Enantio- and Diastereoselective Catalytic Carboalumination of 1-Alkenes and α,ω-Dienes with Cationic Zirconocenes: Scope and Mechanism

Kevin H. Shaughnessy and Robert M. Waymouth*

Department of Chemistry, Stanford University, Stanford, California 94306

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Bis(pentamethylcyclopentadienyl) dimethylzirconium ($Cp^*_2ZrMe_2$) and bis(1-(−)-neomenthylindenyl) dimethylzirconium ($(NMIn)_2ZrMe_2$) upon activation by tris(pentafluorophenyl)borane are efficient catalysts for the carboalumination of a variety of 1-alkenes and nonconjugated dienes. The organoalane products can be oxidized to alcohol products, which are isolated in 50−90% yield. $(NMIn)_2ZrMe_2$ carboaluminates 1-alkenes and dienes with moderate (55−65%) enantioselectivities. In contrast, ethylenebis(tetrahydroindenyl) dimethylzirconium ($(EBTHI)ZrMe_2$) and related zirconocenes give low activities and selectivities in the carboalumination reaction. Study of the interaction of zirconocene methyl cations with trimethylaluminum by ^1H NMR shows that $[(EBTHI)ZrMe][MeB(C_6F_5)_3]$ forms a stable bis(μ-methyl) aluminum adduct. Zirconocene methyl cations derived from $Cp^*_2ZrMe_2$ and $(NMIn)_2ZrMe_2$ react slowly with large excesses of trimethylaluminum to form weakly bound trimethylaluminum adducts. The difference in trimethylaluminum binding to the cationic zirconocene centers is consistent with the significantly lower activity observed when $(EBTHI)ZrMe_2$ is used as the precatalyst.

Introduction

The direct carbometalation of unactivated olefins to give isolable organometallic species has considerable synthetic potential.[1] Despite the potential utility of this transformation, few synthetically useful examples of olefin carbometalation have been reported in the literature. Carbometalation of cyclopropene by main-group organometallic species has been well studied, but is limited to the highly strained olefin cyclopropene.[2−4] Dzhemilev has developed an efficient carbomagnesiation of alkenes catalyzed by zirconocenes.[5−7] Both the mechanism and the stereoselectivity of this reaction have been widely studied.[8−14]

Carbometalation is well accepted as a mechanistic step in reactions such as Heck coupling and olefin polymerization.[15] The catalytic polymerization of alkenes is assumed to involve alkyl migration as the key step to a metal-bound olefin species.[16] Olefin polymerization catalysts are extremely fast carbon−carbon bond formation catalysts, and they are capable of extremely high levels of diastereo- or enantioselectivity in the presence of the appropriate ligands.[17] With the development of homogeneous versions of these catalysts, particularly chiral complexes, efforts have been made to apply these highly active catalysts to small-molecule syntheses.[14,18−24] These catalysts have been used successfully in hydrogenation,[19,25] diolefin cycloisomerization,[26−29] cycloamination,[24] and cyclohydrosilation.[30]

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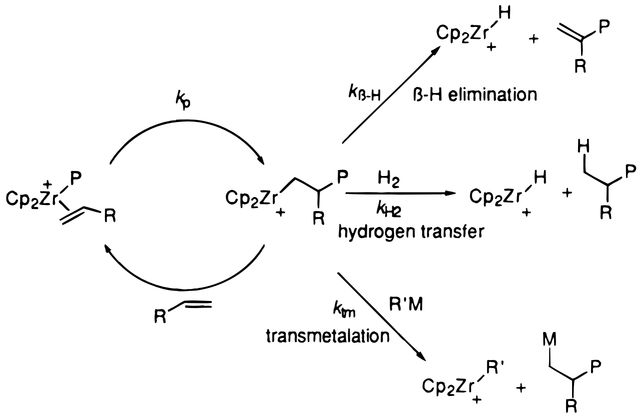
Scheme 1. Chain Transfer Reactions in Ziegler−Natta Polymerization

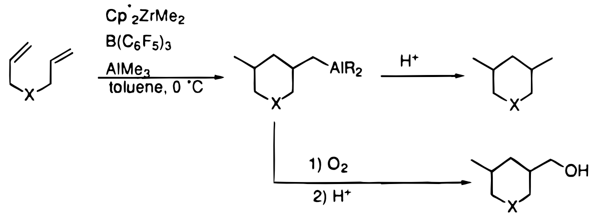


Catalysts active for olefin polymerization can be utilized in carbometalation reactions provided chain transfer (k_{ct}) is fast relative to chain propagation (k_p). Scheme 1 shows the most commonly observed chain transfer reactions in Ziegler−Natta olefin polymerizations. The addition of hydrogen to give high rates of hydrogen transfer has been used in the hydrogenation of olefins with Ziegler−Natta catalysts.[19,25] This strategy has also been used in the cycloisomerization of nonconjugated dienes.[27] β-Hydride elimination ($k_{\beta-H}$) is typically much slower than propagation for group 4 metallocenes except at elevated temperature[29] or at very low zirconium to methylaluminoxane (MAO) ratios.[31] Group 3 metallocenes, which have a much lower $k_p/k_{\beta-H}$ ratio, efficiently dimerize 1-alkenes and cycloisomerize diolefins.[28]

An insertion, transmetalation process is appealing in that it creates a new stereocenter through the formation of a new carbon−carbon bond, as well as a metal−carbon bond which could be used in further elaboration of the substrate. Recently, we[32] and Negishi[33−35] have reported the use of trialkylaluminums in the presence of zirconocenes for the carboalumination of 1-alkenes and nonconjugated olefins. This paper will describe an efficient carboalumination of 1-alkenes and diolefins as well as enantioselective carboaluminations utilizing chiral catalysts. Kinetics and structural studies on the catalyst system reveal the important role of trimethylaluminum as both a transmetalation agent and an inhibitor for the reaction.

Results

Carboalumination of Olefins. The catalytic carbometalation of olefins and the carbocyclization of a variety of 1,5-, 1,6-, and 1,7-dienes can be carried out in the presence of $Cp^*_2ZrMe_2$ (**A**), $B(C_6F_5)_3$, and trimethylaluminum at 0 °C in toluene (eq 1).[32] The organoaluminum products can be oxidized with oxygen to give the corresponding alcohol products in 60−90% yield. Unsubstituted dienes could be cyclized to give cyclopentyl- (**2a**), cyclohexyl- (**2b**), and cycloheptylmethanol (**2c**) products in 60−70% yield and 65% cis diastereoselectivity (Table 1, entry 1). 2-Substituted 1,5-hexadienes are cyclocarbometalated in high yields (70−88%) to cyclopentylmethanols **4a** and **4b** with diastereoselective formation of a quaternary center. This cyclization occurs with complete selectivity for the trans-substituted products as determined by difference NOE analysis of **4b**. Alcohols protected by the *tert*-butyldimethylsilyl (TBS) group can be cyclized at a rate similar to that of the unsubstituted diene (Table 1, entry 5), while the trimethylsilyl-protected analogue gave slow conversion to uncharacterizable oligomeric products. An entry into the piperidine ring structure was provided by cyclization of diallylaniline (**7**), but reaction times were on the order of days rather than hours (Table 1, entry 4).



(1)

Fused-bicyclic and spirocyclic products are also accessible by this approach from suitable dienes or trienes. By changing the substitution pattern of a diolefinic cyclohexane precursor (**11** or **13**), it is possible to produce two regioisomeric bicyclo[4.3.0]nonanes (Table 2, entries 1 and 2). Only two of the four possible diastereomers were observed in each case. Cyclocarboalumination of triene **15** gives the spirocyclo[4.4]nonane **16** in 83% yield as a mixture of two diastereomers. Attempted cyclization of 3-allylmethylenecyclohexane to the bicyclo[3.3.1]nonane **17** resulted instead in the highly chemoselective carbometalation of the terminal olefin to give **18** (Scheme 2).

Carboalumination of 1-hexene yields 2-methylhexan-1-ol (**20**) in 75% yield after oxidation as the sole product observed by GC (Table 3, entry 1). Olefins such as the eugenol derivative **23** also react rapidly under these conditions to give carbometalated product **24** in 74% yield. The carboalumination of 2-siloxy-4-pentene **25** occurred with high yield, but poor diastereoselectivity, affording a 55:45 mixture of diastereomers (Table 3, entry 4). 3-Substituted-1-alkenes are also carboaluminated, albeit slowly and to incomplete conversion (Table 3, entries 5 and 6). Carboalumination of 3-phenyl-1-pentene gives **28**, after 30 h, in good yield (67%) and excellent diastereoselectivity (90% de). Similarly, 3-methyl-1-pentene was carbometalated to 50% yield after 40 h to give 2,3-dimethylpentan-1-ol (**30**) in a diastereomeric ratio of 65:35.

The selectivity for the catalytic carbometalation of olefins is highly dependent on the nature of the ligands and the solvent. In toluene, metallocenes other than

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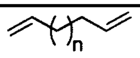
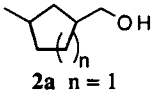
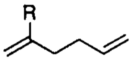
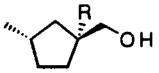
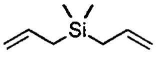
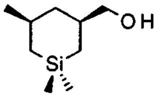
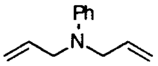
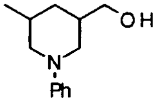
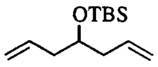
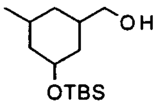
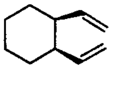
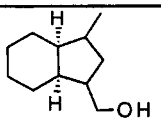
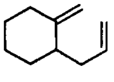
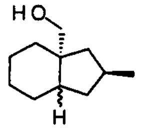
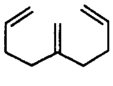
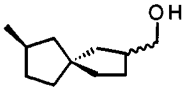
Table 1. Cyclocarbometalation of Nonconjugated Dienes

Entry	Olefin	Rxn Time (h)	Product	% Yield[a]	Diastereomeric Ratio[b]
1	 **1a** n = 1 **1b** n = 2 **1c** n = 3	**1a** = 2 **1b** = 3 **1c** = 3	 **2a** n = 1 **2b** n = 2 **2c** n = 3	**2a** = 70 % **2b** = 60 % **2c** = 67 %	**2a** = 70% cis **2b** = 60% cis **2c** = 65% cis
2	 **3a** R = Me **3b** R = Et	**3a** = 2 **3b** = 2	 **4a** R = Me **4b** R = Et	**4a** = 88 % **4b** = 70 %	**4a** = 100 % trans **4b** = 100% trans
3	 **5**	3	 **6**	61 %	100% cis
4	 **7**	48	 **8**	51 %	70% cis
5	 **9**	3	 **10a-c**	65 %	46:43:11 **10a**:**10b**: **10c**[c]

Reaction run with substrate (2.50 mmol), **A** (0.125 mmol), $B(C_6F_5)_3$ (0.125 mmol), trimethylaluminum (5.0 mmol) in 30 mL toluene at 0 °C. [a]Yields are for isolated products. All compounds are fully characterized (^1H NMR, ^{13}C NMR, FTIR, HRMS, Anal.). [b]Diastereoselectivity ratios (dr) determined by GC of hydrolyzed reaction mixture, or by ^1H NMR. [c]See ref. 38 for isomer designations.

Table 2. Cyclocarboalumination To Give Polycyclic Products

Entry	Starting Material	Time (h)	Product	% Yield[a]	Diastereomeric Ratio[b]
1	 **11**	6	 **12**	90	70:30
2	 **13**	3	 **14**	74	67:33
3	 **15**	2	 **16**	88	50:50

Reaction run with substrate (2.50 mmol), **A** (0.125 mmol), $B(C_6F_5)_3$ (0.125 mmol), trimethylaluminum (5.0 mmol) in 30 mL toluene at 0 °C. [a]Yields are for isolated products. All compounds are fully characterized (^1H NMR, ^{13}C NMR, FTIR, HRMS, Anal.). [b]Diastereoselectivity ratios (dr) determined by ^1H NMR.

$Cp^*_2ZrMe_2$ (**A**) gave slow oligomerization of the substrate; for example, carboalumination of 1,5-hexadiene catalyzed by ethylenebis(tetrahydroindenyl)$ZrMe_2$ (EBTHI)$ZrMe_2$ (**B**)[36] under the conditions of eq 1 gave a 5% yield of 1,3-dimethylcyclopentane (**31**) plus a mixture of oligomeric products after hydrolysis of the reaction mixture after several days. In contrast, the carboalumination of 1,5-hexadiene in toluene with $Cp^*_2ZrMe_2$ was complete in 2 h or less.

The selectivity for carbometalation in chlorinated solvents was higher than that in toluene. Carboalumination of allylbenzene (**21**) using precatalyst $Cp^*_2ZrMe_2$ in methylene chloride gave an 85% yield of 2-methyl-3-phenylpropanol (**22**) in 2 h; under similar conditions

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(36) EBTHI = ethylenebis(5,6,7,8-tetrahydroindenyl).

Scheme 2. Attempted Preparation of Bridged Bicyclic Products

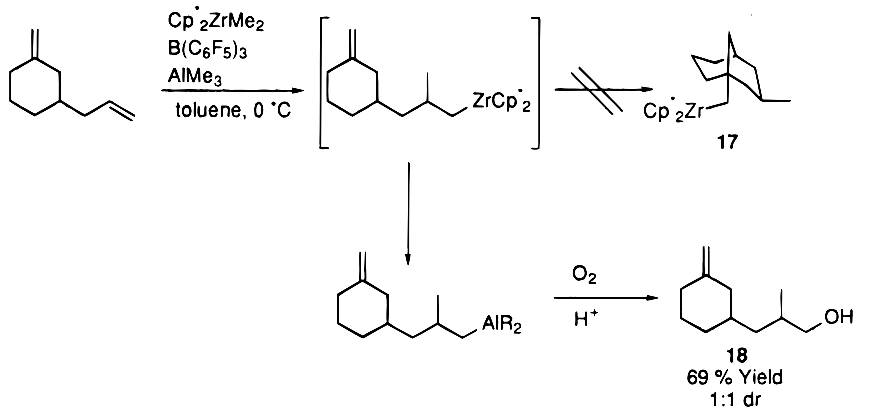
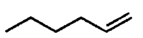
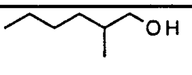
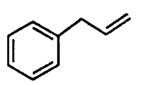
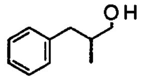
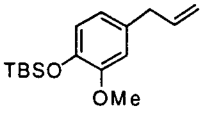
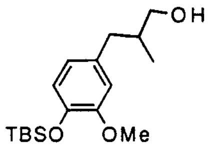
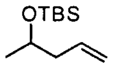
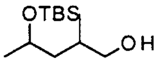
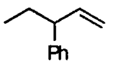
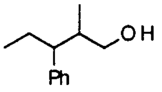
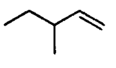
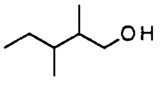


Table 3. Carboalumination of 1-Alkenes

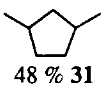
Entry	Starting Material	Time (h)	Product	% Yield^a	Diastereomeric Ratio^b
1	 **19**	2	 **20**	75	
2	 **21**	2	 **22**	69	
3	 **23**	3	 **24**	74	
4	 **25**	3	 **26**	82	55:45
5	 **27**	30	 **28**	67^c	95:5
6	 **29**	40	 **30**	50^c	65:35

Reaction run with substrate (2.50 mmol), A (0.125 mmol), $B(C_6F_5)_3$ (0.125 mmol), trimethylaluminum (5.0 mmol) in 30 mL toluene at 0 °C. ^{a}Yields are for isolated products. All compounds are fully characterized (^{1}H NMR, ^{13}C NMR, FTIR, HRMS, Anal.). ^{b}Diastereoselectivity ratios (dr) determined by ^{1}H NMR. ^{c}Conversion was 80 %. ^{d}Conversion was 70 %.

in toluene the yield was only 69%. Methylene chloride proved less effective with other catalysts. (EBTHI)ZrMe₂ gave low yields in the carboalumination of allylbenzene and incomplete conversion (Table 4, entry 4). Better results were obtained with 1,2-dichloroethane (DCE). The carboalumination of allylbenzene gave high yields of 2-methyl-3-phenylpropan-1-ol (**22**) with each catalyst tried (Table 4, entries 1, 5, 7, and 8). The rate for the carbometalation of 1,5-hexadiene was higher in DCE than in toluene for most catalysts, but the selectivity for dimethylcyclopentane **31** did not always improve in DCE. Precatalyst (EBTHI)ZrMe₂, for example, gave exclusively oligomeric products from 1,5-hexadiene in both DCE and toluene although the rate is markedly increased in DCE.

Carboalumination of allylbenzene in DCE with *rac*-(EBTHI)ZrMe₂ gives a high yield of **22**, although rather slowly, while 1,5-hexadiene is rapidly converted to poly(methylene-1,3-cyclopentane) (pmcp) (Table 5). 1-Hexene, similar to 1,5-hexadiene, gave a low (13%) yield of carbometalated product **20** plus oligomeric products. Olefins such as 4-methyl-1-pentene and diallyldimeth-

Table 4. Solvent Effects in the Carbometalation Reaction

Entry	Catalyst	Solvent	Substrate 1,5-Hexadiene (**1**)[a]	 Allylbenzene (**21**)[a]
1	$Cp^*_2ZrMe_2$ (**A**)	toluene	70 % **2a** 70 % cis 2h	69 % **22** 2h
2	**A**	CH_2Cl_2	---	85% **22** 2 h
3	(EBTHI)$ZrMe_2$ (**B**)	toluene	oligomerization[b] over 24 h.	oligomerization[b] over days
4	**B**	CH_2Cl_2	---	(29 % **22**) (70 % conv.) 24 h
5	**B**	DCE	70 % yield pmcp[c] 1 h, 0 °C	88 % **22** 19 h
6	$(NMIn)_2ZrMe_2$ (**C**)	toluene	 48 % **31** 2 h plus oligomers[b]	---
7	**C**	DCE	62 % **2a**, 3 h 68 % trans	78 % **22** 3 h
8	Cp_2ZrMe_2 (**D**)	DCE	---	71 % **22** 6 h

Reactions were carried out with 2.5 mmol olefin, 5 mmol TMA, 0.125 mmol catalyst precursor, 0.125 mmol borane, 1 mmol decane as GC standard in 30 mL of solvent at room temperature for chlorinated solvents and 0 °C for reactions in toluene. [a]Yields are for isolated products except values in parentheses which are GC yields. Olefin conversion was 100 % unless noted otherwise. [b]Oligomers refers to high retention time products observed in GC which were not characterized or quantified. [c]pmcp = poly(methylene-1,3-cyclopentane)

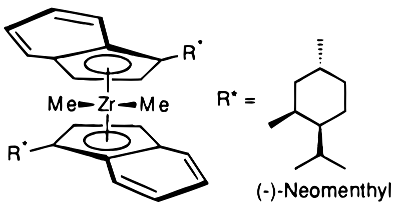


Figure 1. Bis(1-(−)-neomenthylindenyl) dimethylzirconium ($(NMIn)_2ZrMe_2$) (**C**).

ylsilane substrates also gave low yields of carboaluminated products plus oligomeric side products (Table 5, entries 5 and 6). 4-Phenyl-1-butene gave a moderate (33%) yield of the carboaluminated product **37** as well as oligomeric side products.

In contrast to (EBTHI)$ZrMe_2$, bis(1-(−)-neomenthylindenyl) dimethylzirconium[37] ($(NMIn)_2ZrMe_2$, **C**) (Figure 1) gave a high selectivity for carboaluminated products regardless of substrate. The dichloride ($(NMIn)_2ZrCl_2$) has been utilized in the enantioselective carboalumination of olefins by Negishi.[34,35] The enantioselective carbometalation of 1,*n*-dienes **1a**, **1b**, and **3a** proceeded in yields of 62%, 78%, and 67%, respectively (Table 6, entries 1−3). Enantioselective carbometalation of 1-hexene at room temperature gave 2-methylhexanol **20** in 55% ee and 50% yield after oxidation. The yield could be increased to 63% when the carboalumination was carried out at 0 °C. 4-Methyl-1-pentene gives **38** in 58% yield, while carboalumination of olefinic silyl ether **39** occurs in 53% yield at room temperature. Optical yields for the carbometalation of α olefins were in the range 50−66% with this catalyst system.

The diastereoselectivity of ring formation of 1,5-hexadiene catalyzed by $(NMIn)_2ZrMe_2$ is similar in magnitude to that seen with $Cp^*_2ZrMe_2$,[32] but the opposite diastereomer is formed. Cyclocarboalumination of 1,5-hexadiene (**1a**) with precatalyst $(NMIn)_2ZrMe_2$ gives the trans diastereomer as the major product. With 1,6-heptadiene (**1b**), however, the cyclization gives a 70:30 cis:trans ratio, which is similar to that seen with precatalyst $Cp^*_2ZrMe_2$. Cyclocarboalumination of 2-methyl-1,5-hexadiene (**3a**) occurs with preference for the trans diastereomer, but only by a 68:32 ratio rather than the complete diastereoselectivity seen with $Cp^*_2ZrMe_2$.

The enantioselective cyclocarbometalation of dienes results in different levels of enantioselectivity for each diastereomeric product. 1,5-Hexadiene is carbometalated to **2a** in 79% ee for the major trans diastereomer, but only 45% ee for the minor diastereomer. Similar results are seen with the other dienes. 1-Alkenes are carbometalated with 55−65% ee, with allylbenzene and 4-methyl-1-pentene giving the highest enantioselectivities. Optical rotation ($[\alpha]^{25}{}_D$) values of +8.6° ($c = 0.49$, CH_2Cl_2) and +11.1° ($c = 0.82$, CH_2Cl_2) were measured for 2-methyl-1-hexanol (**20**) and 2-methyl-3-phenylpropan-1-ol (**22**), respectively, which are consistent with products of the *R* configuration.[38,39] The same absolute

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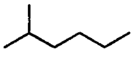
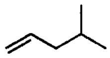
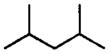
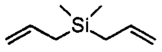
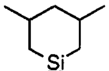
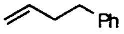
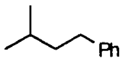
(37) Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590−4601.

Table 5. Carboalumination of Olefins with *rac*-(EBTHI)ZrMe$_2$ (B)

Entry	Olefin	Time^a (h)	Carbometalation product	% Yield^b
1	**21**	19	**22**	78^c
2	**1**	1	**33**	5 plus oligomers
3	**1**	3^d	**33**	5 70 % pmcp^e
4	**19**	1.5	 **32**	13 plus oligomers
5	 **33**	5	 **34**	8 plus oligomers
6	 **6**	5	 **35**	15 plus oligomers
7	 **36**	24	 **37**	33 plus oligomers

Reactions carried out with 2.5 mmol olefin, 5 mmol TMA, 0.125 mmol **B** 0.125 mmol borane, 0.10 mmol decane in 30 mL DCE at 23 °C. ^{a} Time at which conversion ≥ 95 %. ^{b}GC yield of protonated carbometalated product. Oligomers refers to observation of high retention time peaks in GC trace. ^{c}Yield of isolated alcohol formed by oxidation of organoaluminum product. ^{d}Reaction run at 0 °C ^{e}Isolated yield of poly(methyl-1.3-cyclopentane) (pmcp).

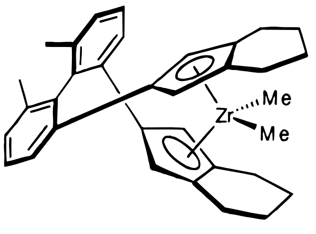


Figure 2. *rac*-[6,6′-Dimethyl-2,2′-bis(5,6,7,8-tetrahydro-2-indenyl)biphenyl] dimethylzirconium (**E**).

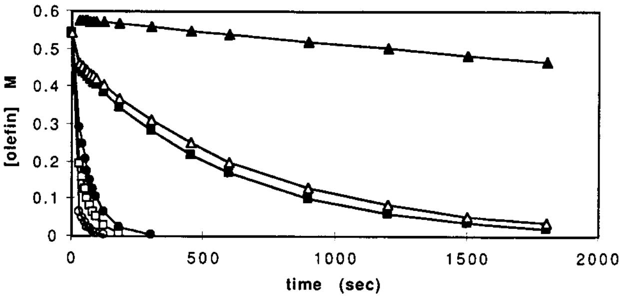


Figure 3. Olefin concentration decay for carbometalations in DCE: (■, □) catalyst = Cp*$_2$ZrMe$_2$, (●, ○) catalyst = (NMIn)ZrMe$_2$, (▲, △) catalyst = (EBTHI)ZrMe$_2$; (□, ○, △) olefin = 1,5-hexadiene, (■, ●, ▲) olefin = allylbenzene.

configuration was reported by Negishi[34] for olefin carbometalation with the (NMIn)$_2$ZrCl$_2$/AlMe$_3$ catalyst system.

The catalyst [6,6′-dimethyl-2,2′-bis(5,6,7,8-tetrahydro-2-indenyl)biphenyl] dimethylzirconium (**E**)[40] (Figure 2) was also explored for the carboalumination reaction (Table 7). Precatalyst **E** proved less efficient in the carboalumination reaction than (NMIn)$_2$ZrMe$_2$. Substrates such as 1-hexene and 1,5-hexadiene gave moderate yields, with incomplete conversion in the case of 1,5-hexadiene. Larger substrates underwent carbometalation sluggishly with this catalyst system. Carboalumination of allylbenzene was only 50% complete after 24 h, giving a 30% yield of isobutylbenzene upon hydrolytic workup. Siloxydecene **39** was only 10% consumed after 24 h with this catalyst.

Kinetics of Carboalumination. The rate of olefin consumption was measured by NMR for both allylbenzene and 1,5-hexadiene for a series of catalysts (Cp*$_2$ZrMe$_2$ (**A**), (EBTHI)ZrMe$_2$ (**B**), (NMIn)$_2$ZrMe$_2$ (**C**)) in both toluene-d_8 and 1,2-dichloroethane-d_4. Plots of ln(olefin) vs time were linear even at high conversion, consistent with first-order behavior in olefin for each system over duplicate runs. The first-order plot for the carboalumination of 1,5-hexadiene by (EBTHI)ZrMe$_2$ in DCE deviated slightly from linearity at longer reaction times, but this is possibly due to the inhomogeneity of the reaction mixture due to poly(1,5-hexadiene) precipitation. Reactions were run under identical conditions except the carboaluminations of 1,5-hexadiene with catalysts Cp*$_2$ZrMe$_2$ and (NMIn)$_2$ZrMe$_2$, which were too fast to observe under the standard conditions. These reactions were carried out at lower [Zr], and the first-order rate constant was determined on the basis of the reaction order in zirconium (vide infra). The olefin decay curves for each system in DCE are shown in Figure 3. The results for the reactions run in toluene give a trend

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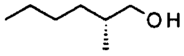
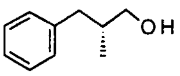
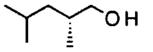
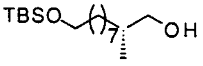
[38] Barth, S.; Effenberger, F. *Tetrahedron: Asymmetry* **1993**, *4*, 823–833.

[39] Drewes, S. E.; Malissar, D. G. S.; Roos, G. H. P. *Chem. Ber.* **1993**, *126*, 2663–2673.

[40] Ellis, W. W.; Hollis, T. K.; Odenkirk, W.; Whelan, J.; Ostrander, R.; Rheingold, A. L.; Bosnich, B. *Organometallics* **1993**, *12*, 4391–4401.

Table 6. Carbometalation of Olefins with $(NMIn)_2ZrMe_2$ (33)

Entry	Olefin	Product	Time (h)	% Conv.[a]	% Yield[b]	Diast. Ratio	% ee[c]
1	**1a**	**2a**	4	94	62	66 % trans	c = 45 t = 79
2	**1b**	**2c**	3	100	67	68 % trans	ND[d]
3	**3a**	**4b**	1	98	78	70 % cis	c = 68 t = 60
4	**19**	 **20**	2[e]	100	63		55 (*R*)[f]
5	**21**	 **22**	3	95	78		66 (*R*)[f]
6	**33**	 **38**	2	100	58		63
7	 **39**	 **40**	4	100	53[c]		53

Reactions carried out with 2.5 mmol olefin, 5 mmol TMA, 0.125 mmol **C**, 0.125 mmol borane, 1.0 mmol decane in 30 mL DCE at room temperature. [a]Conversion determined by GC. [b]Isolated yield of oxidized product except where indicated. [c]Determined from the (R)-(-)-MTPA esters by NMR. [d] Enantiomeric excess not determined due to poorly resolved ^1H and ^{19}F NMR spectra. [e]Reaction run at 0 °C. [f]Absolute configurate determined by comparison of optical rotation with literature values.

Table 7. Carboalumination with E as Precatalyst[a]

entry	olefin	time (h)	product	% conversion[b]	% yield[c]
1	**1a**	3	**2a**	75	45[d]
2	**19**	3.5	**20**	100	46
3	**21**	24	**22**	50	30[e]
4	**39**	24	**40**	10	5[e]

[a] Reactions carried out with 2.5 mmol of olefin, 5 mmol of TMA, 0.125 mmol of **E**, 0.125 mmol of borane, 1.0 mmol of decane in 30 mL of DCE at room temperature. [b] Conversion determined by GC. [c] Isolated yield of oxidized product except where indicated. [d] Isolated as a 3:1 trans:cis ratio of diastereomers. [e] Determined by GC.

Table 8. First-Order Rate Constants for Olefin Carboalumination[a]

		k_{obs} ($\times 10^3$ s^{-1})	
catalyst	solvent	1,5-hexadiene (**1**)	allylbenzene (**21**)
$Cp^*_2ZrMe_2$	DCE-d_4	66.3[b]	1.69
$Cp^*_2ZrMe_2$	toluene-d_8	38.4[b]	2.64
$(EBTHI)ZrMe_2$	DCE-d_4	1.45	0.118
$(EBTHI)ZrMe_2$	toluene-d_8	0.367	0.019
$(NMIn)_2ZrMe_2$	DCE-d_4	95.8[b]	16.8
$(NMIn)_2ZrMe_2$	toluene-d_8	39.9[b]	14.2

[a] Reactions carried out with 0.025 mmol of zirconocene, 0.025 mmol of borane, 0.5 mmol of olefin, 1.0 mmol of TMA and 0.15 mmol of mesitylene as standard in 0.625 mmol of solvent. [b] Reaction carried out with 0.0125 mmol of zirconocene and borane. Value calculated from the measured rate constant and the change in reaction rate measured over this catalyst range in Table 9.

Table 9. [Zr] and [Al] Effects upon Reaction Rate[a]

[Zr] (M)	[Al] (M)	k_{obs} ($\times 10^3$ s^{-1})
0.016	1.27	0.55
0.032	1.27	1.69
0.064	1.27	8.38
0.032	0.64	7.47
0.032	2.54	1.12

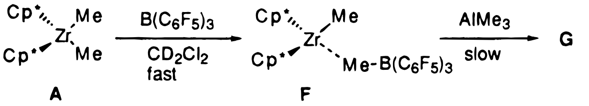
[a] Reactions run with the indicated [Zr] and [Al] with [allylbenzene] = 0.64 M in 0.625 mL of DCE (total volume = 0.79 mL).

similar to that observed in DCE. The observed first-order rate constants are listed in Table 8.

A series of experiments were carried out to determine the reaction order in [Zr] and [Al]. The carboalumination of allylbenzene by $Cp^*_2ZrMe_2$ in DCE was chosen as the model system since it had an intermediate rate which would allow for ease of measurement. Experiments were carried out with [Zr] = 0.016, 0.032, and 0.064 M. First-order rate constants for the consumption of allylbenzene were thus obtained (Table 9). A plot of $\ln(k_{obs})$ vs $\ln([Zr])$ deviated slightly from linearity, but gave a slope of 1.96 ($r^2 = 0.988$). A similar series of experiments carried out over the [Al] concentration range of 0.64−2.54 M revealed that trimethylaluminum inhibits the rate, although above 1.27 M the dependence of reaction rate on [Al] decreased significantly. This asymptotic behavior resulted in a significantly nonlinear $\ln(k_{obs})$ vs $\ln([Al])$ plot.

Investigation of Catalytic Intermediates. The interaction of the zirconocene cations with trimethylaluminum was studied by NMR to investigate the different catalytic behavior observed with precatalysts $Cp^*_2ZrMe_2$ (**A**) and $(NMIn)_2ZrMe_2$ (**C**) compared to $(EBTHI)ZrMe_2$ (**B**). Treatment of zirconocene dimethyl **A** with tris(pentafluorophenyl)borane in CD_2Cl_2 gives a bright yellow solution of the zirconocene methyl cation

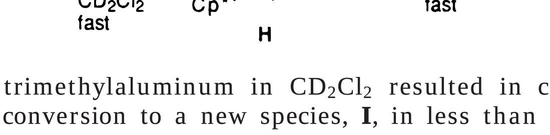
(**F**)[41] (eq 2). At room temperature the ^{1}H NMR spectrum of the cation gives broad peaks at 2.03 ppm (Cp*), 1.90 (Zr−Me), and 0.44 ppm (Me−B) similar to the spectral characteristics previously reported by Marks,[42] although both the Zr−Me and Me−borate peaks are shifted downfield relative to the values reported for **F** in toluene. Upon cooling of the sample to −20 °C, a sharp proton spectrum is obtained showing two Cp−CH_3 peaks (2.06, 1.98; approximately 1:1.2), the Zr−Me peak (1.88 ppm), and the Me−B peak (0.44 ppm). This is in contrast to the previously reported NMR study in toluene, in which the room temperature spectrum of **F** was sharp, with broadening occurring only upon heating to approximately 80 °C.[41]



(2)

Treatment of a CD_2Cl_2 solution of the methylzirconocene cation with a large excess of trimethylaluminum (10−40 equiv of Al:Zr) gives a mixture of cation **F** and a new species **G** which is characterized by a sharp peak at 1.94 ppm (Cp*), and a slightly broad peak at 0.78 ppm with a ratio of 3.5:1 (eq 2). The slightly broadened peak at 0.78 ppm showed no significant change upon cooling of the sample as low as −80 °C, although the Cp* peaks did begin to broaden at this temperature. With an Al:Zr ratio of 40:1, the **F**:**G** ratio is approximately 3:1 within 10 min. After 2 h, the ratio has changed to approximately 2:1. Only after 8−10 h does the reaction near completion with only a trace of **F** being observed. In the kinetic experiments described above, approximately 3:1 **F**:**G** ratios were observed in DCE-d_4 after 15 min. A NOESY-2D spectrum of **G** (**G**:**F** > 5:1, Zr:Al = 20:1) showed an off-diagonal peak between the peak at 0.78 ppm and the excess TMA (−0.25 ppm) as well as between the Cp* ligand and Zr−Me peak at 1.86 ppm. ^{13}C NMR of a sample of **F** shows the Cp* peaks at 122.99 and 11.90 ppm. The excess TMA is observed at −6.77 ppm. Two small broad peaks are observed at 15−16 and 44−44.5 ppm. The pentafluorophenylborane peaks were similar to those observed for tris(pentafluorophenyl)borane. Addition of 10 equiv of 1-hexene to a solution of TMA adduct **F** aged for 1 day results in rapid carbometalation to (2-methylhexyl)dimethylaluminum.

Zirconocene methyl cation **H** was prepared from $Cp^*_2ZrMe_2$ and triphenylmethyl tetrakis(pentafluorophenyl)borate[43] (eq 3). Treatment of this cation with trimethylaluminum in CD_2Cl_2 resulted in complete conversion to a new species, **I**, in less than 20 min. Complex **I** was characterized by a small downfield shift of the Cp* peak (from 2.04 to 2.08 ppm) The Zr−Me peak was not observed, but may obscured by the Cp* peak. No other resonances were observed except the large peak due to free TMA at −0.25 ppm.



(3)

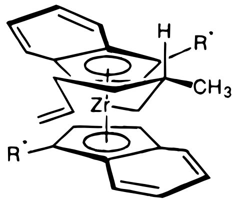


Figure 4. Intermediate **N-*R***.

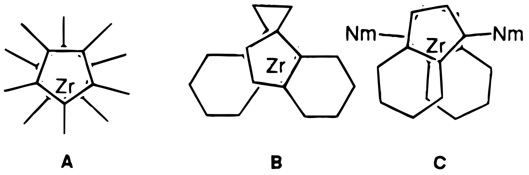


Figure 5. Top views of zirconocene catalysts studied.

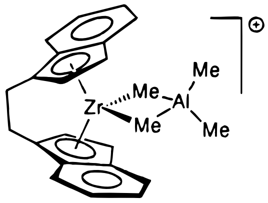
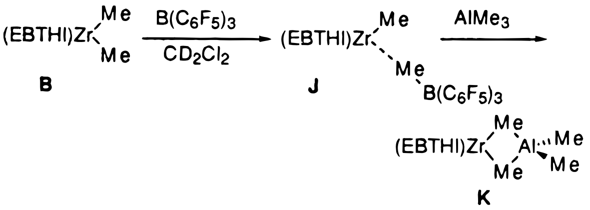


Figure 6. Bis(μ-methyl)aluminum adduct **K**.

Treatment of (EBTHI)$ZrMe_2$ with tris(pentafluorophenyl)borane in CD_2Cl_2 immediately gives a bright yellow solution of the cationic species **J** (eq 4). The room temperature proton NMR spectrum of **J** shows a number of broad resonances which cannot be assigned plus a sharp peak at 0.71 ppm. Cooling of the sample to −20 °C gives a sharp spectra with two sets of ligand peaks. Also observed are the resonances at 0.71 and 0.12 ppm, which are likely the Zr−Me and Me−B resonances, respectively.



(4)

Treatment of **J** with 1 equiv or more of trimethylaluminum in CD_2Cl_2 results in a fast (<5 min) conversion to a new species **K**, which shows a single set of sharp peaks for the ligand. Also observed are the methyl borate (0.49 ppm) and two new peaks at 0.42 and −0.61 ppm in a 1:1 ratio each integrating for 6 protons (Figure 6). The ^{13}C NMR of **K** shows the expected ligand peaks plus the methyl tris(pentafluorophenyl)borate peaks. Two additional peaks are observed at 36.30 (q, $^1J_{C-H} = 112.5$ Hz) and −7.14 (q, $^1J_{C-H} = 114.3$ Hz). The ^{1}H and ^{13}C NMR spectra of complex **K** are consistent with a bis(μ-methyl)aluminum adduct (eq 4) which has been characterized for similar metallocenes by Bochmann.[44]

Treatment of $(NMIn)_2ZrMe_2$ with tris(pentafluorophenyl)borane in CD_2Cl_2 results in the rapid formation

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[41] Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031.

[42] Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623−3625.

[43] Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570−8571.

[44] Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634−1637.

of a bright orange solution of the zirconocene methyl cation **L**. Unlike the other catalysts studied, this cationic species gives a sharp proton spectrum at room temperature displaying a single set of ligand resonances (Figure 6). Low-temperature spectra of **L** did result in uneven broadening of the ligand peaks, most likely due to the freezing out of various ligand rotation modes. The aromatic protons of the indene ligand showed no broadening until −70 °C, well below the point where the neomenthyl peaks began to broaden. Heating the cation in DCE to 70 °C did not result in any significant broadening of the peaks. In addition to the ligand resonances, a peak was observed for Me−B (0.53 ppm). The Me−Zr peak was not observed, likely due to overlap with other peaks.

Treatment of cation **L** with trimethylaluminum resulted in a slow conversion to a new species similar to that observed with the cation **F** derived from $Cp^*_2ZrMe_2$. After 8 h, complete conversion to a new species **M** was observed. Two sets of ligand peaks were observed in a 1:1 ratio. In addition to the ligand resonances, two new peaks were observed at 0.79 and −0.89 ppm in an approximately 3:1 ratio.

Discussion

Carboalumination of Olefins. Catalysts based on zirconocenes and alkylaluminum compounds efficiently carboaluminate a variety of alkenes and dienes to give carbometalated and cyclocarbometalated products in high yield.[32,34,35] Negishi has developed an elegant catalyst system based on the chiral precursor bis(1-(−)-neomenthylindenyl)zirconium dichloride ($(NMIn)_2ZrCl_2$)[37] for the enantioselective carbometalation of terminal olefins.[34,35] This system is experimentally convenient but is specific for this particular metallocene: carbometalation under similar conditions with Cp_2ZrCl_2 is ineffective. In this paper, we report full details of the catalytic carbometalation of olefins with cationic metallocenes and elucidate the role of the nature of the catalyst precursor, the solvent, and the reaction conditions on the selectivity and rate of carbometalation.

The catalyst system based on $Cp^*_2ZrMe_2/B(C_6F_5)_3/$TMA efficiently cyclized dienes to carbocycles and carbobicycles and carboaluminated 1-alkenes in good yields (Tables 1−3). Unsubstituted 1,*n*-dienes were cyclized to five-, six-, and seven-membered rings, and 2-substituted 1,5-dienes were cyclocarbometalated in high (70−88%) yield and produced rings with quaternary centers. Protected nitrogen and oxygen functionalities were tolerated under the reaction conditions, although in the case of diallylaniline the reaction rate was significantly retarded. Unsubstituted dienes cyclized with moderate (66%) selectivity for cis-substituted products independent of ring size. 1,6-Heptadiene was cyclized with 60% cis selectivity, while diallyl dimethylsilane underwent cyclocarbometalation with complete cis selectivity. 2-Substituted 1,5-dienes underwent cyclization with complete trans selectivity. 1,5-Dienes containing a cyclic unit such as **11** or **13** could be carbocylized to give the corresponding bicyclo[4.3.0]-nonanes in high yield with complete cyclization selectivity. Triene **15** also was efficiently cyclized to spirocycle **16** with no evidence of linear or monocyclic products. The bicyclic products were isolated as pairs of diastereomers, but we have not been able to independently assign the identity of each diastereomer. We have tentatively assigned the structures of bicycle **14** and spirocycle **16** on the basis of stereoselectivity we had previously observed in the cyclization of 2-substituted 1,5-dienes.

The catalyst system based on $Cp^*_2ZrMe_2/B(C_6F_5)_3/$TMA efficiently carboaluminated 1-alkenes in good yields and provided an additional approach to what is a limited number of strategies for the direct carbometalation of unfunctionalized olefins.[5−9,12−14,34,35,45] A variety of olefins could be carbometalated by the $Cp^*_2ZrMe_2$-based system including functionalized olefins such as eugenol derivative **23** and 2-TBSO-4-pentene **25**.

Low diastereoselectivities were observed for the carboalumination of olefins substituted in the homoallylic position; carboalumination of siloxypentene **25** occurred with low (55:45) diastereoselectivity, and replacement of the *tert*-butyldimethylsilyl protecting group with the triisopropylsilyl group resulted in no change in the diastereoselectivity.[46] The diastereoselectivity for olefins substituted in the allylic position was higher, but the reactions proceeded at much lower rates: 3-Phenyl-1-pentene (**27**) underwent carboalumination with 90% diastereomeric excess after 30 h to give a 67% yield (Table 3).

The rate and selectivity of this catalyst system for the carbometalation of olefins depended strongly on the nature of the catalyst precursor and the solvent. In toluene, metallocenes other than $Cp^*_2ZrMe_2$ were generally ineffective for carbometalation (in many cases, oligomers or higher polymers were obtained). The rates and selectivities for carbometalation were much higher in chlorinated solvents. Chlorinated solvents had been shown to be effective reaction media for both carboalumination[34] and olefin polymerization reactions.[47] While methylene chloride appeared effective for some metallocenes, the use of dichloroethane improved reaction rates and yields for a variety of metallocenes (Table 4).

The high selectivity for carbometalation in dichloroethane allowed us to investigate a variety of metallocenes to compare the role of the metallocene ligands on the rate and selectivity for olefin carbometalation. For these studies, four metallocenes were investigated: $Cp^*_2ZrMe_2$ (**A**), ethylenebis(tetrahydroindenyl)$ZrMe_2$ ((EBTHI)$ZrMe_2$, **B**),[48,49] bis(1-(−)-neomenthylindenyl) dimethylzirconocene ($(NMIn)_2ZrMe_2$, **C**),[37] and [6,6′-dimethyl-2,2′-bis(5,6,7,8-tetrahydro-2-indenyl)biphenyl] dimethylzirconocene (**E**).[40]

The Brintzinger metallocene **B** generates a highly stereospecific olefin polymerization catalyst[17] and has been shown to be capable of catalyzing a variety of organic transformations with moderate to high enanti-

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(45) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543−2549.

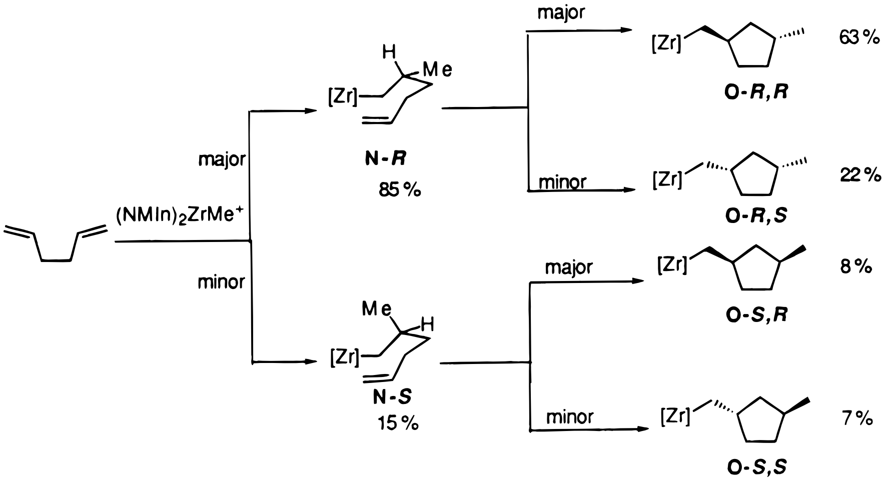
(46) Attempts to use the extremely bulky triphenylsilyl group failed due to the instability of this protecting group under the reaction conditions.

(47) Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1996**, *197*, 855−867.

(48) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233−247.

(49) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63−67.

Scheme 3. Relationship of Diastereoselectivity to Enantioselectivity



oselectivity.[19,22,50,51] However, attempted carbometalation of 1,5-hexadiene, 1-hexene, 4-methyl-1-pentene, and diallylsilane with (EBTHI)ZrMe$_2$/B(C$_6$F$_5$)$_3$/TMA gave poor selectivity for carbometalated products and yielded mostly oligomeric products. For this catalyst, only allylbenzene gave a reasonable selectivity for carbometalated products (Table 5).

The bis(neomenthylindenyl) complex **C** in the presence of methylaluminoxane (MAO) is less highly stereospecific than (EBTHI)ZrCl$_2$ in propylene polymerizations,[37] but the metallocene dichloride in the presence of trialkylaluminum compounds has been successfully used by Negishi for enantioselective carboaluminations in DCE.[34,35] As indicated in Table 6, cations derived from (NMIn)$_2$ZrMe$_2$ and B(C$_6$F$_5$)$_3$ are efficient catalysts for the stereo- and enantioselective carbometalation of a variety of dienes and monoolefins in yields of 55–80%.[52] Less readily polymerizable substrates such as allylbenzene, 4-methyl-1-pentene, and 2-methyl-1,5-hexadiene gave higher yields than simple 1-alkenes (i.e., 1-hexene), presumably due to their higher level of selectivity for carboalumination over oligomerization. The yields obtained under our conditions are approximately 15% lower than those reported by Negishi[34] (except for allylbenzene, which gave nearly identical yields), but the rates are are much higher in the cationic system (NMIn)$_2$ZrMe$_2$/B(C$_6$F$_5$)$_3$ compared to the (NMIn)$_2$ZrCl$_2$/TMA catalyst system.[34] With the cationic system, the carboalumination of 1-octene is 90% complete (65% yield) after 30 min, while Negishi[34] reported reaction times ranging from 12 to 24 h. The lower yields for the cations relative to the dichloride system may be a consequence of the fact that the cations are also active polymerization catalysts in the absence of such a high concentration of trimethylaluminum.

The diastereoselectivity of cyclocarboalumination of dienes mimics trends observed in the cyclopolymerization of dienes with metallocene/MAO catalysts.[53,54] Sterically congested metallocenes such as Cp*$_2$ZrMe$_2$ (**A**) are selective for the formation of cis five-membered rings from hexadienes (Table 1), whereas (NMIn)$_2$ZrMe$_2$ (**C**) selectively form trans rings. For the cyclopolymerization of dienes, catalysts less sterically hindered than Cp*$_2$ZrMe$_2$ favor the formation of trans rings from 1,5-hexadiene.[54–56]

Moderate enantioselectivities (55–65%) were observed for the carbometalation of olefins and the cyclocarbometalation of dienes. For 1-alkenes we observed ee's ranging from 66% for allylbenzene to 55% for 1-hexene. The absolute configurations of 2-methylhexanol (**20**) and 2-methyl-3-phenylpropanol (**22**) were determined to be *R* by comparison of their measured optical rotations with known literature values.[38,39] The formation of *R*-configured products is consistent with *re* insertion as reported by Negishi.[34] While the degree of enantioselectivity is slightly lower than that reported by Negishi,[34] the similar sense and degree of stereoinduction imply very similar intermediates at the stereodifferentiating step (presumably the olefin insertion step) for the two systems.

The cyclocarboalumination of dienes results in different levels of enantioselectivity for the diastereomeric products. For 1,5-hexadiene, *cis*-**2a** was formed in 45% ee, while the major diastereomer, *trans*-**2a**, was formed in 79% ee. The cyclocarboalumination of 1,6-heptadiene gave similar results although the discrepancy was less: 68% ee for *cis*-**2b** and 60% for *trans*-**2b**. From the enantioselectivity observed for each diastereomer and the diastereomeric ratio it is possible to estimate the enantioselectivity of the initial insertion (Scheme 3). In the case of 1,5-hexadiene the initial insertion can be calculated to occur with 70% ee, while the initial insertion of 1,6-heptadiene occurred with 66% ee. These estimates are in reasonable agreement with the enantioselectivity observed for the enantioselective carbometalation of 1-hexene (55%). In contrast, polymerization of propylene with this catalyst precursor at −30 °C yields polypropylene with an isotactic pentad content [mmmm] = 24%, or a calculated ee for propylene polymerization of 46%.[37]

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(50) Yamaura, Y.; Hyakutake, M.; Mori, M. *J. Am. Chem. Soc.* **1997**, *119*, 7615–7616.

(51) Chin, B.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 5650–5651.

(52) These yields are slightly lower than those obtained with Cp*$_2$ZrMe$_2$ in toluene.

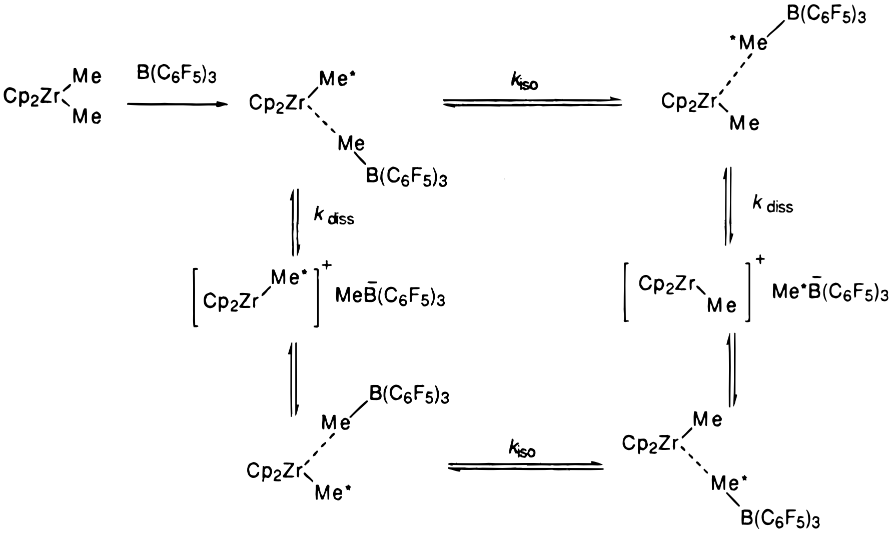
(53) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91–98.

(54) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953–4.

(55) Cavallo, L.; Guerra, G.; Corradini, P.; Resconi, L.; Waymouth, R. M. *Macromolecules* **1993**, *26*, 260–267.

(56) Miller, S. A.; Waymouth, R. M. In *Ziegler Catalysis*; Springer: Berlin, 1995; pp 441–454.

Scheme 4. Fluxional Processes of Zirconocene Methyl Cation as Described by Marks



The diastereoselectivity of intramolecular olefin insertion depends on the enantioface of initial insertion. Intermediate **N-*R*** undergoes cyclization with a relatively high degree of diastereoselectivity giving a 3:1 trans:cis ratio. The diastereoselectivity of cyclization for **N-*S***, however, is essentially 0. These differences reflect the competition between the enantiofacial preference of the coordination site and the diastereofacial preference exerted by the conformational bias of the incipient ring. We have previously proposed that a preference for trans rings in the cyclopolymerization of 1,5-hexadiene is a consequence of a chairlike transition state.[55] Shown in Figure 4 is a possible configuration for intermediate **N-*R***. This conformation is consistent with the moderately high trans diastereoselectivity observed after a *re* insertion. After a misinsertion to give **N-*S***, the analogous chair conformation results in the methyl group being axial. Thus the chairlike conformation will presumably be less favored, resulting in a poor diastereoselectivity after misinsertion (Scheme 3).

The carboalumination reactions catalyzed by $Cp^*_2ZrMe_2$, $(EBTHI)ZrMe_2$, and $(NMIn)_2ZrMe_2$ implied a correlation between the structure of the catalyst and the selectivity for carboalumination. Both Cp* and NMIn ligands (in the conformation shown in Figure 4) project the ligands above and below the coordination sites of the bent metallocene (Figure 5), while $(EBTHI)ZrMe_2$ has less steric bulk in the front quadrant of the catalyst. This suggested to us that ligands positioned near the reaction center might improve the selectivity for carboalumination reactions. Bis(indenyl) catalysts bridged in the 2-position (as described by Bosnich and Halterman[40,57]) constitute a class of chiral bridged metallocenes locked in a conformation similar to that observed in the crystal structure of $(NMIn)_2ZrCl_2$[37] as represented in Figures 1, 4, and 5. The zirconocene *rac*-[6,6′-dimethyl-2,2′-bis(5,6,7,8-tetrahydro-2-indenyl)biphenyl] dimethylzirconocene (**E**) was investigated because it was reported to be the most stable of the 2,2-bridged zirconocenes.[40] The carbometalation of a series of olefins with *rac*-E in DCE yielded a moderate selectivity for carboalumination, but low rates. Substrates such as 1,5-hexadiene and 1-hexene gave moderate (45%) yields of carboaluminated products with rates comparable to those for $(NMIn)_2ZrMe_2$. Allylbenzene, on the other hand, was only 50% consumed after 24 h, while siloxydecene **39** showed essentially no activity with this catalyst system. These results suggest that the 2,2′-bridged catalyst **E** is too sterically congested; as a result, only unhindered olefins show any degree of activity. The carboalumination selectivity is also not particularly high, suggesting that transmetalation must also be slow. While **E** has indenyl rings locked in a conformation similar to that observed in the crystal structure of $(NMIn)_2ZrCl_2$, it would appear that the conformational flexibility provided by the unbridged ligands in catalysts derived from $(NMIn)_2ZrMe_2$ (**C**) affords a kinetic advantage for carboalumination, particularly for more sterically demanding substrates. The conformational flexibility of **C**, however, creates some ambiguity in the assignment of the reactive conformation for the stereodifferentiating olefin insertion step.[34]

Catalytic Intermediates. Formation of zirconocene methyl cations from zirconocene dimethyl compounds and tris(pentafluorophenyl)borane occurs rapidly in CD_2Cl_2. The cationic products in CD_2Cl_2 are spectroscopically similar to those reported by Marks in toluene-d_8,[41,42] but in methylene chloride, cations **F** and **J** (derived from $Cp^*_2ZrMe_2$ and $(EBTHI)ZrMe_2$) have lower barriers to methyl exchange and the disassociation of methylborate[41] (Scheme 4). Thus, as might be expected, more polar solvents appear to facilitate ion exchange processes. The higher activities for carbometalation observed in polar solvents such as DCE might also be a consequence of the weaker interactions between zirconocene methyl cations and trimethylaluminum. In addition, at lower temperature (−20 °C) two species are observed in the spectrum of the ion pair $Cp^*_2ZrMe^+ MeB(C_6F_5)_3^-$ (**F**) in CD_2Cl_2, which we tentatively assign as a mixture of the contact ion pair and the solvent-separated ion pair.

The diastereotopic ligand peaks observed in the −30 °C spectrum of $(EBTHI)ZrMe^+ MeB(C_6F_5)_3^-$ (**J**) indicate that the borate is strongly bound to give a configurationally stable contact ion pair. In contrast, for the cation $(NMIn)_2ZrMe^+ MeB(C_6F_5)_3^-$ (**L**), the borate does

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[57] Halterman, R. L.; Ramsey, T. M. *Organometallics* **1993**, *12*, 2879−2880.

not appear to bind strongly to the metal as the chemical shift for the methylborate in **L** is similar to that observed in $Li^+ MeB(C_6F_5)_3^-$ and that in **F**. The single set of resonances observed for **L** at room temperature is consistent with a solvent-separated ion pair which is less configurationally stable than the cation **J**; the equivalence of the indenyl ligands is consistent with rapid epimerization of the methyl cation **L**.[58]

The interaction of trimethylaluminum with the zirconocene methyl cations **F**, **J**, and **L** depends quite strongly on the nature of the ligands of the metallocene. Treatment of $(EBTHI)ZrMe^+ MeB(C_6F_5)_3^-$ (**J**) with $AlMe_3$ in CD_2Cl_2 results in the rapid formation of a stable bis(μ-methyl)-bridged heterometallic species **K** (Figure 6) as reported by Bochmann.[44] In contrast, $Cp^*{}_2ZrMe^+ MeB(C_6F_5)_3^-$ (**F**) and $(NMIn)_2ZrMe^+ MeB(C_6F_5)_3^-$ (**L**) form weakly bound adducts with $AlMe_3$ of indeterminate structure; treatment of **F** or **L** with trimethylaluminum even at Al:Zr ratios as high as 40:1 results in slow (10−20 h) conversion to a 1:1 trimethylaluminum/zirconocene cation adduct whose NMR spectra do not correspond to a bis(μ-methyl)-bridged heterometallic species corresponding to **K**. The difference in stability of the alkylaluminum adducts is undoubtedly a consequence of the steric congestion at the metal center.

The implications of these observations is significant: the catalytic activity and selectivity for carbometalation appear to be inversely proportional to the stability of the trialkylaluminum adducts: catalysts derived from $Cp^*{}_2ZrMe^+ MeB(C_6F_5)_3^-$ (**F**) and $(NMIn)_2ZrMe^+ MeB(C_6F_5)_3^-$ (**L**) show good selectivity and activity for carbometalation while those from $(EBTHI)ZrMe^+ MeB(C_6F_5)_3^-$ (**J**) are poor carbometalation catalysts. Bochmann has commented on the role of the bis(μ-methyl)-bridged heterometallic species such as **K** on the polymerization activity of metallocene catalysts.[44] The implication of our results is that the inhibitory effects of $AlMe_3$ on polymerization (or carbometalation) activity should be highly dependent on the nature of the metallocene ligands.

Determination of Reaction Kinetics. The rate of olefin consumption for a series of catalysts ($Cp^*{}_2ZrMe_2$, $(EBTHI)ZrMe_2$, and $(NMIn)_2ZrMe_2$) was studied in toluene and DCE and found to be highly dependent upon the catalyst, solvent, and olefin structure. For the carboalumination of 1,5-hexadiene, catalysts derived from $Cp^*{}_2ZrMe_2$ and $(NMIn)_2ZrMe_2$ gave similar rates in both DCE and toluene while the rate constants for reactions run with precatalyst $(EBTHI)ZrMe_2$ were 50 times lower than those for $Cp^*{}_2ZrMe_2$ (Table 8). The results correspond to the reactivities observed for these catalysts. Both $Cp^*{}_2ZrMe_2$ and $(NMIn)_2ZrMe_2$ are efficient carboalumination catalysts, especially in DCE, while $(EBTHI)ZrMe_2$ gives slower conversion and lower carbometalation selectivities.

The carboalumination of allylbenzene is slower than that of 1,5-hexadiene by at least an order of magnitude for catalysts $Cp^*{}_2ZrMe_2$ and $(EBTHI)ZrMe_2$, while for $(NMIn)_2ZrMe_2$ the difference is only a factor of 3−6 depending on the solvent. The rates of carbometalation are faster in DCE than in toluene for all cases except the carbometalation carboalumination of allylbenzene with $Cp^*{}_2ZrMe_2$.[59] The general trend for reactions to occur faster in DCE is likely due, at least in part, to improved ion separation in the cationic catalyst species. By weakening the coordination of the borate anion[41] or TMA, olefin coordination would be facilitated, leading to higher insertion rates.

For the carbometalation of allylbenzene with the $Cp^*{}_2ZrMe_2/B(C_6F_5)_3$ system, the reaction is first order in [olefin] but more complicated for both [Zr] and [Al]. The average order in [Zr] was 1.96. $AlMe_3$ acted as an inhibitor by lowering reaction rates as [Al] increased, but inhibition by $AlMe_3$ appeared to saturate with increasing aluminum concentration. Over the concentration range 0.64−1.27 M the reaction order in [Al] was approximately −2, while above 1.27 M the reaction order was only −0.75 (Figure 4). These results are consistent with trimethylaluminum acting as a competitive inhibitor which undergoes equilibrium binding to the zirconocene alkyl to give an inactive species. Bochmann[44] has proposed that $AlMe_3$ reacts with zirconocene cations to form inactive bis(μ-methyl)aluminum adducts. While this appears to be the case for $(EBTHI)ZrMe_2$, $Cp^*{}_2ZrMe_2$ and $(NMIn)_2ZrMe_2$ appear not to form the bis(μ-methyl)aluminum species, but rather give an equilibrium mixture of weakly bound TMA adduct and methylborate-bound zirconocene cation.

The mechanism of carboalumination must accommodate first-order olefin dependence under all conditions and reaction orders approaching 2 in [Zr] and −2 in [Al]. Hoveyda[14] observed a similar second-order dependence in [Zr] for carbometalations with diethylmagnesium and proposed a rate-determining step involving two zirconocene centers. This seems unlikely for $Cp^*{}_2ZrMe_2$; thus we favor the mechanism described in Scheme 5. From our NMR studies of the catalytic intermediates we have determined that treatment of $Cp^*{}_2ZrMe_2$ with tris(pentafluorophenyl)borane gives ion pair **F**, which in the presence of TMA is slowly converted to a weakly bound adduct assigned tentatively as **G**. Since the rate of conversion of **F** to **G** is significantly slower than the rate of olefin conversion, the contribution of [**G**] to the overall rate can be assumed to be negligible. Although it has not been observed spectroscopically, the aluminum adduct **P** of the zirconocene cation is considered as a kinetically relevant species. Loss of ligand by either **F** or **P** would give the presumed active catalyst **Q**. Rate-limiting coordination of olefin by **Q** followed by rapid alkyl migration would give a new alkylzirconocene cation **S**.

A rate law for the mechanism shown in Scheme 5 can be derived. Here we have made the steady-state assumption for intermediates **Q** and **R** and have assumed both that the formation of **G** does not contribute significantly to the rate and that the total zirconium concentration ($[Zr]_0$) can be approximated by the sum of [**F**] and [**P**]. Using these assumptions, a rate law can

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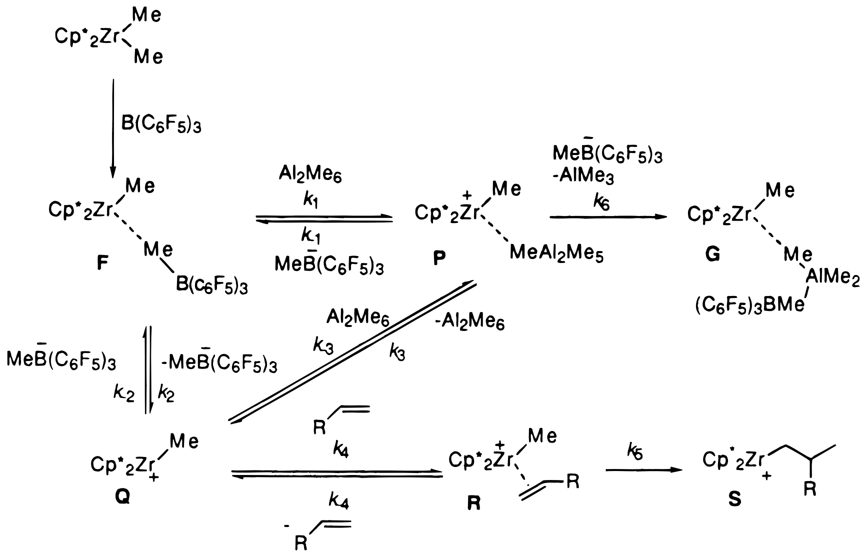
[58] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729−1742.

[59] It should be noted that, for catalysts $Cp^*{}_2ZrMe_2$ and $(EBTHI)ZrMe_2$, addition of TMA to the catalyst solution in toluene results in separation of the catalyst species as an immiscible oil which remains insoluble throughout the reaction, while in DCE the reaction remains homogeneous. Thus, for these catalysts the differences in reaction rate could be attributed in part to the inhomogeneity of the reaction medium.

Scheme 5. Proposed Mechanism for Carboalumination



be derived which has the form shown in eq 5 (see Supporting Information for derivation of the rate law).

$$\text{rate} = -\frac{d[\text{olefin}]}{dt} = k_4[\text{olefin}]\left[\frac{\dfrac{k_2 \frac{k_{-1}}{k_1}[\text{Zr}]_o^2}{[\text{Al}]} + k_3[\text{Zr}]_o}{\left(k_4 - \dfrac{k_4}{k_{-4}+k_5}\right)[\text{olefin}] + k_{-2}[\text{Zr}]_o + k_{-3}[\text{Al}]}\right] \quad (5)$$

While we have no information on the individual rate constants at this time or the validity of the mechanism in Scheme 5, the rate law of eq 5 provides a mechanistic rationale for the reaction orders determined experimentally. Depending on the relative rate constants, the order in [Zr] can approach 2, while the order in [Al] can approach −2. In the absence of TMA, interconversion of **F** and **Q** is moderately fast on the ^{1}H NMR time scale, so we can expect k_2 to be relatively large. Thus, it is possible that the $[\text{Zr}]_0^2$ term is large relative to $k_3[\text{Zr}]_0$, and if $k_{-2}[\text{Zr}]_0$ is small, then the reaction could approach second order in zirconium. At high [Al], the $[\text{Zr}]_0^2$ term would approach 0 and the aluminum dependence would approach −1, while at lower aluminum concentrations the aluminum dependence would approach −2. Equation 5 is also consistent with a first-order dependence of olefin if we assume that $k_{-3}[\text{Al}]$ is large.

The structural data obtained by ^{1}H NMR is consistent with the kinetic trends observed and provides some insight about the carboalumination selectivity of each catalyst. Precatalysts $\text{Cp*}_2\text{ZrMe}_2$ and $(\text{NMIn})_2\text{ZrMe}_2$ have high carboalumination activities and selectivities, while precatalyst $(\text{EBTHI})\text{ZrMe}_2$ has a significantly lower activity and selectivity for formation of carboaluminated products. The NMR analysis suggests that the difference in selectivity arises from the different manner in which $(\text{EBTHI})\text{ZrMe}_2$ interacts with trimethylaluminum. While **J** derived from $(\text{EBTHI})\text{ZrMe}_2$ rapidly forms a very stable trimethylaluminum adduct **K**, ion pairs **F** and **L** are slowly converted to a more stable adduct which retains catalytic activity. The stable adducts formed between trimethylaluminum- and EBTHI-derived zirconocene alkyl cations may result in low transmetalation rates, allowing higher oligomers to form. Since cationic zirconocenes derived from $\text{Cp*}_2\text{ZrMe}_2$ and $(\text{NMIn})_2\text{ZrMe}_2$ do not rapidly form stable adducts with trimethylaluminum, they retain high activities for olefin carboalumination. This weaker binding to TMA may also result in higher transmetalation rates and thus higher carboalumination selectivities.

Conclusion

A detailed investigation of the scope and mechanistic details of a catalytic carbometalation of olefins and dienes is reported. Zirconocenes derived from bis(pentamethylcyclopentadienyl) ligands provide efficient olefin carbometalation catalysts that give high yields with a wide variety of 1-alkenes. The system is also a highly selective diene cyclization catalyst capable of producing not only cyclopentanes but also six- and seven-membered rings as well as fused and spirocyclic structures. High diastereoselectivities are possible with substituted dienes leading, for example, to a highly diastereoselective formation of cyclopentanes containing chiral quaternary centers.

Comparison of the asymmetric version of this reaction with the system previously reported by Negishi shows that use of cationic zirconocene catalysts gives enantioselectivities similar to those obtained with the neutral system, but much higher rates. This high activity apparently leads to the slightly lower yields observed due to competing oligomer formation. The enantioselectivities are slightly lower than those reported by Negishi, but are still high for olefin insertion into a metal−methyl bond.

Characterization of the interaction of trimethylaluminum with the zirconocene cations of successful and unsuccessful carboalumination systems along with our kinetic data provides useful insights for further optimization of catalyst systems for enantioselective carboaluminations. A number of complex issues determine both chemo- and enantioselectivity for these carboalumination systems. The success of the NMIn system and the failure of the EBTHI system show that catalysts which form highly isotactic polyolefins will not necessarily make efficient carboalumination catalysts. While catalysts developed for the preparation of isotactic polyolefins may present convenient systems to explore, it is clear that the factors which govern product and stereoselectivity in polymerizations are significantly different than those in the carboalumination reaction. It is hoped that further structural and kinetic data will lead to more efficient and enantioselective catalyst systems.

Experimental Section

General Considerations. All reactions were run under an argon or nitrogen atmosphere using normal Schlenk techniques. Toluene was distilled from sodium/benzophenone, and chlorinated solvents were distilled from CaH_2 under nitrogen and stored in Straus flasks (Kontes Glassware). Deuterated solvents were treated in the same way as their protio analogues. Trimethylaluminum was purchased from Aldrich and used as received. (*S*)-(−)-Methoxy(trifluoromethyl)phenylacetyl chloride was prepared from the corresponding acid (Aldrich) by a literature procedure.[45] All other reagents and solvents were obtained commercially and used as received except as noted below. GC data was obtained on a HP5980 GC using an SE-30 column (30 m × 0.32 mm i.d. × 0.25 μm coating) with an FID detector. GC yields were determined by comparison of peak areas with an internal standard (decane) using response factors determined with authentic samples. Products were isolated by flash column chromatography using 200−400 mesh silica gel from Aldrich. The enantiomeric excess of alcohols was determined by ^1H and ^{19}F NMR analysis of the corresponding Mosher esters.[60] ^1H, ^{13}C, and ^{19}F NMR were obtained on a Varian Gemini 200 MHz or XL 400 MHz spectrometer. Peak positions are reported in ppm from TMS (0 ppm) and are referenced to added TMS or solvent peaks. ^{19}F NMR are reported in ppm from $CFCl_3$ (0 ppm) and were externally referenced to C_6F_6 (−164.9 ppm) or CF_3COOD (76.2 ppm). FTIR were obtained as thin films on Teflon film IR cards (3M) using a Perkin-Elmer series 1600 FTIR. Electron impact ionization was used for all samples. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Alkene Subtrates. All alkenes and dienes except those described below were purchased from Wiley, Aldrich, or Pfaltz-Bauer. Siloxy-protected alkenes were prepared from the commercially available hydroxyalkenes by literature methods.[61,62] Dienes were stirred over $LiAlH_4$ and then vacuum transferred or vacuum distilled. Dienes were stored in a nitrogen-filled glovebox (Vac Atmospheres or M. Braun Inc.) or in Teflon sealed flasks.

Preparation of 2-allylmethylenecyclohexane (3). 2-Allylcyclohexanone. Lithium diisopropylamide (6.043 g, 56.5 mmol) was dissolved in 100 mL of THF, and the mixture was cooled to −78 °C. Cyclohexanone (5.40 mL, 52.2 mmol) was added by syringe, and the reaction mixture was stirred for 30 min. The solution was then placed in a 0 °C bath and stirred for another 5 min. Allyl bromide (5.40 mL, 62.3 mmol) was then added in one portion. After 2 h an aliquot was removed and analyzed by GC. The reaction was approximately 60% complete, and a small diallyl peak was observed. After 4 h the reaction was quenched by pouring into 100 mL of saturated NH_4Cl solution. This mixture was extracted (3 × 50 mL) with ether, washed with brine, and then dried over $MgSO_4$. The solvent was removed under reduced pressure to yield a yellow oil, which was distilled at 0.15 Torr. The product distilled off at 26 °C and was >95% pure. Distillation gave 3.7688 g, 52% yield of 2-allylcyclohexanone. ^1H NMR ($CDCl_3$, 200 MHz): 5.61−5.78 (m, 1H), 5.02−4.92 (m, 2H), 2.37−2.55 (m, 1H), 2.22−2.34 (m, 3H), 1.79−2.14 (m, 4H), 1.52−1.68 (m, 2H), 1.18−1.41 (m, 1H).

Wittig Olefination of 2-Allylcyclohexanone. Methyltriphenylphosphonium bromide (8.2239 g, 23.0 mmol) was suspended in 60 mL of ether in a two-neck round-bottom flask under argon. Butyllithium, 2.0 M in hexanes (11.5 mL, 23.0 mmol), was added slowly to give a bright yellow solution. This solution was stirred for 4 h, and then 2-allylcylcohexanone (3.2077 g, 23.2 mmol) was added dropwise to give a thick white suspension. The reaction mixture was heated at reflux overnight and then filtered to remove triphenylphosphine oxide. The filtrate was washed (3 × 75 mL) with water and dried over $MgSO_4$. The ether was removed to give a crude oil, which was flash chromatographed (eluted with hexanes) to give 2.527 g, 81% yield of **4**. ^1H NMR ($CDCl_3$, 200 MHz): 5.70−5.86 (m, 1H), 4.96−5.07 (m, 2H), 4.67 (s, 1H), 4.58 (s, 1H), 2.20−2.42 (m, 2H), 1.97−2.09 (m, 3H), 1.82−1.53 (m, 3H), 1.38−1.50 (m, 2H), 1.16−1.27 (m, 1H).

Preparation of 5-Methylene-1,8-nonadiene (15).[63] **1,8-Nonadien-5-one.** 4-Bromobutene and 4-pentenoyl chloride were coupled by a previously reported method.[64] 4-Bromobutenyl-1-magnesium chloride was formed from magnesium powder (1.3394 g, 55.1 mmol) and 4-bromo-1-butene (5.10 mL, 50.2 mmol) in refluxing THF (75 mL total volume). After complete consumption of 4-bromobutene, the reaction mixture was cooled to −78 °C. In an addition funnel, 4-pentenoyl chloride (5.735 g, 48.4 mmol) was diluted with 30 mL of THF. This solution was slowly added to the Grignard solution at such a rate as to keep the temperature below −65 °C. After addition, the reaction mixture was slowly allowed to warm to rt. After 2 h, GC showed compete loss of acid chloride and a large product peak. The reaction was quenched by the addition of 20 mL of NH_4Cl solution. Dilute hydrochloric acid was added to dissolve magnesium salts, and the mixture was extracted (3 × 40 mL) with ether. The combined organics were dried with $MgSO_4$, and the solvent was removed to give a yellow oil. This material was pure by NMR and was used without further purification. Recovered: 6.2929 g, 94% yield of the dienone. ^1H NMR ($CDCl_3$, 200 MHz): 5.70−5.94 (m, 2H), 4.95−5.08 (m, 4H), 2.49−2.56 (m, 4H), 2.31−2.44 (m, 4H).

Wittig Olefination of 1,8-Nonadien-5-one. Methylenetriphenylphosphine ylide was prepared from methyltriphenylphosphonium bromide (16.0886 g, 45 mmol) and butyllithium, 2.0 M in hexanes (22.5 mL, 45 mmol). This was reacted with 1,8-nonadien-5-one (6.2929 g, 45.5 mmol) as described above. After workup and chromatography, 2.4088 g (40%) of **15** was recovered. This was distilled at 57 °C (35 mmHg). ^1H NMR ($CDCl_3$, 200 MHz): 5.73−5.90 (m, 2H), 4.92−5.08 (m, 4H), 4.76 (s, 2H), 2.08−2.22 (m, 8H).

3-Allyl-1-methylenecyclohexane (13). 3-Allylcyclohexanone. Cyclohex-2-enone was allylated by the method of Lipshutz.[65] Methyllithium, 1.4 M in ether (193 mL, 0.270 mol), was dissolved in 200 mL of THF at −78 °C. To this was added allyltributyltin (83.3 mL, 0.269 mol), and the mixture was stirred for 15 min at −78 °C. In another flask, copper(I) iodide (51.4456 g, 0.270 mol) and lithium bromide (23.570 g, 0.272 mol) were dissolved in 300 mL of THF, and the mixture was cooled to −78 °C. The allyllithium solution was added to the copper solution via a precooled cannula, giving a dark orange solution. To this were added trimethylsilyl chloride (22.0 mL, 0.271 mol) and cyclohexenone (8.6 mL, 0.090 mol). The reaction

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mixture was stirred at −78 °C for 1 h and then allowed to warm to room temperature. The reaction was quenched by the addition of 200 mL of saturated NH_4Cl solution. The resulting mixture was extracted with ether (3 × 200 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was removed to give a yellow oil. The oil was dissolved in 250 mL of THF and treated with a 75% aqueous solution of tetrabutylammonium fluoride (100 mL, 0.270 mol). After 15 min of stirring, the mixture was taken up in 500 mL of ether, the water layer was removed, the organic layer was dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The product was distilled (main fraction bp 35 °C at 0.2 mmHg), giving the product in 85% purity with the major contaminant identified as methyltributyltin. This material was used without further purification. ^{1}H NMR ($CDCl_3$, 200 MHz): 5.61−5.84 (m, 1H), 5.04 (brs, 1H), 4.96−4.98 (m, 1H), 2.43−2.24 (m, 3H), 2.21−1.97 (m, 4H), 1.88−1.94 (m, 2H), 1.50−1.74 (m, 1H), 1.20−1.43 (m, 1H).

3-Allyl-1-methylenecyclohexane. Wittig Olefination of 3-Allylcyclohexanone. Methylenetriphenylphosphine ylide was prepared from methyltriphenylphosphonium iodide (25.0705 g, 62.1 mmol) and butyllithium, 2.5 M in hexanes (25 mL, 62.5 mmol). The olefination was carried out as described above on 3-allylcyclohexanone (7.25 g, 52.5 mmol). After chromatography the material was distilled at 110−115 °C. Recovered: 3.23 g (45%) of 3-allyl-1-methylenecyclohexane (**13**). ^{1}H NMR ($CDCl_3$, 200 MHz): 5.69−5.89 (m, 1H), 4.96−5.06 (m, 2H), 4.61 (s, 2H), 2.35−2.19 (m, 2H), 2.04−1.94 (m, 3H), 1.88−1.64 (m, 3H), 1.58−1.20 (m, 2H), 1.20−1.00 (m, 1H). ^{13}C NMR (50 MHz): 149.23, 137.19, 115.62, 107.07, 41.33, 41.15, 38.93, 35.04, 32.21, 26.95.

Zirconocene Dimethyl Complexes. Zirconocene complexes $Cp^*_2ZrMe_2$[66,67] and (EBTHI)$ZrMe_2$[48,49] were prepared according to literature procedures. Tris(pentafluorophenyl)borane was prepared as described by Massey.[68]

Bis(1-(−)-Neomenthylindenyl) Dimethylzirconium (C). The zirconocene dichloride complex was prepared by the method of Erker.[37] The zirconocene dichloride (1.3183 g, 1.97 mmol) was dissolved in 75 mL of THF and cooled to −78 °C. Methyllithium, 1.4 M in hexanes (3 mL, 4.20 mmol), was added, and the reaction mixture was stirred at −78 °C for 30 min. The reaction mixture was then allowed to warm to room temperature and stirred at rt for 2 h. The solvent was removed under vacuum, and the remaining residue was extracted with hot hexanes (3 × 50 mL). The hot extracts were filtered through a Celite-covered frit to give a brown solution. This was concentrated and placed in a freezer overnight to give a tan powder. The solvent was removed via cannula, and the remaining solid was dissolved in fresh hexanes (50 mL) and heated until the solid was completely dissolved. The solution was allowed to cool and then placed in a freezer. Large, pale-yellow needles formed. The solvent was removed and the crystals were dried under vacuum to give 695.7 mg (56% yield) of **C**. ^{1}H NMR (CD_2Cl_2, 400 MHz): 7.66 (d, J = 8.59 Hz, 2H), 7.24 (d, J = 8.51, 2H), 7.17−7.13 (m, 2H), 7.03−7.00 (m, 2H) 6.13 (d, J = 3.05 Hz, 2H), 5.87 (d, J = 3.29 Hz, 2H), 3.52−3.50 (m, 2H), 2.10−1.99 (m, 2H), 1.95−1.85 (m, 2H) 1.72−1.54 (m, 4H), 1.48−1.35 (m, 2H) 1.33−1.25 (m, 2H) 1.13−1.05 (m, 2H) 1.04 (d, J = 6.65 Hz, 6H), 0.65 (d, J = 6.17 Hz, 6 H), 0.19 (d, J = 6.31 Hz, 6 H), −1.64 (s, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz): 126.23, 125.16, 125.08, 123.77, 123.72, 123.33, 121.85, 111.60, 93.62, 47.92, 39.73, 39.24, 35.70, 33.86, 29.30, 28.89, 23.86, 22.54, 22.33, 18.76. Elemental anal. Calcd for $C_{40}H_{56}Zr$: C, 76.49; H, 8.99. Found: C, 76.19; H, 9.14.

[6,6′-Dimethyl-2,2′-bis(5,6,7,8-tetrahydroinden-2-yl)-biphenyl] Dimethylzirconium (E). 6,6′-Dimethyl-2,2′-bis(5,6,7,8-tetrahydroinden-2-yl)biphenylzirconium dichloride was prepared as described by Bosnich et al.[40] The dichloride (825.4 mg, 1.43 mmol) was dissolved in 40 mL of THF under nitrogen, and the mixture was cooled to −78 °C. Methyllithium, 1.4 M in ether (2.25 mL, 3.15 mmol), was added via syringe, causing the color to change from yellow to orange. After 15 min at −78 °C, the reaction mixture was allowed to warm to room temperature. After 2 h, the solvent was removed under reduced pressure to give a pale yellow solid. The solid was taken up in hot hexanes (50 mL) and filtered through a Celite-covered frit. This process was repeated three times to give a colorless solution. The solution was concentrated to 30 mL and heated to redissolve some precipitate. The solution was placed in a freezer overnight to give the product as white needles. The solvent was decanted and the crystals were dried in vacuo to give 407 mg (53%) of fine needles. ^{1}H NMR (toluene-d_8, 400 MHz): 7.27 (d, J = 7.70 Hz, 2H), 6.98 (t, J = 7.64 Hz, 2H), 6.91 (d, J = 7.26 Hz, 2H), 6.07 (d, J = 2.44 Hz, 2H), 4.07 (d, J = 2.68 Hz, 2H), 2.55−2.74 (m, 4H), 2.11−2.29 (m, 4H), 1.79 (s, 6H), 1.67−1.70 (m, 4H), 1.38−1.52 (m, 4H), −0.32 (s, 6H). Also observed:hexane of crystallization (0.33 mol/mol of Zr). ^{13}C NMR (toluene-d_8, 100 MHz): 137.32, 136.21, 133.31, 129.27, 128.12, 127.44, 125.63, 124.20, 119.59, 108.76, 108.13, 43.63, 25.07, 24.10, 23.32 (2C), 20.00. Recrystallization of this material always resulted in the inclusion of solvent that could not be removed under vacuum; thus, elemental analyses could not be obtained.

Carboalumination Reactions. General Procedure for Carboalumination Reactions. In a drybox the zirconocene dimethyl (0.125 mmol) and $B(C_6F_5)_3$ (0.125 mmol) were placed in a 50 mL Schlenk tube and were dissolved in 5 mL of solvent to give a bright yellow or orange solution. Trimethylaluminum (5.0 mmol) was then added to the catalyst solution. The substrate (2.50 mmol) and decane (0.2 mL) were dissolved in 25 mL of solvent, and the apparatus was brought out of the drybox and attached to a vacuum/argon manifold. The catalyst solution was cooled to 0 °C for reactions run in toluene and left at room temperature for those run in chlorinated solvents. The olefin solution was added dropwise to the catalyst over 30 min. After addition was completed, the reaction was monitored by GC until all starting material had been consumed. To obtain hydrolyzed products the reaction was quenched at this point with 10 mL of dilute HCl while the mixture was cooled at 0 °C (**CAUTION**: hydrolysis is very exothermic!) and isolated as described below.

Oxidation Procedure. After complete consumption of the substrate, the reaction flask was cooled to 0 °C and oxygen was bubbled through the reaction mixture. After 1 h, the flask was sealed and stirred at room temperature for several hours. The reaction was quenched with either a 10% hydrochloric acid or a 10% sodium hydroxide solution (10 mL). The quenched mixture was extracted with ether (3 × 10 mL). The combined organic layers were dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure to leave a colored oil. Products were purified on silica gel columns eluted first with hexane (100 mL) and then with 15% ethyl acetate in hexane. Removal of solvent gave products as oils in >95% purity by GC.

(3-Methylcyclopentyl)methanol (2a).[32] The ^{1}H and ^{13}C NMR spectra and GC retention time of this material were identical to those of the previously reported product. Enantiomeric excess of **2a** produced by (NMIn)$_2$ZrMe$_2$ was determined by ^{1}H NMR of the methyl group of the Mosher ester.[60] Enantiomeric excess = 79% for the trans diastereomer and 45% for the cis diastereomer.

(3-Methylcyclohexyl)methanol (2b).[32] The ^{1}H and ^{13}C NMR spectra and GC retention time of this material were

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identical to those of the previously reported product. Enantiomeric excess of **2b** produced by (NMIn)$_2$ZrMe$_2$ was determined by ^{1}H NMR of the methyl group of the Mosher ester.[60] Enantiomeric excess = 68% for the cis diastereomer and 60% for the trans diastereomer.

(3-Methylcycloheptyl)methanol (2c).[32] The ^{1}H and ^{13}C NMR spectra and GC retention time of this material were identical to those of the previously reported product.

(1,3-Dimethylcyclopentyl)methanol (4a).[32] The ^{1}H and ^{13}C NMR spectra and GC retention time of this material were identical to those of the previously reported product. The Mosher ester of **4a** produced by (NMIn)$_2$ZrMe$_2$ was prepared[60] and analyzed by ^{1}H, ^{19}F, and ^{13}C NMR. The NMR spectra did not give resolved peaks for the diastereomers of the Mosher ester, so the enantiomeric excess could not be determined.

(1-Ethyl-3-methylcyclopentyl)methanol (4b).[32] The ^{1}H and ^{13}C NMR spectra and GC retention time of this material were identical to those of the previously reported product.

(3,3,5-Trimethyl-3-silacyclohexyl)methanol (6).[32] The ^{1}H and ^{13}C NMR spectra and GC retention time of this material were identical to those of the previously reported product.

(5-Methyl-1-phenylpiperidin-3-yl)methanol (8).[32] The ^{1}H and ^{13}C NMR spectra and GC retention time of this material were identical to those of the previously reported product.

(3-*tert*-Butyldimethylsiloxy-5-methylcyclohexyl)methanol (10).[32] The ^{1}H and ^{13}C NMR spectra and GC retention time of this material were identical to those of the previously reported product.

(9-Methylbicyclo[4.3.0]cyclonon-7-yl)methanol (12). ^{1}H NMR (CDCl$_3$, 400 MHz): 3.58−3.61 (dd, *J* = 4.75, 10.35 Hz, 1H, major diastereomer), 3.40−3.45 (dd, *J* = 7.52, 10.35 Hz, 1H, major diastereomer), 3.38−3.52 (m, 2H, minor diastereomer), 2.03−2.17 (m, 1H), 1.91−2.02 (m, 1H), 1.58−1.82 (m, 4 H), 1.40−1.58 (m, 4H), 1.22−1.38 (m, 2H), 1.03−1.17 (m, 1H), 0.91 (d, *J* = 6.65 Hz, 3H, minor diastereomer), 0.88 (d, *J* = 6.91 Hz, 3H, major diastereomer). ^{13}C NMR (CDCl$_3$, 100 MHz): major diastereomer, 67.38, 44.20, 42.20, 41.09, 37.17, 34.72, 26.44, 25.42, 22.75, 21.53, 15.05; minor diastereomer, 67.47, 45.58, 45.44, 41.24, 36.38, 34.40, 29.27, 25.85, 24.72, 22.35, 19.81. Elemental anal. Calcd for C$_{11}$H$_{20}$O: C, 78.50; H, 11.98. Found: C, 78.48; H, 11.87.

(8-Methylbicyclo[4.3.0]cyclonon-1-yl)methanol (14). ^{1}H NMR (CDCl$_3$, 400 MHz): 3.60−3.62 (m, 1H, major diastereomer), 3.48−3.53 (m, 1H, minor diastereomer), 3.36−3.41 (m, 1H, minor diastereomer), 3.31−3.36 (m, 1H, major diastereomer), 2.18−2.29 (m, 1H, major diastereomer), 1.98−2.10 (m, 1H, minor diastereomer), 1.77−1.90 (m, 2H), 1.67−1.75 (m, 1H), 1.22−1.55 (m, 8H), 1.05 (d, *J* = 7.26 Hz, 3H, minor diastereomer), 1.00 (d, *J* = 7.85 Hz, 3H, major diastereomer), 0.85−0.93 (m, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz): major diastereomer, 68.98, 46.40, 43.91, 42.59, 39.16, 37.81, 30.49, 28.59, 26.17, 23.02, 21.88; minor diastereomer, 68.78, 46.40, 43.91, 42.59, 40.51, 39.02, 30.86, 29.39, 27.30, 22.62, 21.83. Elemental anal. Calcd for C$_{11}$H$_{20}$O: C, 78.51; H, 11.98. Found: C, 78.42; H, 11.66.

(7-Methylspiro[4.4]cyclonon-2-yl)methanol (16). ^{1}H NMR (CDCl$_3$, 400 MHz): 3.50−3.52 (m, 2H), 2.16−2.22 (m, 1H), 1.96−2.07 (m, 1H), 1.75−1.82 (m, 2H), 1.66−1.72 (m, 2H), 1.48−1.60 (m, 6H), 1.28−1.37 (m, 1H), 1.11−1.22 (m, 2H), 0.98 (d, *J* = 6.65 Hz, 3H, diastereomer A), 0.97 (d, *J* = 6.65 Hz, 3H, diastereomer B). ^{13}C NMR (CDCl$_3$, 100 MHz): diastereomer A, 68.16, 51.24, 48.84, 43.72, 41.63, 39.81, 39.68, 34.32, 33.62, 28.49, 21.53; diastereomer B, 68.16, 51.24, 48.92, 43.72, 41.57, 40.07, 39.63, 34.35, 34.06, 28.33, 21.53. Elemental anal. Calcd for C$_{11}$H$_{20}$O: C, 78.51; H, 11.98. Found: C, 78.30; H, 12.02.

2-Methyl-3-(3-methylenecyclohexyl)propan-1-ol (18). ^{1}H NMR (CDCl$_3$, 200 MHz): 4.58 (brs, 2H), 2.51−3.43 (dd, *J* = 5.53, 10.46 Hz, 1H), 3.40−3.31 (dd, 6.69, 10.35 Hz, 1H), 2.13−2.35 (m, 2H), 1.90−2.05 (m, 2H), 1.50−1.87 (m, 4H), 1.34−1.50 (m, 1H), 1.21−1.33 (m, 2H), 0.94−1.08 (m, 1H), 0.89 (d, *J* = 6.59 Hz, 3H), 0.88 (d, 6.77 Hz, 3H). ^{13}C NMR (CDCl$_3$, 50 MHz): diastereomer A, 149.28, 106.83, 68.42, 42.48, 40.26, 36.14, 35.03, 32.51, 32.00, 26.90, 16.68; diastereomer B, 149.16, 106.92, 68.42, 41.24, 40.26, 36.18, 35.03, 33.36, 32.51, 26.98, 16.72.

2-Methyl-1-hexanol (20).[32,34] The ^{1}H NMR spectrum and GC retention time of this material are identical to those of the previously reported product. The enantiomeric excess of **20** produced by (NMIn)$_2$ZrMe$_2$ was determined to be 55% by ^{19}F NMR of the trifluoromethyl group of the Mosher ester.[60] $[\alpha]^{25}_{D} = +8.6$ ($c = 0.49$, CH$_2$Cl$_2$). Literature value for (2*S*)-2-methyl-1-hexanol: $[\alpha]^{25}_{D} = -12.7$ (15.9, diethyl ether).[38]

2-Methyl-3-phenylpropan-1-ol (22).[34] The ^{1}H and ^{13}C NMR spectra of this material were identical to those of the previously reported product. The enantiomeric excess of **22** produced by (NMIn)$_2$ZrMe$_2$ was determined by ^{1}H and ^{19}F NMR of the Mosher ester.[60] Enantiomeric excess = 66%. $[\alpha]^{25}_{D} = +11.1$ ($c = 0.82$, CH$_2$Cl$_2$). Literature value for (2*S*)-2-methyl-3-phenylpropan-1-ol: $[\alpha]^{25}_{D} = -11.02$ ($c = 2.75$, C$_6$H$_6$).[39]

2-Methyl-3-(4-*tert*-butyldimethylsiloxy-3-methoxyphenyl)propan-1-ol (24). ^{1}H NMR (CDCl$_3$, 200 MHz): 6.76 (d, *J* = 7.97 Hz, 1H), 6.58−6.66 (m, 2H), 3.79 (s, 3H), 3.40−3.60 (m, 2H), 2.61−2.71 (dd, *J* = 6.53, 13.45 Hz, 1H), 2.30−2.44 (dd, *J* = 7.87, 13.51 Hz, 1H), 1.82−2.00 (m, 1H), 0.99 (s, 9H), 0.90 (d, *J* = 6.78 Hz, 3H), 0.14 (s, 6H). ^{13}C NMR (CDCl$_3$, 50 MHz): 150.63, 143.05, 134.05, 121.20, 120.26, 113.00, 67.74, 55.45, 39.47, 37.86, 26.71, 18.41, 16.52, −4.68. Elemental anal. Calcd for C$_{17}$H$_{30}$O$_3$Si: C, 65.76; H, 9.74. Found: C, 66.05; H, 9.98.

4-(*tert*-Butyldimethysiloxy)-2-methylpentan-1-ol (26).[69] ^{1}H NMR (CDCl$_3$, 400 MHz): 3.80−4.15 (m, 1H), 3.29−3.51 (m, 2H) 1.70−2.00 (m, 1H), 1.43−1.65 (m, 2H) 1.13, 1.20 (t, *J* = 6.95, 6.23 Hz, 3H), 0.85−0.95 (m, 12H), 0.08 (s, major diastereomer, 6H), 0.06 (s, minor diastereomer, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz): major diastereomer, 68.57, 67.48, 43.67, 31.77, 25.87, 24.67, 18.30, 16.94, −4.61, −4.96; minor diastereomer, 68.75, 66.83, 44.42, 32.64, 27.79, 22.51, 18.06, 14.23, −4.13, −4.71. FTIR: 3344.0, 2956.6, 2858.1, 1463.2, 1375.0, 1254.0, 1158.5, 1131.6, 1070.4, 1043.2, 835.2, 806.7, 774.4 cm^{-1}. Elemental anal. Calcd for C$_{12}$H$_{28}$O$_2$Si: C, 62.01, H, 12.14. Found: C, 61.65, H, 12.27.

2-Methyl-3-phenylpentan-1-ol (28). ^{1}H NMR (CDCl$_3$, 200 MHz): 7.11−7.29 (m, 5H), 3.40−3.60 (m, 2H), 3.52−3.63 (m, 1H), 1.81−1.98 (m, 1H), 1.62−1.81 (m, 3H), 0.72−0.78 (m, 6H). ^{13}C NMR (CDCl$_3$, 50 MHz): 142.73, 128.79 (2C), 127.96 (2C), 125.96, 66.35, 48.92, 40.27, 25.78, 13.78, 12.42.

2,3-Dimethylpentan-1-ol (30). ^{1}H NMR (CDCl$_3$, 200 MHz): 3.33−3.62 (m, 2H), 1.62−1.78 (m, 1H), 1.60−1.00 (m, 3H), 0.74−0.90 (m, 9H). ^{13}C NMR (CDCl$_3$, 50 MHz): major diastereomer, 66.73, 39.09, 35.04, 27.50, 1.89, 11.96, 11.24; minor diastereomer, 66.00, 40.37, 36.26, 25.28, 16.35, 13.62, 11.84.

2,4-Dimethylpentan-1-ol (38).[34] The ^{1}H and ^{13}C NMR spectra of this material were identical to those of the previously reported product. The enantiomeric excess of **38** produced by (NMIn)$_2$ZrMe$_2$ was determined by ^{19}F NMR of the trifluoromethyl group of the Mosher ester.[60] Enantiomeric excess = 63%.

2-Methyl-10-(*tert*-butyldimethylsiloxy)decan-1-ol (40). ^{1}H NMR (CDCl$_3$, 400 MHz): 3.60 (t, *J* = 6.63 Hz, 2H), 3.49−3.53 (dd, *J* = 5.76, 10.48 Hz, 1H), 3.39−3.43 (dd, *J* = 6.57, 10.46 Hz, 1H), 1.55−1.63 (m, 1H), 1.47−1.53 (m, 2H), 1.34−1.41 (m, 1H), 1.28 (brs, 11H), 1.06−1.15 (m, 1H), 0.91 (d, *J* = 6.72 Hz, 3H), 0.90 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz): 68.38, 63.31, 35.74, 33.11, 32.84, 29.85, 29.58, 29.40, 26.95, 25.96 (3C), 25.77, 18.35, 16.56, −5.29. Elemental anal.

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[69] White, J. D.; Amedio, J. C., Jr. *J. Org. Chem.* **1989**, *54*, 736−738.

Calcd for $C_{17}H_{38}O_2Si$: C, 67.48; H, 12.66. Found: C, 67.39; H, 12.56. The enantiomeric excess of **40** produced by $(NMIn)_2ZrMe_2$ was determined by ^{19}F NMR of the trifluoromethyl group of the Mosher ester.[60] Enantiomeric excess = 53%.

Kinetics Experiments. In the drybox, zirconocene dimethyl complex (0.025 mmol) and tris(pentafluorophenyl)borane (0.025 mmol) were weighed into a vial and dissolved in 0.625 mL of solvent. To this were added trimethylaluminum (96 μL, 1.0 mmol) and mesitylene (21 μL, 0.15 mmol). The resulting solution was transferred to an NMR tube and sealed with a septum. The sample was taken to the NMR and shimmed and then removed from the instrument. Olefin (0.5 mmol) was added via syringe, and the tube was shaken and quickly returned to the NMR. After reshimming the magnet, spectra were taken periodically until the olefin was mostly consumed. The concentration of olefin was determined by comparing the normalized integration of isolated olefin peaks (vinyl peaks for 1,5-hexadiene and allyl peaks for allylbenzene) with those of the mesitylene internal standard. From the ratio of olefin to mesitylene, the olefin concentration was determined. Plots of ln([olefin]) vs time gave the first-order rate. Rate constants were determined from the average of at least two independent experiments.

Reactions involving 1,5-hexadiene and catalysts $Cp^*{}_2ZrMe_2$ or $(NMIn)_2ZrMe_2$ occurred too quickly under the conditions described above to be observed with reasonable accuracy. For these systems, the reactions were run with 0.0125 mmol (0.016 M) of zirconocene and borane with all other conditions identical. Reaction rate constants at standard conditions (0.032 M zirconocene) were extrapolated from the values measured using the apparent reaction order determined over this concentration range.

Determination of [Zr] and [Al] Effects upon Reaction Rate. Reactions to determine the affect of changing [Zr] or [Al] were run exactly as described for the determination of reaction half-life. Catalyst $Cp^*{}_2ZrMe_2$ was used as the catalyst, allylbenzene was used as the olefin, and DCE-d_4 was used as the solvent. Duplicate reactions were run with [Zr] values of 0.016, 0.032, and 0.064 M, while [Al] was kept constant at 1.27 M. A second series of duplicate reactions were run with a constant [Zr] of 0.032 M and [Al] values of 0.64, 1.27, and 2.54 M.

NMR Characterization of Catalytic Intermediates. [Bis(pentamethylcyclopentadienyl) Methylzirconium] [Methyltris(pentafluorophenyl)borate] (F). In a drybox, dimethylzirconocene **A** (19.8 mg, 0.05 mmol) and tris(pentafluorophenyl)borane (25.6 mg, 0.05 mmol) were placed in a small vial and dissolved in 0.5 mL of CD_2Cl_2 to give an orange solution. ^1H NMR (400 MHz): 2.04 (brs, 30 H), 1.89 (brs, 3H), 0.48 (brs, 3H). ^1H NMR (CD_2Cl_2, 400 MHz, −30 °C): 2.05, 1.98 (s, 1:1.3, 30H), 1.90, 1.88 (s, 1:1, 3H), 0.44 (s, 3H).

[Bis(pentamethylcyclopentadienyl) Methylzirconium] [Tetrakis(pentafluorophenyl)borate] (H). In a drybox, dimethylzirconocene **A** (9.8 mg, 0.025 mmol) and triphenylmethyl tetrakis(pentafluorophenyl)borate (23.1 mg, 0.025 mmol) were dissolved in 0.5 mL of CD_2Cl_2 to give a red-orange solution. ^1H NMR (CD_2Cl_2, 400 MHz): 2.04 (s, 30 H).

[Ethylenebis(tetrahydroindenyl) Methylzirconium] [Methyltris(pentafluorophenyl)borate] (J). In a drybox, dimethylzirconocene **B** (19.5 mg, 0.05 mmol) and tris(pentafluorophenyl)borane (25.6 mg, 0.05 mmol) were placed in a small vial and dissolved in 0.5 mL of CD_2Cl_2 to give a yellow solution. ^1H NMR (CD_2Cl_2, 400 MHz, −20 °C): 6.77 (d, J = 2.38 Hz, 1H), 5.85 (d, J = 2.51 Hz, 1H), 5.61 (d, J = 2.75 Hz, 1H), 5.48 (d, J = 2.44 Hz, 1H), 3.09−3.12 (m, 2H), 2.89−2.93 (m, 2H), 2.78−2.85 (m, 2H), 2.51−2.73 (m, 4H), 2.23−2.32 (m, 2H), 2.01−2.10 (m, 1H), 1.70−1.89 (m, 4H), 1.53−1.66 (m, 1H), 1.25−1.48 (m, 4H), 0.71 (s, 3H), 0.12 (brs, 3H).

[Bis(1-(−)-neomenthylindenyl Methylzirconium] [Methyltris(pentafluorophenyl)borate] (L). In a drybox, dimethylzirconocene **C** (19.5 mg, 0.05 mmol) and tris(pentafluorophenyl)borane (25.6 mg, 0.05 mmol) were placed in a small vial and dissolved in 0.5 mL of CD_2Cl_2 to give a red solution. ^1H NMR (CD_2Cl_2, 400 MHz): 7.75 (d, J = 8.55 Hz, 2H), 7.65 (d, J = 8.48 Hz, 2H), 7.36 (t, J = 6.51, 8.31 Hz, 2H), 7.19 (t, J = 7.26, 8.00 Hz, 2H), 6.71 (s, 2H), 5.85 (s, 2H), 3.70−3.72 (m, 2H), 2.10−2.15 (m, 3H), 1.95−1.93 (m, 2H), 1.48−1.62 (m, 4H), 1.22−1.40 (m, 4H), 0.95−1.15 (m, 1H), 1.03 (d, J = 6.35 Hz, 6H), 0.64 (d, J = 6.48 Hz, 6H), 0.53 (brs, 3H), 0.24 (s, 3H), 0.02 (d, J = 6.41 Hz, 6H).

[Bis(pentamethylcyclopentadienyl) Methylzirconium] [Methyltris(pentafluorophenyl)borate]−Trimethylaluminum Adduct (G). In a drybox, dimethylzirconocene **A** (19.8 mg, 0.05 mmol) and tris(pentafluorophenyl)borane (25.6 mg, 0.05 mmol) were placed in a small vial and dissolved in 0.5 mL of CD_2Cl_2 to give an orange solution. To this solution was added trimethylaluminum (96 μL, 1.0 mmol, 20 equiv) to give a yellow solution. Slow conversion to **G** was observed over several hours. Complete conversion required in excess of 8 h. ^1H NMR (CD_2Cl_2, 400 MHz): 1.98 (s, 3H), 1.89 (s, 30 H), 0.78 (s, 9H). ^{13}C NMR (100 MHz): 148.85−151.52 (d, $^1J_{C-F}$ = 236.7 Hz, 2C), 140.37−142.98 (d, $^1J_{C-F}$ = 254.4 Hz, 1C), 135.71−138.64 (d, 236.4 Hz, 2C), 122.99, 44.00−44.50 (brs), 14.50−16.00 (brs), 11.90. A NOESY 2-D NMR was taken of the sample using a delay time of 18 s (T_1 calculated to be 5.3 s by inversion recovery). Off-diagonal resonances were observed between the resonances at 1.98 and 1.89 ppm and between the 0.78 ppm peak and the excess TMA peak at −0.25 ppm.

[Bis(pentamethylcyclopentadienyl) Methylzirconium] [Tetrakis(pentafluorophenyl)borate]−Trimethylaluminum Adduct (I). In a drybox, dimethylzirconocene **A** (19.8 mg, 0.05 mmol) and triphenylmethyl tetrakis(pentafluorophenyl)borate (46.2 mg, 0.05 mmol) were dissolved in 0.5 mL of CD_2Cl_2 to give a red-orange solution. To this was added trimethylaluminum (96 μL, 1.0 mmol) to give **I** after 15 min. ^1H NMR (CD_2Cl_2, 400 MHz): 2.08 ppm (s, 30H)

[Ethylenebis(tetrahydroindenyl)zirconium Bis(μ-methyl)aluminumdimethyl] [Methyltris(pentafluorophenyl)borate] (K). In a drybox, dimethylzirconocene **B** (29.1 mg, 0.075 mmol) and tris(pentafluorophenyl)borane (38.4 mg, 0.075 mmol) were placed in a small vial and dissolved in 0.5 mL of CD_2Cl_2 to give a yellow solution. To this was added trimethylaluminum (14 μL, 0.15 mmol). Complete conversion to **K** was observed after 10 min. ^1H NMR (CD_2Cl_2, 300 MHz): 6.22 (d, J = 2.75 Hz, 2H), 5.67 (d, J = 2.81 Hz, 2H), 3.48−3.58 (m, 2H), 2.23−2.38 (m, 2H), 2.92−3.04 (m, 2H), 2.80−2.92 (m, 4H), 2.41−2.62 (m, 4H), 1.74−1.82 (m, 4H), 1.53−1.72 (m, 4H), 0.50 (s, 3H), 0.44 (s, 6H), −0.59 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 147.04−150.72 (d, $^1J_{C-F}$ = 241.1 Hz, 2C), 139.41 (s), 136.18−139.83 (d, $^1J_{C-F}$ = 243.3 Hz, 2C), 136.55 (s), 134.993−138.75 (d, $^1J_{C-F}$ = 242.6 Hz), 129.52 (brs, C−B), 126.84 (s), 116.00 (d, $^1J_{C-H}$ = 175.8 Hz), 113.29 (d, $^1J_{C-H}$ = 173.4 Hz), 36.30 (q, $^1J_{C-H}$ = 112.5 Hz), 30.70 (t, J = 129.5 Hz), 24.66, 24.08, 22.49, 21.91 (overlapping peaks, $^1J_{C-H}$ could not be determined), −7.14 (q, $^1J_{C-H}$ = 114.3 Hz).

[Bis(1-(−)-neomenthylindenyl Methylzirconium] [Methyltris(pentafluorophenyl)borate]−Trimethylaluminum Adduct (M). In a drybox, dimethylzirconocene **C** (19.5 mg, 0.05 mmol) and tris(pentafluorophenyl)borane (25.6 mg, 0.05 mmol) were placed in a small vial and dissolved in 0.5 mL of CD_2Cl_2 to give a red solution. To this solution was added trimethylaluminum (96 μL, 1.0 mmol), which resulted in a darkening of the solution. Monitoring by ^1H NMR showed slow conversion to **M**, which was complete after approximately 8 h. ^1H NMR (CD_2Cl_2, 400 MHz): 7.67−7.74 (m, 1H), 7.49 (d, J = 8.67 Hz, 1H), 7.39−7.42 (m, 1H), 7.32−7.35 (m, 1H), 7.23 (d, J = 8.57 Hz, 1H), 7.08−7.14 (m, 3H), 6.71 (d, J = 3.03 Hz, 1H), 6.41 (d, J = 3.27 Hz, 1H), 6.39 (d, J = 2.61 Hz, 1H), 5.90 (d, J = 3.03 Hz, 1H), 3.54−3.61 (m, 1H), 3.36−3.42 (m, 1H), 1.98−2.11 (m, 2H), 1.83−1.96 (m, 2H), 1.74−1.82 (m, 1H), 1.68−1.72 (m, 1H), 1.58−1.68 (m, 4H), 1.18−1.45 (m, 4H), 1.03−1.17 (m, 2H), 1.08 (d, J = 6.62, 3H), 1.02 (d, J = 6.58

Hz, 3H), 0.83−0.99 (m, 2H), 0.79 (s, 9H), 0.59−0.63 (m, 6H), 0.10−0.15 (m, 6H), −0.89 (s, 3H).

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Supporting Information Available: Derivation of rate law, plot of reaction order in Al, and ^{1}H NMR spectra of cations **J** and **L** and the $AlMe_3$ adducts (5 pages). Ordering information is given on any current masthead page.

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