Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 4768–4773
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Enantioselective methylalumination of α-olefins

Robby A. Petros, James M. Camara, Jack R. Norton *

Columbia University, Department of Chemistry, New York, NY 10027, United States

Received 1 May 2007; received in revised form 18 June 2007; accepted 18 June 2007
Available online 26 June 2007

Abstract

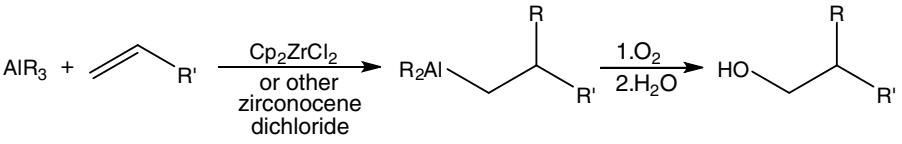
The ability of various enantiopure zirconocenes to catalyze the asymmetric methylalumination of allylbenzene has been tested. The enantioselectivity of an ethylene(Ind)$_2$ZrCl$_2$/MAO system is the same as that of authentic methyl cation generated with Ph_3C^+ from ethylene(Ind)$_2$ZrMe$_2$, confirming that the methyl cation is the active catalyst from ethylene(Ind)$_2$ZrCl$_2$/MAO.

Keywords: Ansa-metallocenes; Asymmetric carboalumination; Insertion

1. Introduction

Carboalumination, generally catalyzed by Zr complexes, leads to the synthesis of aliphatic primary alcohols from α-olefins (Eq. (1)) [1]. A stoichiometric amount of an aluminum alkyl ($AlMe_3$ or $AlEt_3$) is used, along with a catalytic amount of Cp_2ZrCl_2, $Cp^*_2ZrCl_2$, or (NMIn)$_2$ZrCl$_2$ (bis(1-neomenthylindenyl)zirconium dichloride). While early reactions were rather sluggish, one equivalent of water has been shown to dramatically accelerate the rate [2]. This effect has parallels in the well-established chemistry of olefin polymerization, where the reaction of a zirconocene dichloride with methylaluminoxane (MAO) is commonly used to generate the active catalyst. Since the synthesis of MAO involves the partial hydrolysis of $AlMe_3$, it seems likely that carboalumination is catalyzed by 14-electron alkylzirconium cations like those that catalyze olefin polymerization [3].

Carboalumination has been carried out asymmetrically[4] with a catalyst (bis(1-neomenthylindenyl)zirconium dichloride, (NMIn)$_2$ZrCl$_2$) introduced by Gerhard Erker [5]. Racemic (EBTHI)ZrMe$_2$ and [6,6′-dimethyl-2,2′-bis(5,6,7,8-tetrahydro-2- indenyl)biphenyl]ZrMe$_2$ have been tested as catalysts because the same compounds are readily available in enantiopure form; however, these reactions have proven sluggish and have given oligomerization as well as carboalumination [4c]. Asymmetric carboalumination of α-olefins has not been reported with an enantiopure metallocene other than (NMIn)ZrCl$_2$, although low ee's have been obtained with Cp_2ZrCl_2 and organoaluminums bearing enantiopure alkoxide ligands [6].



(1)

We have, therefore, examined the ability of several enantiopure zirconocenes *S*,*S*-**1a**–**d** (Fig. 1) to catalyze the asymmetric carboalumination of allylbenzene and styrene.

* Corresponding author. Tel.: +1 2128547644; fax: +1 2128547660.
E-mail address: jrn11@columbia.edu (J.R. Norton).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.06.028

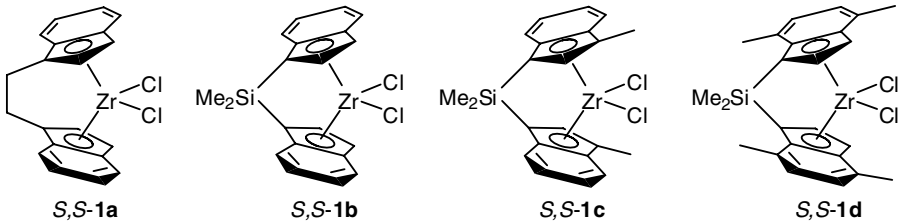
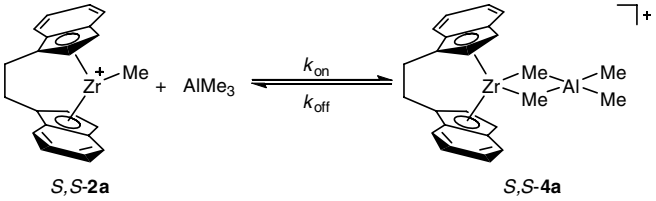


Fig. 1. Structures of *S*,*S*-**1a**–**d**.

2. Results and discussion

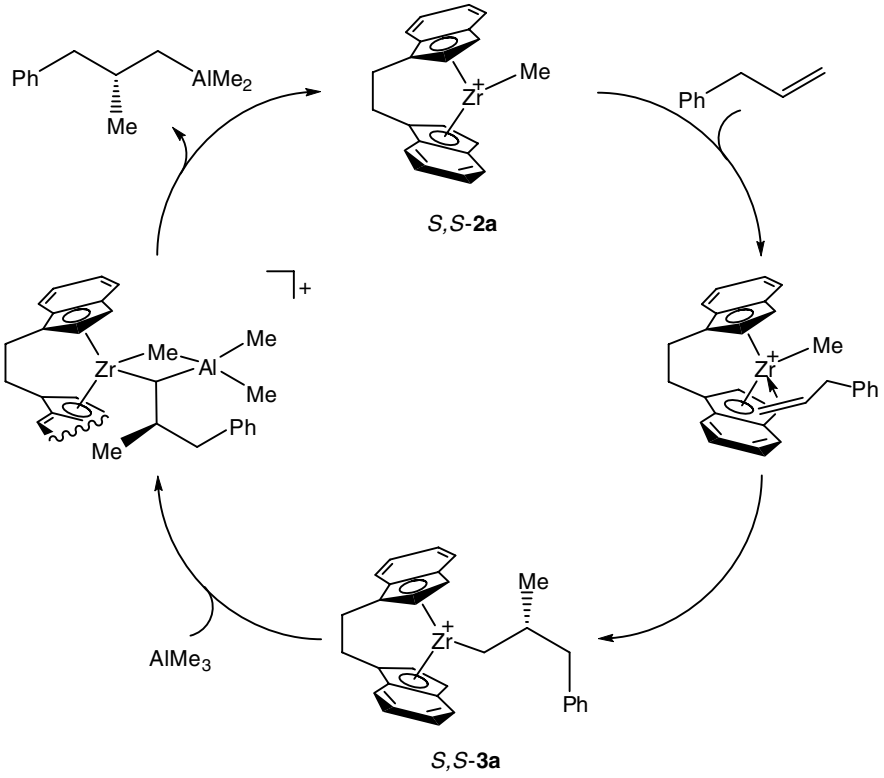
2.1. Choice of catalysts

If we assume that carboalumination is catalyzed by an alkylzirconium cation (Scheme 1), the use of *S*,*S*-**1a** as a precatalyst will generate *S*,*S*-**2a** as the active catalyst upon activation with MAO. Coordination and insertion of the olefin substrate will then (as shown for allylbenzene in Scheme 1) give another alkylzirconium cation *S*,*S*-**3a**. However, the mechanism is complicated by association (Eq. (2)) between the alkylzirconium cation *S*,*S*-**2a** and $AlMe_3$ to form the heterobimetallic cation *S*,*S*-**4a**. A similar equilibrium binds $AlMe_3$ to *S*,*S*-**3a** and is responsible for exchange of the resulting alkyl onto Al.



(2)

We have already reported that k_{off}, the rate constant for dissociation of a Zr/Al heterobimetallic species, is a useful predictor of effectiveness in catalyzing carboalumination [7]. Presumably this is because the activity of the cations is suppressed by equilibria like Eq. (2) and the equilibrium constants of such equations reflect k_{off}. Because **4a** has a relatively high k_{off}, about 0.17 s^{-1} in benzene at 300 K, it is an attractive carboalumination catalyst [7]. The same is



Scheme 1. Mechanism of carboalumination catalyzed by *S*,*S*-**2a**.

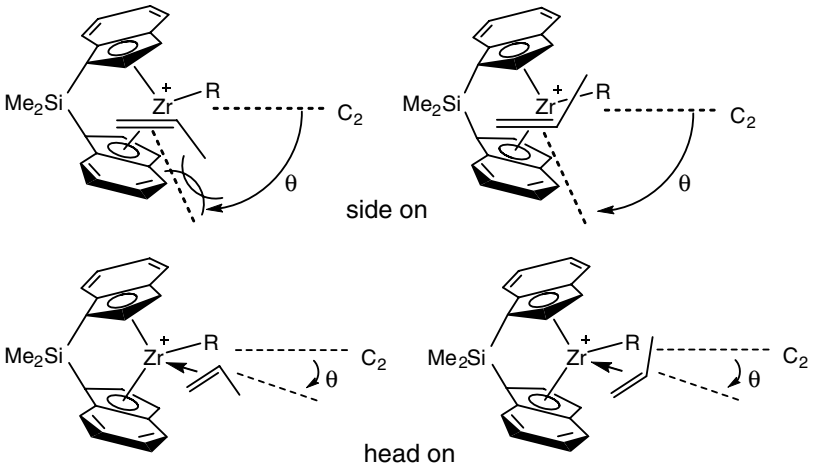
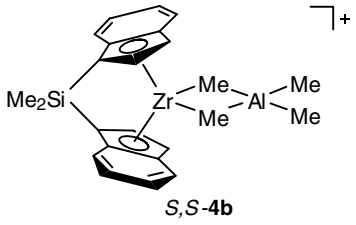


Fig. 2. "Side on" and "head on" coordination modes of propylene to an alkylzirconocene cation [8]. The enantioface selectivity is plainly greater when coordination is "side on".

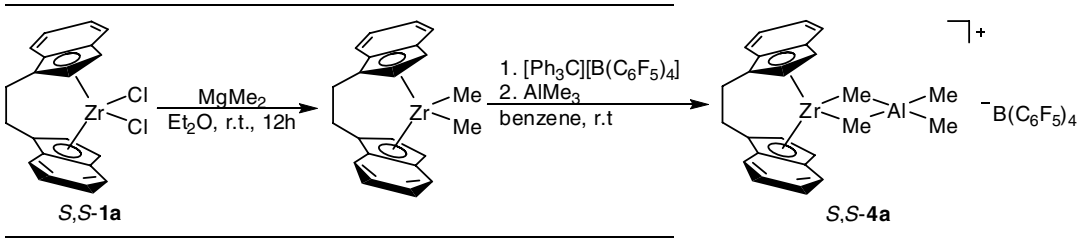
true of its silicon-bridged indenyl analog **4b**. New selective population inversion experiments like the ones in our previous paper (involving inversion of the terminal methyl peak of **4b**, and analysis of the return of the magnetization to equilibrium) [7] give a k_{off} value of 0.16(1) s^{-1} for **4b** in benzene at 300 K.



S,S-**4b**

2.2. Preparation of enantiopure zirconocenes

These reactions were carried out in the absence of light to avoid photoracemization [9]. Enantiopure (*S,S*)-(EBI)$ZrCl_2$ (*S,S*-**1a**) [10] was first converted to its dimethyl derivative [11], then treated with $[Ph_3C][B(C_6F_5)_4]$ and $AlMe_3$ to form the heterobimetallic cation **4a** (Eq. (3));[12] **4a** was assumed to be pure (*S,S*) because these transformations had not involved the indenyl framework. Enantiopure (*S,S*)-(SBI)$ZrCl_2$ (*S,S*-**1b**), (*S,S*)-(3-MeInd)$_2$-$ZrCl_2$ (*S,S*-**1c**), and (*S,S*)-(4,7-Me_2Ind)$_2ZrCl_2$ (*S,S*-**1d**) were prepared in collaboration with the Jordan group by procedures that will be published separately [13].



S,S-**1a** *S,S*-**4a** (3)

When we considered using enantiopure **1b** as a catalyst for *asymmetric* carboalumination, we thought that adding bulk to the front of the catalyst would discourage "head on" olefin coordination, encourage "side on" coordination, and increase enantioface selectivity (Fig. 2). Waymouth and Pino emphasized the importance of the site of olefin coordination when they used zirconocene catalysts for the enantioselective hydrogenation of α-olefins [8]. Accordingly, we decided to try enantiopure (*S,S*)-(3-MeInd)$_2ZrCl_2$ (*S,S*-**1c**) and (*S,S*)-(4,7-Me_2Ind)$_2ZrCl_2$ (*S,S*-**1d**) as catalysts. The ligand environment that they should produce is compared in Fig. 3 with that expected from *S,S*-**1b**.

2.3. Catalysis of asymmetric carboalumination

Enantiopure *S,S*-**1a**, *S,S*-**1b**, *S,S*-**1c**, *S,S*-**1d**, and *S,S*-**4a** were then tested as catalysts for the methylalumination of allylbenzene (Eq. (4)) and styrene (Eq. (5)). The reactions were carried out in benzene with [Zr] from 0.9 to 1.1 mM, and [substrate] from 4 to 10 mM. Generation of the active catalytic species was accomplished either by (1) adding a stoichiometric amount of $[Ph_3C][B(C_6F_5)_4]$ to a solution of the zirconocene dimethyl, letting these reagents react for 2 h, and adding $AlMe_3$; or by (2) adding ≈40 equivalents of MAO to a solution of the zirconocene dichloride, which resulted in its immediate conversion to

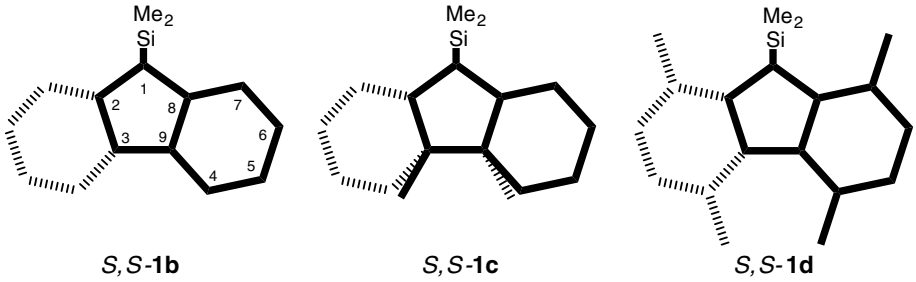


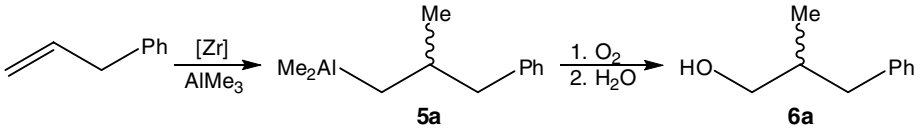
Fig. 3. Top-down view of catalysts *S*,*S*-**1b–d** with bold lines representing the indenyl ligand on top and hashed ones the ligand on bottom. Zr and Cl have been omitted for clarity.

Table 1
Asymmetric catalysis of the carboalumination of allylbenzene and styrene at 300 K by *S*,*S*-**1a–d** and [(*S*,*S*)-(EBI)Zr(μ-Me)$_2$AlMe$_2$][B(C$_6$F$_5$)$_4$] (**4a**)

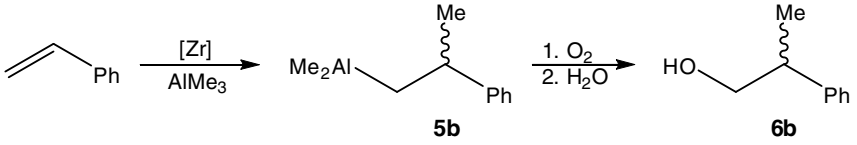
Catalyst precursor	Substrate	Product	% Conv	% ee
(*S*,*S*)-(EBI)ZrCl$_2$ (*S*,*S*-**1a**)[a]	Allylbenzene	**6a**	88	29
(*S*,*S*)-(SBI)ZrCl$_2$ (*S*,*S*-**1b**)[a]	Allylbenzene	**6a**	83	25
(*S*,*S*)-Me$_2$Si(3-Me-Ind)$_2$ZrCl2 (*S*,*S*-**1c**)[a]	Allylbenzene	**6a**	72	25
(*S*,*S*)-Me$_2$Si(4,7-Me$_2$-Ind)$_2$ZrCl$_2$ (*S*,*S*-**1d**)[a]	Allylbenzene	**6a**	65	33
[(*S*,*S*)-(EBI)Zr(μ-Me)$_2$AlMe$_2$][B(C$_6$F$_5$)$_4$] (*S*,*S*-**3a**)[b]	Styrene	**6b**	89	80
[(*S*,*S*)-(EBI)Zr(μ-Me)$_2$AlMe$_2$][B(C$_6$F$_5$)4] (*S*,*S*-**3a**)[c]	Allylbenzene	**6a**	80	29

[a] 1.2×10^{-6} mol Zr, 1.8×10^{-4} mol MAO, 1.2×10^{-5} mol allylbenzene in 1.17 mL C_6D_6; 3–6 h.
[b] 8×10^{-7} mol Zr, 8×10^{-7} mol [Ph$_3$C][B(C$_6$F$_5$)$_4$], 9×10^{-6} mol AlMe$_3$, 3×10^{-6} mol styrene in 0.7 mL C_6D_6; 24 h.
[c] 1.6×10^{-6} mol Zr, 1.6×10^{-6} mol [Ph$_3$C][B(C$_6$F$_5$)$_4$], 1.7×10^{-5} mol AlMe$_3$, 1.2×10^{-5} mol allylbenzene in 1.7 mL C_6D_6; 3 h.

active catalyst. In method (2) enough MAO was added to convert a significant fraction of the zirconocene dichloride to the active catalyst **2** while keeping free [AlMe$_3$] low enough that its association with **2** was minimized (at much higher [MAO] the reaction became exceedingly slow). The reactions were allowed to proceed 4–16 h, until the conversion was at least 50%. The results are shown in Table 1.



(4)



(5)

Styrene gives much greater enantioselectivity than allylbenzene, although the reaction is considerably slower with styrene as substrate. Presumably the vinyl phenyl substituent slows coordination of the olefin but increases the facial selectivity with which it occurs due to increased interaction with the ligand framework of the catalyst.

None of these catalysts show as much enantioselectivity as the Erker catalyst (NMIn)$_2$ZrCl$_2$, which catalyzes the methylalumination of allylbenzene with 70% ee [1a]. The methyl substituents in *S*,*S*-**1c** and *S*,*S*-**1d** are presumably not big enough to block "head on" coordination (although *S*,*S*-**1d** is better than *S*,*S*-**1b** and *S*,*S*-**1c**). Furthermore, methylalumination is probably difficult because the methyl group is too small to orient the incoming olefin; Zambelli found a similar lack of selectivity for the insertion of a propylene into an enantiopure methyltitanocene cation [14].

The results in Table 1 do, however, suggest one important conclusion. The alkylzirconium cation *S*,*S*-**2a**, present in equilibrium with the Zr/Al cation *S*,*S*-**4a** in the last entry, gives the same ee as the catalyst generated from the dichloride *S*,*S*-**1a** in the first entry – consistent with our assumption that MAO and *S*,*S*-**1a** generate *S*,*S*-**2a** and *S*,*S*-**4a**.

3. Experimental

Inert atmosphere techniques, including glove box (<2 ppm O_2) and Schlenk line methods, were used to handle air and moisture sensitive compounds. Benzene and

THF were distilled from sodium/benzophenone under N_2 prior to use. Toluene, Et_2O, CH_2Cl_2, and hexanes were purified by passage through a column of alumina as described by Grubbs [15]. Benzene-d_6 was degassed, and then stored over 4 Å molecular sieves under nitrogen. (*S*,*S*)-(EBI)$ZrCl_2$ (*S*,*S*-**1a**) was a gift from Prof. Richard F. Jordan (University of Chicago, prepared by Matthew LoCoco). Racemic (SBI)$ZrMe_2$ was prepared by literature methods [16], and converted to racemic **4b** by known procedures [17].

NMR spectra were recorded on a Bruker DMX-500 (500 MHz for ^1H), and were referenced by assigning the residual solvent peak (C_6D_5H) to 7.15 δ. Chiral HPLC was performed on a Varian instrument (model 9012 solvent delivery system) with variable wavelength detector (model 9050) using a Chiralcel OD-H column (Daicel Industries) with flow rate = 1 mL/min, 95:5 *n*-hexanes:*i*PrOH, $\lambda = 220$ nm.

3.1. Measurement of k_{off} for racemic *4b*[1]

Selective population inversion experiments were performed at 300 K with a $180^{\circ}_{selective}$-τ-$90^{\circ}_{nonselective}$ – acquire ^1H NMR pulse sequence [18]. Spectra were taken at each of 20 different mixing times (τ). The peak areas were recorded and the data fit using CIFIT [19]. The entire experiment was repeated six times, giving k_{off} values that averaged 0.16(1) s^{-1}.

3.2. 2-Me-3-Ph-1-propanol (*6a*) [20]

Racemic **6a** was synthesized for comparison with the enantioenriched products of asymmetric carboalumination reactions. *trans*-2-Me-3-Ph-2-propen-1-ol (1.5 g, 9.5 mmol) in EtOH (20 mL) was hydrogenated in a Fisher–Porter bottle under 50 psi H_2 using Adams's catalyst (70 mg). Both enantiomers are known compounds: (*S*)-**6a**, CAS 22436-06-2; (*R*)-**6a**, CAS 77943-96-5. ^1H NMR (500 MHz, C_6D_6): δ 7.18 (m, *Ph*, 2H), 7.06 (m, *Ph*, 4H), 3.18 (m, $PhCH_2CHMeCH_2OH$, 2H), 2.64 (m, $PhCH_2CHMeCH_2OH$, 1H), 2.23 (m, $PhCH_2CHMeCH_2OH$, 1H), 1.70 (m, $PhCH_2CHMeCH_2OH$, 1H), 0.90 (br s, $PhCH_2CHMeCH_2OH$, 1H), 0.79 (d, $J_{H-H} = 6.8$ Hz, $PhCH_2CHMeCH_2OH$, 3H).

3.3. (S,S)-(EBI)$ZrMe_2$ [11]

Me_2Mg was prepared by mixing a solution of MeMgBr (240 μL, 3 M in Et_2O) with dioxane (70 μL, 0.77 mmol) in Et_2O (30 mL) and stirring overnight. This solution was added by cannula filter to a solution of (*S*,*S*)-(EBI)$ZrCl_2$ (*S*,*S*-**1a**) (100 mg, 0.24 mmol) dissolved in Et_2O (20 mL). The remaining solid was washed with Et_2O (10 mL), which was again added to the solution containing the zirconocene dichloride. The mixture was stirred overnight. The solvent was removed under vacuum leaving a yellow solid, which was dissolved in benzene (20 mL) and filtered. The remaining solid was washed with benzene (7 mL). The filtrates were combined and brought to dryness under vacuum. The remaining yellow solid was washed with hexanes and dried under vacuum (56 mg, 62% yield). ^1H NMR (500 MHz, C_6D_6): δ 7.31 (d, C_6H, $J_{H-H} = 8.5$ Hz, 2H), 7.06 (m, C_6H, 4H), 6.89 (m, C_6H, 2H), 6.41 (d, C_5H, $J_{H-H} = 3.3$ Hz, 2H), 5.65 (d, C_5H, $J_{H-H} = 3.3$ Hz, 2H), 2.83–2.66 (m, CH_2CH_2, 4H), −0.97 (s, $ZrMe_2$, 6H).

3.4. Methylalumination reactions

Reactions catalyzed by **4** were carried out as in the following example (with *S*,*S*-**4a**). An NMR tube was charged with (*S*,*S*)-(EBI)$ZrMe_2$ (1.6 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (1.6 μmol), 900 μL C_6D_6, and wrapped in aluminum foil to exclude light. After 2 h, $AlMe_3$ (400 μL, 29.2 mM, C_6D_6) was added. After an additional 1 h, allylbenzene (400 μL, 18.1 mM, C_6D_6) was added and the reaction was allowed to sit for 3 h. The reaction was approximately 80% complete (as judged by a decrease in the signal for $PhCH_2CHCH_2$, δ 4.97) with the expected aluminum alkyl >90% (by ^1H NMR) of the product (**5a**). ^1H NMR (500 MHz, C_6D_6): δ 2.56 (d, $PhCH_2CHCH_3CH_2AlMe_2$, $J = 8.3$ Hz, 1H), 1.93 (bs, $PhCH_2CHCH_3CH_2AlMe_2$, 2H), 1.12 (d, $PhCH_2CHCH_3CH_2AlMe_2$, $J = 5.3$ Hz, 3H), and from −0.22 to −0.08 (m, $PhCH_2CHCH_3CH_2AlMe_2$, 2H); a peak for $PhCH_2CHCH_3CH_2AlMe_2$ was not observed due to overlap with $AlMe_3$. These chemical shifts are in agreement with those reported previously for the same compound in CD_2Cl_2 [20]. O_2 was bubbled through the sample for 20 min; addition of 0.1 mL of water completed the conversion of the aluminum alkyl to the corresponding alcohol, 2-methyl-3-phenyl-1-propanol (**6a**). The ee of the product (**6a**) was 29%, determined by a direct comparison of its chiral HPLC trace with that of racemic **6a**.

The methylalumination of styrene was carried out by substituting styrene for allylbenzene in the procedure above. The % ee for the methylalumination of styrene was determined by comparing the chiral HPLC trace of enantioenriched **6b** (prepared with enatiopure *S*,*S*-**4a** as the catalyst) with that of racemic **6b** (prepared with racemic **4a** as the catalyst). Both enantiomers of **6b** are commercially available.

Methylalumination reactions catalyzed by *S*,*S*-**1** were carried out as in the following example (with *S*,*S*-**1b**). In a glovebox, an NMR tube was charged with (*S*,*S*)-(SBI)$ZrCl_2$ (*S*,*S*-**1b**) (600 μL, 3.3 mM, C_6D_6), MAO (178 μL, 0.9 M, C_6D_6), and then allylbenzene (55 μL, 98 mM, C_6D_6). The tube was then wrapped in aluminum foil to exclude light. The sample was monitored for 6 h by ^1H NMR, during which time the reaction reached

[1] For complete details for selective population inversion experiments see [7].

75% completion (judged by the decrease in the signal for $PhCH_2CHCH_2$, δ 4.97). O_2 was bubbled through the sample for 20 min; addition of 0.1 mL of water completed the conversion of the aluminum alkyl to the corresponding alcohol, 2-methyl-3-phenyl-1-propanol (**6a**). The ee of the product alcohol (**6a**) was determined to be 25%, by chiral HPLC as above.

Acknowledgements

This work was supported by the National Science Foundation, Grant CHE-0451385. We owe special thanks to Prof. Richard F. Jordan and Dr. Matthew LoCoco for supplying a sample of (*S*,*S*)-(EBI)$ZrCl_2$ (*S*,*S*-**1a**).

References

[1] (a) U.M. Dzhemilev, A.G. Ibragimov, O.S. Vostrikova, G.A. Tolstikov, Bull. Acad. Sci. USSR Div. Chem. Sci. 34 (1985) 196–197;
(b) E.-I. Negishi, D.Y. Kondakov, Chem. Soc. Rev. 25 (1996) 417–426;
(c) F. Zeng, E.-I. Negishi, Org. Lett. 3 (2001) 719–722;
(d) E.-I. Negishi, S.Q. Huo, Pure Appl. Chem. 74 (2002) 151–157;
(e) S.Q. Huo, J.C. Shi, E.-I. Negishi, Angew. Chem. Int. Ed. 41 (2002) 2141–2143.

[2] (a) P. Wipf, S. Ribe, Org. Lett. 2 (2000) 1713–1716;
(b) P. Wipf, S. Ribe, Org. Lett. 3 (2001) 1503–1505;
(c) P. Wipf, D.L. Waller, J.T. Reeves, J. Org. Chem. 70 (2005) 8096–8102.

[3] (a) R.F. Jordan, W.E. Dasher, S.F. Echols, J. Am. Chem. Soc. 108 (1986) 1718–1719;
(b) X.M. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 113 (1991) 3623–3625;
(c) X.M. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10015–10031;
(d) E.Y.-X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391–1434.

[4] (a) P. Wipf, S. Ribe, Org. Lett. 3 (2001) 1503–1505;
(b) P. Wipf, S. Ribe, Org. Lett. 2 (2000) 1713–1716;
(c) K.H. Shaughnessy, R.M. Waymouth, Organometallics 17 (1998) 5728–5745;
(d) Z. Tan, B. Liang, S.Q. Huo, J.C. Shi, E.-I. Negishi, Tetrahedron: Assym. 17 (2006) 512–515;
(e) B. Liang, T. Novak, Z. Tan, E.-I. Negishi, J. Am. Chem. Soc. 128 (2006) 2770–2771;
(f) T. Novak, Z. Tan, B. Liang, E.-I. Negishi, J. Am. Chem. Soc. 127 (2005) 2838–2839;
(g) E.-I. Negishi, Dalton Trans. (2005) 827–848;
(h) E.-I. Negishi, Z. Tan, B. Liang, T. Novak, Proc. Natl. Acad. Sci. USA 101 (2004) 5782–5787;
(i) S.Q. Huo, J.C. Shi, E.-I. Negishi, Angew. Chem. Int. Ed. 41 (2002) 2141–2143;
(j) E.-I. Negishi, D.Y. Kondakov, Chem. Soc. Rev. 25 (1996) 417–426.

[5] (a) G. Erker, Pure Appl. Chem. 64 (1992) 393–401;
(b) G. Erker, M. Aulbach, M. Knickmeier, D. Wingbermuhle, C. Kruger, M. Nolte, S. Werner, J. Am. Chem. Soc. 115 (1993) 4590–4601.

[6] L.M. Khalilov, L.V. Parfenova, S.V. Pechatkina, A.G. Ibragimov, J.P. Genet, U.M. Dzhemilev, I.P. Beletskaya, J. Organomet. Chem. 689 (2004) 444–453.

[7] R.A. Petros, J.R. Norton, Organometallics 23 (2004) 5105–5107, The rate constants in Table 1 are first order and their units should have been given as s^{-1}; the temperature, 300 K, should have been given.

[8] R. Waymouth, P. Pino, J. Am. Chem. Soc. 112 (1990) 4911–4914.

[9] (a) A. Barbieri, A. Droghetti, S. Sostero, O. Traverso, J. Photochem. Photobio. A 129 (1999) 137–142;
(b) E. Polo, A. Barbieri, S. Sostero, M.L.H. Green, Eur. J. Inorg. Chem. (2002) 405–409.

[10] M.D. LoCoco, R.F. Jordan, J. Am. Chem. Soc. 126 (2004) 13918–13919.

[11] Preparation of rac-(EBI)$ZrMe_2$ from racemic 1a: ref. 8 in: S. Rodewald, R.F. Jordan, Ibid 116 (1994) 4491–4492.

[12] Preparation of racemic 3a from rac-(EBI)$ZrMe_2$: K.P. Bryliakov, N.V. Semikolenova, D.V. Yudaev, V.A. Zakharov, H.-H. Brintzinger, M. Ystenes, E. Rytter, E.P. Talsi, J. Organomet. Chem. 683 (2003) 92–102.

[13] R.M. Buck, M.D. LoCoco, R.A. Petros, J.M. Camara, J.R. Norton, R.F. Jordan, in preparation.

[14] P. Longo, A. Grassi, C. Pellecchia, A. Zambelli, Macromolecules 20 (1987) 1015–1018.

[15] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, Organometallics 15 (1996) 1518–1520.

[16] M.D. LoCoco, R.F. Jordan, J. Am. Chem. Soc. 126 (2004) 13918–13919.

[17] M. Bochmann, S.J. Lancaster, Angew. Chem. Int. Ed. 33 (1994) 1634–1637.

[18] A.D. Bain, G.J. Duns, F. Rathgeb, J. Vanderkloet, J. Phys. Chem. 99 (1995) 17338–17343.

[19] A.D. Bain, CIFIT, Chemistry Department, McMaster University, 2003.

[20] E.-I. Negishi, D.Y. Kondakov, US Pat. Appl. 6,002,037, 1999.