Pt−C(9), 2.008(6), C(1)−C(2), 1.380(9).

change in stereochemistry is presumably acid-catalyzed. The greatest steric effects in **3** and **5** are clearly between the coordinated alkene and the PhCH═N group, and the cis stereochemistry, in which the phenyl group is directed away from the alkene, appears to be necessary to allow alkene coordination. As depicted in Figures 1 and 2, the bulk of the cyclohexyl group lies below the square plane of platinum(II) and steric hindrance between the cyclohexyl and PhCH═ groups is minimized by displacement of the PhCH═ group to a position above the plane. As a result, the positions of greatest and least steric hindrance are for the alkene substituents syn to the PhCH═ group but above and below the plane, respectively. In **5** the phenyl group of the styrene ligand does indeed adopt the position syn to the free imine group and below the plane. The structure of **5** thus makes very clear the basis of the high stereoselectivity of olefin coordination in these complexes.

In summary, these are the first examples of chiral square-planar platinum(II) complexes [PtR(alkene)(diimine)]$^+$ with diimine ligands that have the properties of sterically precluding easy olefin exchange as well as effecting highly stereoselective α-olefin coordination.[4−6] The structure of [Pt(η^2-CH_2═CHC_6H_5){*cis*-1-(N═CHC_6H_4)-2-(N═CHC_6H_5)C_6H_{10}}]BF_4 (**5**), is important in elucidating the basis of the stereoselectivity, and so it is a good model complex in the design of new, asymmetric d^8-metal polymerization catalysts.[1−3]

Acknowledgment. We thank the NSERC (Canada) for financial support and for the award of a Postgraduate Scholarship to C.R.B.

Supporting Information Available: Tables of X-ray data for complexes **3** and **5**, text giving details of synthesis and complete spectral data for new complexes, and figures giving examples of NMR spectra (22 pages). Ordering information is given on any current masthead page.

OM980566K