Zirconium−Benzyl Complexes of a Tridentate C_2-Symmetric Dialkoxo Ligand. Diastereoselectivity of Olefin Single-Insertion Reactions

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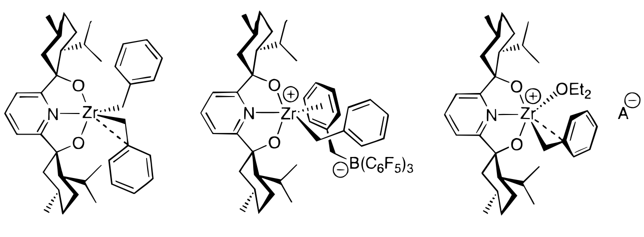
Summary: Complexes such as Zr(BMP)(CH$_2$Ph)[(η^6-PhCH$_2$)B(C$_6$F$_5$)$_3$] (BMP^{2-} = 2,6-bis[(1S,2S,5R)-(−)-menthoxo]pyridyl) were synthesized and shown to undergo single insertion of ethylene into their Zr−carbon bonds to yield, for example, Zr(BMP)(CH$_2$CH$_2$CH$_2$Ph)][(η^6-PhCH$_2$)B(C$_6$F$_5$)$_3$], whereas α-olefins and cyclooctadiene afford diastereomeric mixtures of the general formula [Zr(BMP)(η^1:η^6-CHRCHR′CH$_2$Ph)]$^+$[B(CH$_2$Ph)(C$_6$F$_5$)$_3$]$^-$.

Numerous examples of non-cyclopentadienyl zirconium catalysts for the polymerization of olefins have now been reported,[1] among which complexes of chelating diamido or dialkoxo ligands have attracted particular interest, owing to their analogy with the highly efficient *ansa*-metallocene catalysts. However, only a few attempts to design chiral C_2-symmetric complexes of this type have been described,[2] despite the fact that the corresponding *ansa*-zirconocenes, which polymerize propene and other α-olefins stereospecifically to give isotactic polymers,[3] have led to a series of commercial applications.[4] In this paper, we report our studies on the production and reactivity of new zirconium complexes that contain a tridentate, C_2-symmetric, stereochemically rigid dialkoxo ligand:[5] 2,6-bis[(1*S*,2*S*,5*R*)-(−)-menthoxo]pyridyl (BMP^{2-}; Chart 1). Notably, zwitterionic and cationic benzyl complexes of this ligand are shown to insert one molecule of α-olefins into their zirconium−carbon bond, leading to spectroscopically distinguishable diastereoisomeric complexes whose relative proportions give direct information on the stereoselectivity of this fundamental step.

Chart 1



1 2 3a,b

Protonolysis of Zr(CH$_2$Ph)$_4$ [6] with 1 equiv of the diol (BMP)H$_2$ [5] gives yellow crystals of the dibenzyl complex Zr(BMP)(CH$_2$Ph)$_2$ (**1**; Chart 1) in good yield.[7] X-ray structure analysis of **1**[7,8] shows (Figure 1) that in the solid state the complex adopts a distorted-trigonal-bipyramidal geometry. The coordination mode of the BMP^{2-} ligand is, as expected, meridional, the two oxygen atoms occupying the axial sites; the O−Zr−O angle, however, is significantly inferior to 180°. As desired, this confers approximate C_2 symmetry to the Zr(BMP) framework, the discrepancies observed arising essentially from the differences between the two benzyl ligands: these adopt an "*endo, exo*" configuration,[9] and one of them is clearly coordinating in an η^2 fashion.[10] Such a structure is probably maintained in solution.[11]

Addition of 1 equiv of B(C$_6$F$_5$)$_3$ [12] to a bright yellow solution of **1** in C$_6$D$_6$ or C$_6$D$_5$Br at 25 °C leads to immediate fading of the solution and quantitative (by NMR) formation of the zwitterionic adduct Zr(BMP)(CH$_2$Ph)[(η^6-PhCH$_2$)B(C$_6$F$_5$)$_3$] (**2**; Chart 1). This new complex, in which the benzylborate anion coordinates to the cationic metal center via its phenyl ring, shows characteristic ^{1}H, ^{13}C, and ^{19}F NMR features.[13−16] If **2**

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† Deceased, April 23, 2000.

[1] Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

[2] (a) Van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008. (b) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem.* **1996**, *506*, 343. (c) Woodman, P.; Hitchcock, P. B.; Scott, P. *J. Chem. Soc., Chem. Commun.* **1996**, 2735. (d) Fokken, S.; Spaniol, T. P.; Okuda, J.; Sernetz, F. G.; Mülhaupt, R. *Organometallics* **1997**, *16*, 4240. (e) Jeon, Y.-M.; Park, S. J.; Heo, J.; Kim, K. *Organometallics* **1998**, *17*, 3161.

[3] Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *35*, 1143.

[4] Morse, P. M. *Chem. Eng. News* **1998**, *76(27)*, 11; **1998**, *76(49)*, 25.

[5] Bellemin-Lapponaz, S.; Coleman, K. S.; Dierkes, P.; Masson, J.-P.; Osborn, J. A. *Eur. J. Inorg. Chem.*, in press.

[6] Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

[7] Experimental details are contained in the Supporting Information.

[8] Crystallographic data for **1** at 173 K: triclinic, space group *P*1, $a = 10.3692(3)$ Å, $b = 10.3812(3)$ Å, $c = 17.6043(3)$ Å, $\alpha = 84.299(9)°$, $\beta = 87.855(9)°$, $\gamma = 68.667(9)°$, $V = 1756.4(1)$ Å^3, $Z = 2$, $d_{calcd} = 1.25$ g cm^{-3}, $R = 0.026$, $R_w = 0.035$, GOF = 1.034.

[9] Guerin, F.; McConville, D. H.; Vittal, J. J.; Yap, A. P. *Organometallics* **1998**, *17*, 5172.

[10] (a) Latesky, S. L.; McMullen, A. K.; Nicollai, G. P.; Rothwell, I. P. *Organometallics* **1985**, *4*, 902. (b) Jordan, R. F.; Lapointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (c) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Abdul Malik, K. M. *Organometallics* **1994**, *13*, 2235.

[11] The ^{1}H and ^{13}C NMR spectra of **1** at room temperature in C$_6$D$_6$[7] are in fact consistent with an averaged C_2-symmetric structure with equivalent benzyl groups. However, the geminal coupling constant of the latter ($^2J_{HH} = 9.3$ Hz) and their C$_{ipso}$ chemical shift (δ 144.78) are intermediate between the values expected for η^1- and η^2-benzyl ligands,[10] suggesting that the molecular structure found in the solid state is maintained in solution and that rapid exchange of the two benzyl ligands occurs.

[12] Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

10.1021/om000299u CCC: $19.00

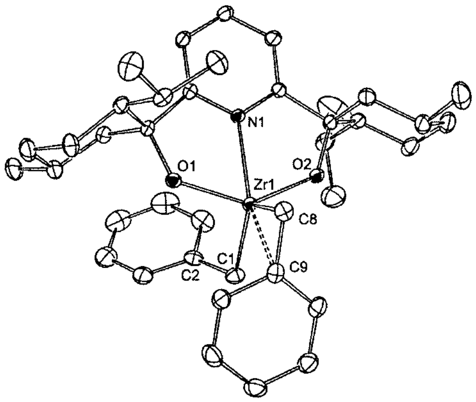


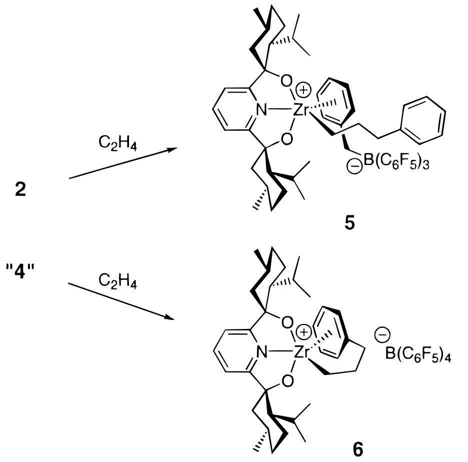
Figure 1. Molecular structure of **1**. Selected interatomic distances (Å) and angles (deg): Zr(1)−O(1) = 1.989(2), Zr(1)−O(2) = 2.001(3), Zr(1)−N(1) = 2.272(2), Zr(1)−C(1) = 2.300(4), Zr(1)−C(8) = 2.298(4), Zr(1)−C(2) = 3.054(4), Zr(1)−C(9) = 2.599(3); O(1)−Zr(1)−O(2) = 140.89(9), Zr(1)−C(8)−C(9) = 84.5(1), Zr(1)−C(1)−C(2) = 105.9(1).

is then treated in C_6D_5Br with 1 equiv of Et_2O, the free anion[17] is instantaneously liberated and the compound $[Zr(BMP)(\eta^2\text{-}CH_2Ph)(OEt_2)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**3a**; Chart 1) builds up as separated ion pairs in quantitative yield (by NMR). The cationic complex is now stabilized by diethyl ether ligation.[10b,16,18] Its other ^1H and ^{13}C NMR characteristics[16,18] are not very different from those of the $Zr(BMP)(CH_2Ph)^+$ fragment in **2**, except those showing[10,14] η^2-coordination of the benzyl ligand ($^2J_{HH}$ = 8.5 Hz, $^1J_{CH}$ = 141 Hz, $\delta(C_{ipso})$ 137.98 ppm), whose existence suggests that the metal center is electronically more unsaturated in **3a** than in **2**.

If one of the benzyl ligands of **1** is abstracted with 1 equiv of $[CPh_3]^+[B(C_6F_5)_4]^-$ [19] instead of $B(C_6F_5)_3$, the expected "naked" cationic complex $[Zr(BMP)(\eta^n\text{-}CH_2Ph)]^+[B(C_6F_5)_4]^-$ (**4**) is not clearly distinguished in the NMR spectra of the reaction mixture; however, further addition of 1 equiv of diethyl ether cleanly affords the ^1H NMR spectrum of $[Zr(BMP)(\eta^2\text{-}CH_2Ph)(OEt_2)]^+$, the cationic species already present in **3a**, indicating that the complex $[Zr(BMP)(\eta^2\text{-}CH_2Ph)(OEt_2)]^+[B(C_6F_5)_4]^-$ (**3b**) has been obtained as the sole product. Also, reaction with ethylene leads to a single well-defined product (vide infra). This strongly suggests that the initial reaction product is a mixture of components that all contain the "naked" cationic fragment $Zr(BMP)(\eta^n\text{-}CH_2Ph)^+$ in masked forms, possibly within differently aggregated entities,[20] with $[B(C_6F_5)_4]^-$ as counteranion. It will therefore be designated by "**4**".

Neither **1**, in the presence of MAO, nor **2** or "**4**" is an active catalyst for the polymerization of ethylene at room temperature and low pressure (1−6 bar). Bromobenzene solutions of **2** and "**4**" turn readily colorless when placed under an atmosphere of ethylene, but no polyethylene formation ensues. In situ NMR studies[16] show that **2** is cleanly converted into the zwitterionic complex $[Zr(BMP)(CH_2CH_2CH_2Ph)][(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$ (**5**),[21] whereas "**4**" affords the ionic complex $[Zr(BMP)(\eta^1{:}\eta^6\text{-}CH_2CH_2CH_2Ph)]^+[B(C_6F_5)_4]^-$ (**6**)[22] as a single detectable high-yield product (Scheme 1). Both **5** and **6** result from the stoichiometric insertion of a molecule of ethylene into the zirconium−carbon bond of the two precursors. This leads to a zirconium−trimethylene sequence whose six hydrogens are pairwise diastereotopic in both complexes. The other NMR data of **5** are similar to those of structurally analogous **2**, η^6-coordination of the benzylborate anion being in particular well established. In **6**, which differs in the poorer coordination ability of the anion, it is the phenyl group of the γ-substituted *n*-propyl ligand which stabilizes the cationic center by π-bonding it, as revealed in particular by its nonsymmetric character and the 20 ppm downfield shift of the corresponding C_{ipso} signal (δ 161.7). This ligand hence adopts a chelating structure similar to that found in a few previous studies,[20,23] which certainly prevents further insertion of ethylene into the zirconium−carbon bond of **6**. The inactivity of **5**, on the other hand, may be explained by stronger anion coordination in **5** than in **2**, resulting probably from less steric pressure in **5**.

Scheme 1



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(13) (a) Pellechia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1993**, *115*, 1160. (b) Wright, J. M.; Landis, C. R.; Ros, M. A. M. P.; Horton, A. D. *Organometallics* **1998**, *17*, 5031 and references therein.

(14) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

(15) Selected NMR data for **2** (C_6D_6, 25 °C): ^1H NMR δ 3.48 (broad, 1H, $BC\mathit{H}H'Ph$), 3.40 (broad, 1H, $BCH\mathit{H}'Ph$), 2.60 (d, $^2J_{HH}$ = 11.2 Hz, 1H, $ZrC\mathit{H}H'Ph$), 1.50 (d, $^2J_{HH}$ = 11.2 Hz, 1H, $ZrCH\mathit{H}'Ph$); ^{13}C NMR δ 174.10 and 173.39 (C_o and $C_{o'}$ py), 157.80 (C_{ipso} $BCH_2\mathit{Ph}$), 148.51 (C_{ipso} $ZrCH_2\mathit{Ph}$), 65.87 ($Zr\mathit{C}H_2Ph$); ^{19}F NMR δ −130.91 (d, 6F, F_o), −161.62 (t, 3F, F_p), −165.63 (t, 6F, F_m).

(16) Full NMR data and assignments can be found in the Supporting Information.

(17) Pellechia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473.

(18) Selected NMR data for **3a** (C_6D_5Br, 25 °C): ^1H NMR δ 3.46 (broad, 2H, CH_2 Et_2O), 3.33 (broad, 4H, CH_2 Et_2O + $BC\mathit{H}_2Ph$), 2.72 (d, $^2J_{HH}$ = 8.5 Hz, 1H, $ZrC\mathit{H}H'Ph$), 2.68 (d, $^2J_{HH}$ = 8.5 Hz, 1H, $ZrCH\mathit{H}'Ph$); ^{13}C NMR δ 173.55 and 173.35 (C_o and $C_{o'}$ py), 148.68 (C_{ipso} $BCH_2\mathit{Ph}$), 137.98 (C_{ipso} $ZrCH_2\mathit{Ph}$), 70.06 (broad, $\mathit{C}H_2$ Et_2O), 63.60 ($^1J_{CH}$ = 141 Hz (t), $Zr\mathit{C}H_2Ph$).

(19) (a) Ewen, J. A.; Elder, M. J. (Fina) Eur. Pat. Appl. 426637, 1991. (b) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.

(20) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424.

(21) Selected NMR data for **5** (C_6D_5Br, 25 °C): ^1H NMR δ 2.36 (m, 1H, $C_\gamma \mathit{H}H'Ph$), 2.23 (m, 1H, $C_\gamma H\mathit{H}'Ph$), 1.82 (m, 1H, $C_\beta \mathit{H}H'$), 1.74 (m, 1H, $C_\beta H\mathit{H}'$), 1.23 (m, 1H, $ZrC_\alpha \mathit{H}H'$), 0.23 (m, 1H, $ZrC_\alpha H\mathit{H}'$); ^{13}C NMR δ 173.72 and 173.33 (C_o and $C_{o'}$ py), 156.54 (C_{ipso} $BCH_2\mathit{Ph}$), 141.63 (C_{ipso} $Zr(CH_2)_3\mathit{Ph}$), 63.77 ($Zr\mathit{C}_\alpha H_2$), 41.40 ($\mathit{C}_\gamma H_2$), 34.39 ($\mathit{C}_\beta H_2$).

(22) Selected NMR data for **6** (C_6D_5Br, 25 °C): ^1H NMR δ 2.59−2.33 (m, 4H, $C_\beta \mathit{H}_2 C_\gamma \mathit{H}_2 Ph$); ^{13}C NMR δ 174.2 and 173.3 (C_o and $C_{o'}$ py), 161.7 (C_{ipso} $Zr(CH_2)_3\mathit{Ph}$), 60.5 ($Zr\mathit{C}_\alpha H_2$), 42.1 ($C_\gamma H_2$), 36.1 ($C_\beta H_2$).

(23) (a) Pellechia, C.; Grassi, A.; Zambelli, A. *J. Chem. Soc., Chem. Commun.* **1993**, 947. (b) Pellechia, C.; Grassi, A.; Zambelli, A. *Organometallics* **1994**, *13*, 298. (c) Pellechia, C.; Immirzi, A.; Zambelli, A. *J. Organomet. Chem.* **1994**, *479*, C9. (d) Thorn, M. G.; Etheridge, Z. C.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1998**, *17*, 3636.

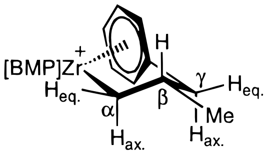
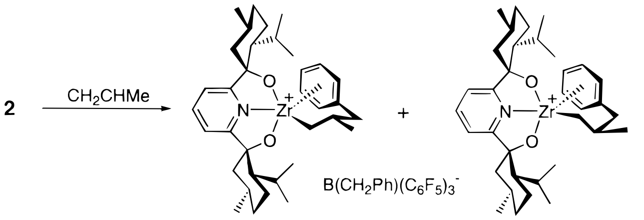


Figure 2. Configuration of the chelating alkyl ligand of **7a**/**7b**.

This latter assumption is consistent with the fact that, if zwitterionic **2** reacts similarly with propene to yield a colorless single-insertion complex, the benzylborate anion in this compound is no more interacting with Zr as in **5**. In this case, the regiospecific 1,2-insertion of propene affords the complex $[Zr(BMP)(\eta^1{:}\eta^6\text{-}CH_2CHMeCH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**7a**/**7b**), which exhibits an ionic[24] chelated[25] structure analogous to that of **6** and exists as a mixture of two diastereoisomers differing in the relative configuration of the chiral Zr(BMP) framework and β-carbon of the alkyl ligand (Scheme 2), giving rise to distinct NMR spectra.[26] The molecular structure of each diastereoisomer was unambiguously deduced from ^1H, ^{13}C, and ^{19}F NMR studies, including $^1H-^1H$ COSY and $^1H-^{13}C$ correlation experiments.[16] It is similar to that of analogous achiral complexes described in the literature.[20,23] In particular, full assignment of the six ^1H NMR resonances of the $Zr-CH_2CHMeCH_2-$ units[26] allows us to conclude that, for both isomers, the β-Me substituent lies in the equatorial position of the chelate rings, and the four bonds linking the α- and γ-equatorial hydrogens adopt a stereorigid W conformation[27] (Figure 2), as shown by the observation on the COSY spectrum of a characteristic long-range $^4J_{HH}$ coupling between these two protons in each compound. By integration of several distinct pairs of signals, we find the diastereoisomeric ratio **7a**/**7b** = 45/55,[28] which shows that the diastereoselectivity of the reaction of **2** with propene is real but low (de = 9%).

Scheme 2



7a/7b

With the hope that higher α-olefins would undergo enhanced steric interactions with the BMP^{2-} ligand and hence insert more stereoselectively, we also reacted **2** with 1-hexene and 4,4-dimethyl-1-pentene. Addition to **2** of a few equivalents of $CH_2{=}CHR$ (R = *n*-Bu, CH_2-*t*-Bu) at room temperature in C_6D_5Br leads readily to the corresponding 1,2-insertion complexes $[Zr(BMP)(\eta^1{:}\eta^6\text{-}CH_2CHRCH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ as a mixture of diastereoisomers (R = *n*-Bu, **8a**/**8b**; R = CH_2-*t*-Bu, **9a**/**9b**).[16] Surprisingly, however, the diastereoselectivity of 1-hexene insertion is extremely low (**8a**/**8b** = 50/50), and that of 4,4-dimethyl-1-pentene is opposite to that found for propene (**9a**/**9b** = 60/40, de = 20%). This strongly suggests that a second stereodirecting effect opposite to that of chiral BMP^{2-} contributes to determine the stereochemistry of complexes **7**−**9**. This second effect could result from the nonsymmetric orientation of the benzyl ligand in the anion-free, highly electron deficient benzyl−olefin intermediate adduct. Also styrene, which often inserts with the reverse regiochemistry,[29] undergoes 1,2-insertion into the Zr−carbon bond of **2** to yield $[Zr(BMP)(\eta^1{:}\eta^6\text{-}CH_2CHPhCH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**10a**/**10b**, de = 33%).[16] The electronic effects favoring 2,1-insertion[29] thus seem less pronounced in these nonmetallocene complexes and are overridden by the steric effect of the BMP^{2-} ligand.

Reaction of **2** with 1,5-cyclooctadiene is much slower but leads similarly to the single-insertion complex $[Zr(BMP)(\eta^1{:}\eta^6\text{-}CHCH_2CH_2CHCHCH_2CH_2CHCH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**11**) after 72 h at room temperature.[16] In this case, only one isomer could be detected in the ^1H and ^{13}C NMR spectra, showing that the olefin insertion is stereospecific and that stereoselection at chiral C_α, which can more safely be ascribed to steric effects of the chiral BMP^{2-} ligand, is much higher than at C_β.

It may be anticipated from these studies that aromatic-free alkyl complexes of the BMP^{2-} ligand might lead to higher insertion stereoselectivities and actual polymerization activity.

Acknowledgment. We are grateful to J.-P. Masson for supplying a sample of $[BMP]H_2$, to N. Kyritsakas and A. De Cian (Service Commun de Radiocristallographie, ULP Strasbourg) for solving the X-ray structure of **1**, and to R. Graf and J.-D. Sauer for running the 2D NMR experiments. The CNRS and the Ministère de l'Education Nationale, de la Recherche et de la Technologie are acknowledged for financial support.

Supporting Information Available: Text, figures, and tables giving general experimental procedures, experimental data for **1**, X-ray structure data for **1**, and NMR data for compounds **1**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) The free anion has been characterized by ^1H, ^{13}C, and ^{19}F NMR.[16]

(25) The ^{13}C NMR characteristics of the π-bound phenyl ring are similar to those of **6**.[16]

(26) Selected NMR data for **7a** (C_6D_5Br, 25 °C): ^1H NMR δ 2.81 (m, 1H, $C_\gamma H_{eq}$), 2.68 (m, 1H, $C_\beta H$), 2.03 (t, $^2J_{HH} = {^3J_{HH}} = 11.7$ Hz, 1H, $C_\gamma H_{ax}$), 1.25 (m, 1H, $ZrC_\alpha H_{ax}$), 0.83 (m, 3H, $C_\beta H\mathit{Me}$), 0.43 (m, 1H, $ZrC_\alpha H_{eq}$); ^{13}C NMR δ 68.23 ($C_\alpha H_2$), 50.86 ($C_\beta H$), 43.22 ($C_\gamma H_2$), 26.34 ($C_\beta H\mathit{Me}$). Selected NMR data for **7b** (C_6D_5Br, 25 °C): ^1H NMR δ 2.79 (m, 1H, $C_\gamma H_{eq}$), 2.59 (m, 1H, $C_\beta H$), 1.97 (t, $^2J_{HH} = {^3J_{HH}} = 11.7$ Hz, 1H, $C_\gamma H_{ax}$), 1.14 (m, 1H, $ZrC_\alpha H_{ax}$), 0.84 (m, 3H, $C_\beta H\mathit{Me}$), 0.53 (m, 1H, $ZrC_\alpha H_{eq}$); ^{13}C NMR δ 69.59 ($C_\alpha H_2$), 50.16 ($C_\beta H$), 43.22 ($C_\gamma H_2$), 26.21 ($C_\beta H\mathit{Me}$).

(27) Barfield, M.; Chakrabarti, B. *Chem. Rev.* **1969**, *69*, 757.

(28) This ratio is obtained instantaneously and remains unmodified after 24 h at room temperature.

(29) (a) Guram, A. S.; Jordan, R. F. *Organometallics* **1991**, *10*, 3470. (b) Rodewald, S.; Jordan, R. F. *J. Am. Chem. Soc.* **1994**, *116*, 4491.