Stereoselective Olefin Insertion Reactions of Chiral (EBI)Zr(η^2-pyrid-2-yl)$^+$ and (EBTHI)Zr(η^2-pyrid-2-yl)$^+$ Complexes

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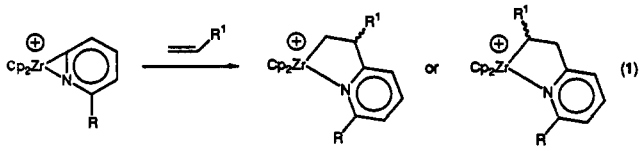
Active isoselective α-olefin polymerization catalysts are generated from Brintzinger's C_2-symmetric *ansa* zirconocene complexes (EBI)$ZrCl_2$ (**1**, EBI = ethylenebis(indenyl)) and (EBTHI)$ZrCl_2$ (**2**, EBTHI = ethylenebis(tetrahydroindenyl))[1] via activation with suitable cocatalysts.[2] The active species in these systems are believed to be chiral [$^{ch}Cp_2Zr(R)$][A] ion pairs ($^{ch}Cp_2$ = chiral *ansa* biscyclopentadienyl).[3,4] There is great current interest in exploiting the stereodirecting properties of $^{ch}Cp_2M$ frameworks in other reactions.[5] Achiral $Cp_2Zr(\eta^2$-pyrid-2-yl)$^+$ species insert olefins to yield azazirconacycles (eq 1), providing the basis for



an extensive body of stoichiometric and catalytic chemistry.[6] Here we describe highly regio- and stereoselective olefin insertion reactions of chiral $^{ch}Cp_2Zr(\eta^2$-pyrid-2-yl)$^+$ species derived from **1** and **2** which may be incorporated into a catalytic process.[6a]

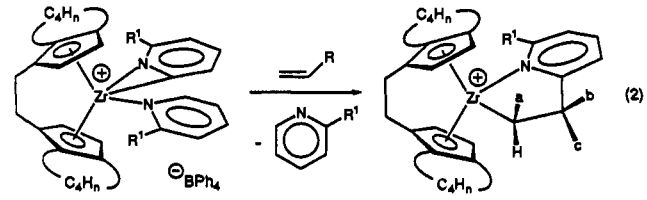
Protonolysis[7] of *rac*-(EBI)$ZrMe_2$ (**3**)[8] and *rac*-(EBTHI)$ZrMe_2$ (**4**) with [$HN(^nBu)_3$][BPh_4] in the presence of excess 2-picoline yields *rac*-(EBI)Zr(η^2-6-Me-pyrid-2-yl)(2-picoline)$^+$ (**5**, 91%) and *rac*-(EBTHI)Zr(η^2-6-Me-pyrid-2-yl)(2-picoline)$^+$ (**6**, 91%) as the BPh_4^- salts (eq 2; the *S,S* ligand configurations are illustrated).

Table 1. Products of Olefin Insertion Reactions of **5**, **6**, **15**, **18**, and **19** (See Eqs 2 and 3 for Positions of the Substituents R^1, a, b, and c)

product	ligand	anion	R^1	a	b	c	de (%)[a]
7	EBI	BPh_4^-	Me	H	H	Me	83
8	EBTHI	BPh_4^-	Me	H	H	Me	64
9	EBI	BPh_4^-	Me	H	H	Bu	83
10	EBTHI	BPh_4^-	Me	H	H	Bu	66
11	EBI	BPh_4^-	Me	Ph	H	H	>98
12[b]	EBTHI	BPh_4^-	Me	Ph	H	H	>98
13a[c]	EBI	BPh_4^-	Me	TMS	H	H	>98
13b[d]	EBI	BPh_4^-	Me	H	H	TMS	
14a[e]	EBTHI	BPh_4^-	Me	TMS	H	H	>98
14b[d]	EBTHI	BPh_4^-	Me	H	H	TMS	
16	EBI	$MeB(C_6F_5)_3^-$	Me	Me	Me	H	>98
17	EBI	$MeB(C_6F_5)_3^-$	Me	Me	H	Me	>98
20	EBI	$MeB(C_6F_5)_3^-$	Ph	H	H	Me	>98
21	EBI	$MeB(C_6F_5)_3^-$	H	H	Me	H	21

[a] NMR detection limit ca. 2%. [b] Stereochemistry assigned by analogy to **11**. [c] Ratio of **13a**/**13b** = 88/12. [d] Regiochemistry confirmed by GC/MS analysis of hydrolysis products. Stereochemistry at Cβ assigned by analogy to **7** and **8**. [e] Ratio of **14a**/**14b** = 94/6.

Complexes **5** and **6** exist as mixtures of "N-inside" and "N-outside" isomers which differ in the orientation of the η^2-pyridyl ligand.[9]



5 n = 4, (EBI) R = Me, Bu, Ph, TMS **7-14**
6 n = 8, (EBTHI)
R^1 = Me

Pyridyl complexes **5** and **6** readily insert α-olefins (23 °C, CH_2Cl_2, 1 equiv of 2-picoline is liberated) to yield azazirconacyles **7-14** (eq 2 and Table 1), which were isolated as crystalline mixtures of stereo-/regioisomers. In general, these mixtures could not be separated by recrystallization, and structural assignments were made by 1-D and 2-D NMR methods.[10] Propene and 1-hexene undergo 1,2 insertion, yielding **7–10** as mixtures of diastereomers which differ in the configuration of Cβ. Surprisingly, in the major diastereomer, the β-substituent points *toward* the C_6 ring of the EBI/EBTHI ligand.[11] This stereoselectivity is opposite that of α-olefin insertions of (EBTHI)Zr(R)$^+$ species (R > Me).[12] The de values are similar for the two olefins but are markedly

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(8) *Rac*-**3** was prepared (90%) by reaction of *rac*-**1** with Me_2Mg in Et_2O followed by workup with dioxane. Reaction of **1** with MeLi/Et_2O yielded *rac*-**3** contaminated with 50% *meso*-**3** at 23 °C and ca. 5% at −42 °C.

(9) Isomer ratios are 2.3/1 (**5**) and 3.7/1 (**6**) at −20 °C; structures were not assigned. Isomer exchange is rapid at 23 °C.

(10) Yields for eq 2: 100% NMR, 67–84% isolated. Yields for eq 3: 95–100% NMR, 90% isolated. Characterization data and stereo/regiochemical assignments are given as supplementary material.

(11) The configuration of the major diastereomer of **7–10** is *S,S,S* (or *R,R,R*), where the first two entries denote the configurations of the EBI/EBTHI bridgehead carbons and the third denotes that of the metallacycle β-carbon. The minor diastereomer configuration is *S,S,R* (or *R,R,S*).

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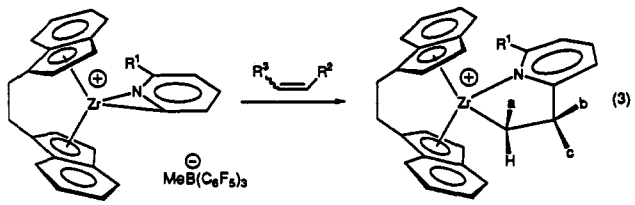
higher for the EBI system and increase at lower temperatures (**5** reacts with 1-hexene to yield **9** with 89% de at −10 °C).

To probe stereoselection at the developing Cα, several olefins which, for electronic reasons,[6d,e] undergo 2,1 insertion were examined. Styrene reacts regio- and stereospecifically with **5** and **6** to yield **11** and **12**, in which the Ph substituent points *away from* the EBI/EBTHI C_6 ring.[13] Vinyltrimethylsilane reacts similarly to yield **13a** and **14a**. In these cases, minor amounts of the regioisomeric 1,2 insertion products **13b** and **14b** are also observed.

Disubstituted olefins do not displace the 2-picoline ligand of **5** or **6** and thus are not inserted. However, the base-free species [(EBI)Zr(η^2-6-Me-pyrid-2-yl)][$CH_3B(C_6F_5)_3$] (**15**)[14] reacts stereospecifically with *cis*- and *trans*-2-butene to yield cis insertion products **16** and **17**, respectively (eq 3 and Table 1). In both



(3)

15 R^1 = CH_3; **18** R^1 = Ph; **19** R^1 = H

R^2, R^3 = H or Me

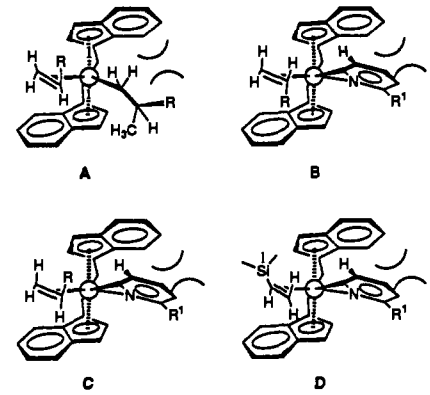
16, 17, 20, 21

cases, the α-Me group points *away from* the EBI C_6 ring.[15] The configuration of Cα of **16** is analogous to that of 2,1 insertion products **11**, **12**, **13a**, and **14a**, while that at Cβ is opposite that of the major diastereomers of **7–10**. This result and the higher stereoselectivities observed for the 2,1 insertions indicate that the stereodirecting forces have a stronger influence at the developing Cα than at the developing Cβ.

The *o*-phenyl-η^2-pyridyl species [(EBI)Zr(η^2-6-Ph-pyrid-2-yl)][$MeB(C_6F_5)_3$] (**18**) and the parent unsubstituted species [(EBI)Zr(η^2-pyrid-2-yl)][$MeB(C_6F_5)_3$] (**19**) were examined to probe the influence of the ortho substituent (R^1) on the insertion stereoselectivity (eq 3). Complex **18** reacts stereospecifically with propene to yield **20**, which is structurally analogous to the major diastereomer of **7**. In contrast, the reaction of **19** with propene yields **21** with low and reversed (vs **7**) stereoselectivity.[16]

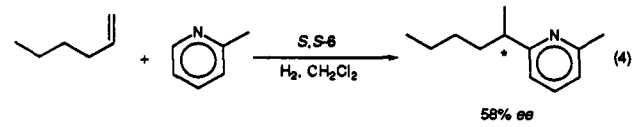
Molecular modeling studies of (EBTHI)Zr(CH_2CHMeR)(propene)$^+$ "activated complexes" (R = growing polypropylene chain) have provided insight to the origin of the stereoselectivity of α-olefin insertions of (EBTHI)Zr(R)$^+$ species.[17] In the favored adduct **A** (Chart I), which leads to product, olefin/CH_2CHMeR and olefin/EBTHI steric interactions both favor an olefin orientation in which the olefin substituent points away from the CH_2CHMeR chain and the EBTHI C_6 ring. Similar studies of (EBI)Zr(η^2-6-R^1-pyrid-2-yl)(olefin)$^+$ activated complexes **B–D** provide a working rationale for the stereoselectivities in eqs 2 and

Chart 1



3.[18] These calculations suggest that steric interactions between the pyridyl ortho substituent (R^1 = Me, Ph, or H) and an EBI C_6 ring cause the η^2-pyridyl ligand to twist out of the metallocene equatorial plane. For adducts leading to 1,2 insertion, olefin/η^2-pyridyl interactions thus favor diastereomer **B**, in which the olefin substituent points *toward* the other EBI C_6 ring, over diastereomer **C**. This preference is counteracted by steric interactions between the olefin and the EBI C_6 ring in **B**. For small α-olefins (propene, hexene) and medium or large R^1 substituents (Me, Ph), the olefin/pyridyl steric interactions are dominant, **B** is favored, and high stereoselectivity is observed. When R^1 = H, the pyridyl ligand is not significantly twisted, and olefin/pyridyl interactions are comparatively less important. In this case **B** is less favored than **C**, and stereoselectivity is reduced/reversed. In (EBI)Zr(η^2-6-R^1-pyrid-2-yl)(olefin)$^+$ adducts leading to 2,1 insertion (e.g., **D**) and in (EBI)Zr(η^2-6-R^1-pyrid-2-yl)(2-butene)$^+$ adducts, interactions between the pro-Cα olefin substituent (positioned in the narrow part of the metallocene wedge) and the EBI ligand determine the stereochemistry.

The utility of $^{ch}Cp_2Zr(\eta^2$-pyridyl)$^+$ species in asymmetric catalysis was tested with the (*S,S*)-(EBTHI)Zr system.[1c] At 50 °C in the presence of H_2, (*S,S*)-(EBTHI)Zr(η^2-6-Me-pyrid-2-yl)(2-picoline)$^+$ ((*S,S*)-**6**, generated in situ from (*S,S*)-**4** and [$HNBu_3$][BPh_4] in the presence of excess 2-picoline) catalyzes the conversion of 1-hexene and 2-picoline to (*R*)-2-Me,6-(2-hexyl)-pyridine with 58% ee (eq 4).[6a] The activity (ca. 0.1



(4)

turnover/h at 50 °C, total 6.2 turnovers, 3 mol % catalyst) is ca. 10x lower than the activity of the achiral Cp_2ZrMe_2-derived catalyst under comparable conditions. The ee is in line with the de (64%) observed for the reaction of *rac*-**4** with 1-hexene at 23 °C.

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Supplementary Material Available: Complete characterization data and detailed discussions of stereo/regio-chemical assignments for new compounds (61 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(13) The configurations of the major diastereomer of **13a** and **14a** is *S,S,S* (or *R,R,R*), where the first two entries denote the configurations of the EBI/EBTHI bridgehead carbons and the third denotes that of the metallacycle α-carbon.

(14) **15** was generated in situ from **3**, $B(C_6F_5)_3$, and 1 equiv picoline; see: Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

(15) The configuration of **16** is *S,S,R,R* (or *R,R,S,S*), where the first two entries denote the configurations of the EBI bridgehead carbons and the third and fourth entries denote the configuration of Cα and Cβ. The configuration of **17** is *S,S,R,S* (or *R,R,S,R*).

(16) Control experiments indicate that the counterion and the presence/absence of excess 2-picoline do not influence the stereoselectivity.

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(18) Calculations were performed using Rappé's Universal Force Field as implemented in the Cerius 3.2 package (Molecular Simulations): Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024. Structural constraints imposed on **A–D** are similar to those used in studies of (EBTHI)Zr(R)(olefin)$^+$ systems.[17]