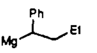
36 h at 25 °C gave, after hydrolysis, only a 22% yield of 2,3-dimethylundecane. The reaction of either 1-decene or styrene with MeMgBr (2 equiv) in the presence of 0.2 equiv of Cp_2ZrCl_2 in THF at 25 °C did not produce the desired methylation product. It did, however, produce a good yield of Cp_2ZrMe_2 based on Zr.



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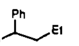

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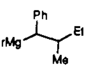

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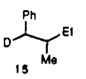

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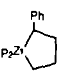

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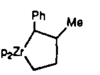

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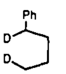

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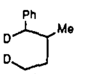

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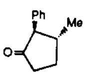

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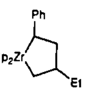

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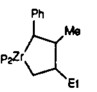

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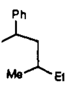

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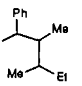

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Acknowledgment. We thank Kawakami Memorial Foundation, Japan, and the National Science Foundation (CHE-8921899) for support of this research. We also thank Professor R. M. Waymouth of Stanford University for informing us of his related study prior to publication.

Registry No. 1a, 133817-48-8; **1c**, 133817-49-9; **2a**, 133817-34-2; **2b**, 133817-36-4; **2c**, 133817-37-5; **4**, 119366-91-5; **5**, 133817-29-5; **6**, 133817-30-8; *cis*-**7**, 133817-32-0; *trans*-**7**, 133817-31-9; **10**, 133817-33-1; **13**, 4397-69-7; (*R**,*R**)-**14**, 133817-38-6; (*R**,*S**)-**14**, 133817-39-7; **15**, 133817-40-0; **16**, 133817-50-2; **17**, 133817-41-1; **18**, 133817-42-2; **19**, 133817-43-3; **20**, 133869-10-0; **21**, 133817-51-3; **22**, 133817-44-4; **23**-*1*-d_1, 133817-45-5; **23**-*4*-d_1, 133817-46-6; Cp_2ZrCl_2, 1291-32-3; $Cp_2Zr(Bu\text{-}n)_2$, 80005-41-0; Cp_2ZrMe_2, 12636-72-5; $Cp_2ZrEt(C_{10}H_{23}\text{-}n)$, 133817-52-4; $Cp_2ZrCl(C_{10}H_{23}\text{-}n)$, 133817-53-5; EtMgBr, 925-90-6; *n*-PrMgBr, 927-77-5; MeMgBr, 75-16-1; 1-decene, 872-05-9; 3-methylundecane, 1002-43-3; 5-ethyl-1-tridecene, 133817-35-3; 3-ethylundecane, 17312-58-2; 1-octene, 111-66-0; styrene, 100-42-5; (*E*)-β-methylstyrene, 873-66-5; (*E*)-stilbene, 103-30-0; (*Z*)-stilbene, 645-49-8; 2,3-dimethylundecane, 17312-77-5; 3-iodomethylundecane, 133817-47-7.

Supplementary Material Available: Representative synthetic procedures and spectral data (2 pages). Ordering information is given on any current masthead page.

Zirconium-Catalyzed Diene and Alkyl-Alkene Coupling Reactions with Magnesium Reagents

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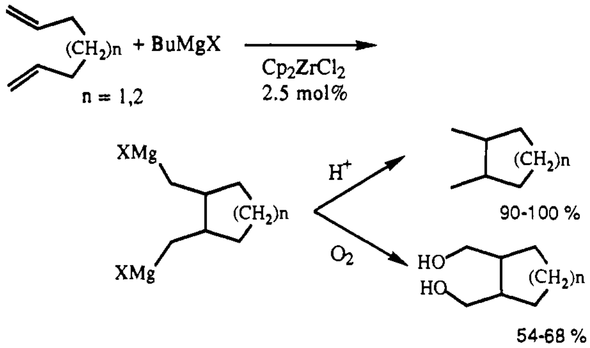
Received December 10, 1990

Zirconium complexes have found extensive application as stoichiometric reagents in organic synthesis.[1] The development of chiral zirconocenes[2,3] and their successful application as stereospecific olefin polymerization catalysts[4,5] have stimulated renewed interest in the development of early-transition-metal chemistry for enantioselective synthesis.[3] However, the multistep synthesis and resolution of these chiral metallocenes presents a severe limitation in the application of these complexes for stoichiometric organic transformations; practical applications will likely require catalytic methods. As part of our efforts to develop the catalytic chemistry of group 4 metallocenes,[5] we were attracted to a report[6] of catalytic carbometalation of olefins mediated by zirconocenes and dialkylmagnesium reagents. Herein we report our studies of these reactions and the development of a zirconium *catalyst* for the reductive coupling of dienes to yield magnesium reagents.

Zirconocene derivatives generated from zirconocene dichloride and butyllithium[7] have previously been shown to be highly efficient stoichiometric reagents for the regio- and stereoselective reductive cyclization of nonconjugated dienes,[8] diynes, and enynes.[9] We have found that, in the presence of Bu_2Mg[10] or BuMgCl, the diene cyclization reactions are *catalytic in zirconium*. For example, treatment of 1,7-octadiene with Bu_2Mg (1.5 equiv) or BuMgCl (3.0 equiv) in the presence of 2.5% zirconocene dichloride in ether at room temperature for 24 h yields, upon hydrolysis, 1,2-dimethylcyclohexane in excellent yield (eq 1, Table I). Deuterolysis of the reaction mixture with 10% D_2SO_4/D_2O affords 1,2-bis(deuteriomethyl)cyclohexane (93% d_2).[11] Oxidative workup (O_2, Et_2O, −78 °C)[12] gives the diol product, 1,2-bis(hydroxymethyl)cyclohexane. The stereochemistry of the cyclization of 1,7-octadiene (82:18 cis:trans) is similar to that seen in stoichiometric reactions.[8] In contrast, the catalytic cyclization of 1,6-heptadiene with Bu_2Mg occurs with lower stereoselectivity (36:64 cis:trans) than is observed in stoichiometric reactions with BuLi (3:97 cis:trans).[8] At this time, the origin of the different stereoselectivities is not known; it is possible that the metallacycle intermediates can isomerize[9b] under the reaction conditions (Scheme I).[13] Further studies are underway to address this possibility.



(1)

The use of Et_2Mg in place of Bu_2Mg gave a complex mixture of products in the reaction with octadiene. However, treatment of terminal alkenes with Et_2Mg or EtMgBr in the presence of

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(1) (a) Harrington, P. J. *Transition Metals in Total Synthesis*; Wiley: New York, 1990; p 414. (b) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and Hafnium Compounds*; Ellis Horwood Limited: Chichester, 1986. (c) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65–72.

(2) (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, D. S.; Britzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. (b) Wild, F. R. W. P.; Zsolnai, L.; Huttner, D. S.; Britzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63.

(3) (a) Collins, S.; Kuntz, B. A.; Hong, Y. *J. Org. Chem.* **1989**, *54*, 4154–4158. (b) Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883–892. (c) Halterman, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1987**, *109*, 8105–8107. (d) Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D. *Organometallics* **1989**, *8*, 1707–1713. (e) Erker, G.; van der Zeijden, A. A. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 512. (f) Couturier, S.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1980**, *195*, 291.

(4) (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255 and references therein. (b) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507–508. (c) Kaminsky, W.; Moller-Lindenhof, N. *Bull. Soc. Chim. Belg.* **1990**, *99*, 103 and references therein. (d) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (e) Spalek, W.; Antberg, M.; Dolle, V.; Klein, R.; Rohrmann, J.; Winter, A. *New J. Chem.* **1990**, *14*, 499.

(5) (a) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911–4914. (b) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953–4954.

(6) (a) Dzhemilev, V. M.; Vostrikova, O. S. *J. Organomet. Chem.* **1985**, *285*, 43–51. (b) Dzhemilev, V. M.; Vostrikova, O. S.; Tolstikov, A. *J. Organomet. Chem.* **1986**, *304*, 17.

(7) Negishi, E.-i.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829–2832.

(8) (a) Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 6435–6437. (b) Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E.-i. *Tetrahedron Lett.* **1989**, *30*, 5105–5108.

(9) (a) Negishi, E.-i.; Swanson, D. R.; Cedarbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917–920. (b) Swanson, D. R.; Rousset, C. J.; Negishi, E.-i. *J. Org. Chem.* **1989**, *54*, 3521–3523. (c) RajanBabu, T. V.; Nugent, W. A.; Taber, D. T.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128–7135. (d) Negishi, E.-i.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (e) Lund, E. C.; Livinghouse, T. *J. Org. Chem.* **1989**, *54*, 4487–4488.

(10) Conveniently prepared from the Grignard reagent. Saheki, Y.; Sasada, K.; Satoh, N.; Kawaichi, N.; Negoro, K. *Chem. Lett.* **1987**, 2299–2300.

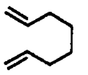
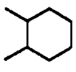
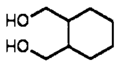
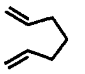
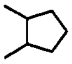
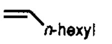
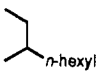
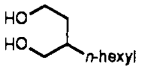
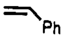
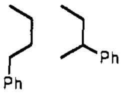
(11) Determined by ^{13}C NMR and high-resolution mass spectrometry. Budzikiewicz, H.; Djerassi, C.; Williams, D. H. *Structural Elucidation of Natural Products By Mass Spectrometry*; Holden Day: **1964**, p 34–36.

(12) Walling, C.; Ciaoffari, A. *J. Am. Chem. Soc.* **1970**, *92*, 6609.

(13) The temperature of the catalytic reactions is 25 °C, whereas stoichiometric reactions are carried out between −78 and 25 °C.

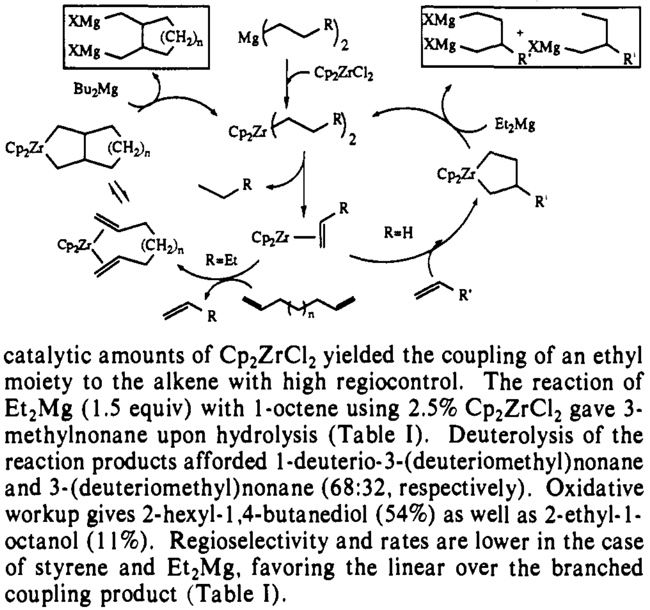
0002-7863/91/1513-6268$02.50/0

Table I. Zirconium-Catalyzed Coupling Reactions

alkene	Mg reagent	workup[a]	products	conversn, %	yield, %	isomer ratio
	Bu_2Mg	a		80[b]	100[c]	82:18 c/t
	BuMgCl			80[b]	94[c]	82:18 c/t
	Bu_2Mg	b			68[d]	80:20 c/t
	Bu_2Mg	a		89	92[c]	36:64 c/t
	Et_2Mg	a		97	89[c]	
	EtMgBr			94	96[c]	
	Et_2Mg	b			54[d]	
	Et_2Mg	a		61	54[c,e]	87:13

[a] Conditions: (a) H_2O/HCl quench, 0 °C; (b) oxidation with O_2 at −78 °C (ref 12). [b] Low conversion likely due to catalyst deactivation. [c] By GC, based upon converted olefin. [d] Isolated yields. [e] Styrene dimer (5–10%) also observed.

Scheme I. Proposed Catalytic Cycle for Diene and Alkyl-Alkene Coupling



catalytic amounts of Cp_2ZrCl_2 yielded the coupling of an ethyl moiety to the alkene with high regiocontrol. The reaction of Et_2Mg (1.5 equiv) with 1-octene using 2.5% Cp_2ZrCl_2 gave 3-methylnonane upon hydrolysis (Table I). Deuterolysis of the reaction products afforded 1-deuterio-3-(deuteriomethyl)nonane and 3-(deuteriomethyl)nonane (68:32, respectively). Oxidative workup gives 2-hexyl-1,4-butanediol (54%) as well as 2-ethyl-1-octanol (11%). Regioselectivity and rates are lower in the case of styrene and Et_2Mg, favoring the linear over the branched coupling product (Table I).

Reactions carried out with ethylmagnesium reagents in ether yield both mono- and difunctionalized products. Deuterolysis of the reaction products obtained with EtMgBr shows a 36:64 ratio of dideuterated versus monodeuterated products compared to the 68:32 ratio obtained with Et_2Mg. In THF, only monodeuterated products are observed.[14] Significantly, the regiochemistry of monofunctionalization is also quite high: the monodeuterated product obtained from 1-octene and EtMgBr was exclusively 3-(deuteriomethyl)nonane (90% yield, THF).

The experimental results in the presence of butylmagnesium reagents can be interpreted in terms of a mechanism based on known stoichiometric chemistry (Scheme I),[8] where dibutylzirconocene is formed by the reaction of Cp_2ZrCl_2 and Bu_2Mg. Elimination of butane forms a zirconocene–butene adduct;[9d,15] displacement of butene by the diene followed by cyclization forms a metallacycle. Transmetalation[16] of the metallacycle to BuMgX completes the catalytic cycle by regenerating the dibutylzirconocene species.[17]

The alkane products obtained in the presence of the EtMgX reagents are similar to those reported previously by Dzhemilev[6] for the catalytic carbometalation of olefins; however, in light of our deuterium labeling studies, the formation of diols upon oxidation, and our results with diene coupling, it is unlikely that these reactions proceed via a carbometalation mechanism. In Scheme I, we present an alternate mechanism involving the formation of a zirconium ethylene complex (R = H) from diethylzirconocene.[15c,d] The difference in the reactivity between EtMgX and BuMgX reagents is likely due to the higher substitutional lability of the zirconium butene adduct relative to the zirconium ethylene adduct. As ethylene is not readily displaced, it couples directly to terminal olefins to form substituted zirconacyclopentanes, which transmetalate to form dimagnesium substituted products or monomagnesium products, depending on the reaction conditions.[18,19]

In summary, we have reported a novel catalytic reaction for zirconium which shows great potential as a powerful new method for carbocyclic ring construction. A particular advantage of this catalytic system is the organomagnesium functionality of the products,[20] allowing for further functionalization. Moreover, the mechanistic implications of this system are intriguing: subtle transmetalation equilibria between Zr and Mg alkyls are key to the success of this catalytic system. Further studies on the mechanism of this reaction and investigations with chiral metallocenes are in progress.

Acknowledgment. We gratefully acknowledge the NIH for a Biomedical Research Grant and the donors of the Petroleum

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(14) Negishi, and co-workers have reported similar results. See: Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E.-i. *J. Am. Chem. Soc.*, preceding paper in this issue.

(15) (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047–1058. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (c) Binger, P.; Muller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Kruger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035. (d) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761.

(16) The transmetalation of metallacycles to inorganic reagents has been extensively investigated by the Du Pont group. (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310–2312. (b) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137–7141. (c) Tumas, W.; Suriano, J. A.; Harlow, R. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 75.

(17) The detection of stoichiometric and roughly equal quantities of butane and 1-butene in the reaction head gas provides support for this mechanism.

(18) The mechanism of the transmetalation reaction and the origin of the unusual solvent and substrate dependence are under investigation. See also ref 14.

(19) Nugent and Dzhemilev have recently reported similar catalytic cycles using Et_3Al reagents: Nugent, W., personal communication. Dzhemilev, U. M.; Ibragimov, A. G.; Zolotarev, A. P.; Muslukhov, R. R.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, *38*, 207; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1989**, *38*, 194.

(20) The nature of the magnesium products has not been unambiguously determined, but they are likely mixtures of di-Grignard products and magnesacycles.

Research Fund, administered by the American Chemical Society, for partial support of this work. We thank Dr. W. Nugent for helpful discussions and Professor Negishi for sharing results prior to publication.

Registry No. 1,7-Octadiene, 3710-30-3; 1,6-heptadiene, 3070-53-9; 1-octene, 111-66-0; ethenylbenzene, 100-42-5; *cis*-1,2-dimethylcyclohexane, 2207-01-4; *trans*-1,2-dimethylcyclohexane, 6876-23-9; *cis*-1,4-cyclohexanedimethanol, 3236-47-3; *trans*-1,4-cyclohexanedimethanol, 3236-48-4; *cis*-1,2-dimethylcyclopentane, 1192-18-3; *trans*-1,1-dimethylcyclopentane, 822-50-4; 3-methylnonane, 5911-04-6; 2-hexyl-1,4-butanediol, 18755-31-2; *n*-butylbenzene, 104-51-8; (1-methylpropyl)benzene, 135-98-8; 1-deuterio-2-(deuteriomethyl)nonane, 122348-19-0; *cis*-1,2-bis(deuteriomethyl)cyclohexane, 133816-67-8; *trans*-1,2-bis(deuteriomethyl)cyclohexane, 133816-68-9; dibutylmagnesium, 1191-47-5; butylmagnesium chloride, 693-04-9; diethylmagnesium, 557-18-6; ethylmagnesium bromide, 925-90-6; zirconocene dichloride, 1291-32-3.

Supplementary Material Available: Experimental details and spectral data (3 pages). Ordering information is given on any current masthead page.

Enantioselective Cyclopolymerization: Optically Active Poly(methylene-1,3-cyclopentane)

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The impressive stereoselectivity of homogeneous Ziegler–Natta catalysts[1] presents an unprecedented opportunity for the molecular design of polymers that are difficult or impossible to prepare with conventional heterogeneous catalysts. The availability of chiral metallocene precursors[2] provides an opportunity to prepare new chiral polymers.[3,4] However, the symmetry of high molecular weight stereoregular vinyl polymers is such that they generally contain mirror planes of symmetry and thus are achiral.[5-8] Herein we report a synthetic route to polymers that do not have this fundamental symmetry limitation. The enantioselective cyclopolymerization of 1,5-hexadiene yields a novel example of an optically active polyolefin whose chirality derives from configurational main-chain stereochemistry.[6,7,9]

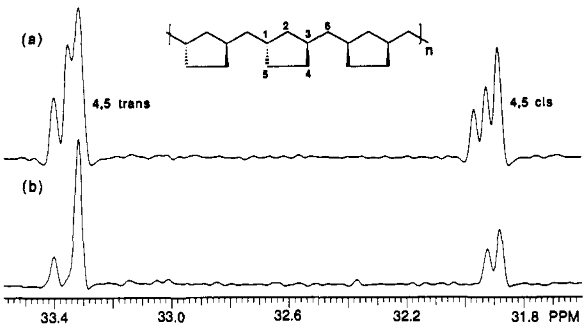
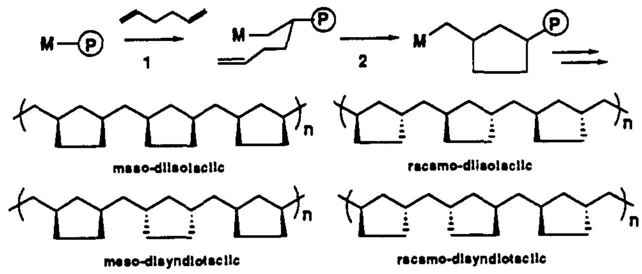


Figure 1. Resolution-enhanced ^{13}C NMR spectra (100 MHz, $CDCl_3$, 40 °C) of $C_{4,5}$ for PMCP prepared with (a) Cp_2TiCl_2 and (b) *rac*-(EBTHI)ZrBINOL.

Scheme I



Cyclopolymerization[10] of 1,5-hexadiene with homogeneous[11] Ziegler–Natta catalysts yields poly(methylenecyclopentane) (PMCP), a polymer for which four structures of maximum order[8] are possible (Scheme I). Of these, only the racemo diisotactic polymer contains no mirror planes of symmetry and is thus chiral by virtue of its main-chain stereochemistry. There are two criteria for chirality in these materials: (1) the polymer must be predominantly isotactic, and (2) the polymer must contain predominantly trans rings. The enantioface selectivity of olefin insertion determines the tacticity of the polymer (the relative stereochemistry of every other stereocenter), and the diastereoselectivity of the cyclization step determines whether cis or trans rings are formed. We have previously shown that the cis/trans diastereoselectivity is influenced by the size of the catalyst precursor, leading to the first examples of *trans*-PMCP and *cis*-PMCP.[12,13] In an effort to control the enantioface selectivity of olefin insertion (and therefore the tacticity), we investigated chiral metallocenes of the Brintzinger type[2] $(EBI)ZrX_2$ and $(EBTHI)ZrX_2$ (EBI = ethylenebis(1-indenyl), EBTHI = ethylenebis(tetrahydro-1-indenyl). Shown in Figure 1 are the ^{13}C NMR resonances of carbons C_4 and C_5 of the repeating unit of polymers produced at 25 °C from (a) Cp_2TiCl_2 and (b) the chiral precursor *rac*-(EBTHI)ZrBINOL (BINOL = 1,1′-bi-2-naphtholate). The ratio of resonances at 33.3 and 31.9 ppm indicates[12,14] that both catalysts exhibit a trans ring selectivity (between 63 and 68%). Closer analysis reveals fine structure in these resonances: the differences in the two spectra imply that the ^{13}C chemical shifts of these carbons are sensitive to stereochemistry between rings (i.e., tacticity), but do not provide unambiguous information about the microstructure.

Cyclopolymerization of 1,5-hexadiene in the presence of the optically active catalyst precursor (−)-(*R*)-ethylenebis(tetra-

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