1870 *Organometallics* **2000,** *19,* 1870−1878

Catalytic Carboalumination of Olefins with Cyclopentadienylamidotitanium Dichloride Complexes

Dan B. Millward, Adam P. Cole, and Robert M. Waymouth*

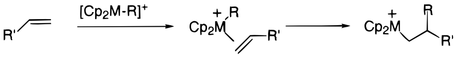
Department of Chemistry, Stanford University, Stanford, California 94305

Received September 7, 1999

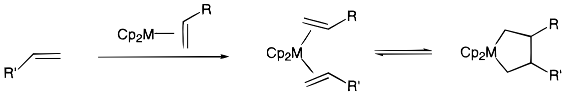
The half-sandwich metallocene η^5-$(C_5Me_4)SiMe_2N(tBu)TiCl_2$ reacts with a stoichiometric amount of dibutylmagnesium in tetrahydrofuran to form a robust monobutyl monochloride η^5-$(C_5Me_4)SiMe_2N(tBu)Ti(Bu)Cl$. X-ray crystallography reveals an undistorted η^1-butyl ligand. In the presence of an excess of triethylaluminum the dichloride η^5-$(C_5Me_4)SiMe_2N(tBu)TiCl_2$ serves as a catalyst for the carboalumination of olefins. The organometallic products of these reactions can be oxidized to 1,4-butanediols. The enantioselective carboalumination of allylbenzene by the chiral complex η^5-$(Ind)SiMe_2N[CH(Me)Ph]TiCl_2$, derived from (−)α-methylbenzylamine, affords 2-benzyl-1,4-butanediol in 53% yield and 28% enantiomeric excess.

Introduction

Group 4 metallocenes catalyze the carbometalation of alkenes and alkynes.[1−3] Mechanistic descriptions of these reactions fall into one of two classes; one involving olefin insertion into a metal−carbon bond (eq 1), the other a reductive coupling of olefins through the formation of a metallacycle (eq 2). The latter mechanism requires formation of a formally reduced metal center, which is believed to occur through β-hydride elimination and reductive elimination processes. The pathway followed depends on substrates, reagents, catalyst structure, and solvent.[4−9]



(1)



(2)

Complexes containing the cyclopentadienyl-amido (CpA) family of ligands have engendered considerable interest since their introduction by Bercaw,[10] especially as olefin polymerization catalysts.[11−17] These complexes form highly productive catalysts and generate polymers with higher molecular weights than those produced by bis(cyclopentadienyl) metallocenes; this tendency is typically attributed to a decreased tendency toward β-hydride elimination, a common chain transfer process with Ziegler−Natta catalysts.[18] The CpA ligands differ from their *ansa*-metallocene analogues in that they are formally 10- rather than 12-electron donors and tend to be more open about the metal center. As bis(cyclopentadienyl) metallocene complexes have proven sluggish in some carbometalation reactions;[19] we initiated studies on the reactivity and catalytic behavior of $CpATiCl_2$ complexes with metal alkyls and α-olefins. Here we report that these complexes are competent catalysts for the carboaluminations of olefins and exhibit reactivity consistent with both mechanistic classes of carbometalation reactions (eqs 1 and 2).

Results

The metallocene η^5-$(C_5Me_4)SiMe_2N(t\text{-}Bu)TiCl_2$ (**1**) (Figure 1) reacts cleanly and quantitatively with an equimolar amount of dibutylmagnesium (2 alkyl equivalents) in tetrahydrofuran to form η^5-$(C_5Me_4)SiMe_2N(t\text{-}Bu)Ti(Bu)Cl$ (**2**), as determined by ^1H NMR. Crystals of **2** suitable for X-ray diffraction studies were obtained from pentane; the resulting crystal structure is presented in Figure 2. The bonding and geometry of complex **2** is similar to previously characterized CpA complexes such

---

(1) Hoveyda, A.; Xu, Z. *J. Am. Chem. Soc.* **1991**, *113*, 5079−5080.

(2) Hoveyda, A.; Morken, J. P.; Houri, A. F.; Xu, Z. *J. Am. Chem. Soc.* **1992**, *114*, 6692−6697.

(3) Negishi, E.; Kondakov, D. Y.; Choueiry, D.; Kasai, K.; Takahashi, T. *J. Am. Chem. Soc.* **1996**, *118*, 9577−9588.

(4) Kondakov, D. Y.; Negishi, E.-i. *J. Am. Chem. Soc.* **1995**, *117*, 10771−10772.

(5) Kondakov, D. Y.; Negishi, E.-i. *J. Am. Chem. Soc.* **1996**, *118*, 1577−1578.

(6) Dzhemilev, U. M.; Ibragimov, A. G.; Zolotarev, A. P.; Muslukhov, R. R.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 2831−2841.

(7) Houri, A. F.; Didiuk, M. T.; Xu, Z.; Horan, N. R.; Hoveyda, A. *J. Am. Chem. Soc.* **1993**, *115*, 6614−6624.

(8) Shaughnessy, K. H.; Waymouth, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 5873−5874.

(9) Shaughnessy, K. H.; Waymouth, R. M. *Organometallics* **1998**, *17*, 5728−5745.

(10) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867−869.

(11) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587−2598.

(12) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649.

(13) Pannell, R. B.; Canich, J. A. M.; Hlatky, G. G. (Exxon) PCT Int. Appl. 94/00500, 1994.

(14) Rosen, R. K.; Nickias, P. N.; Devore, D. D.; Stevens, J. C.; Timmers, F. J. (Dow) U.S. Patent 5,274,696, 1994.

(15) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S.-y. (Dow) Eur. Pat. Appl. 416,815, 1991.

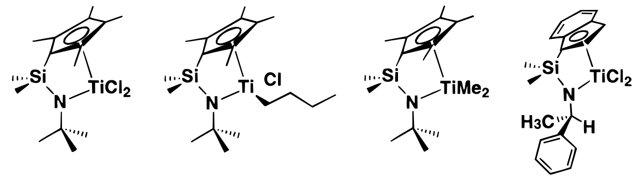
(16) Canich, J. A. M. (Exxon) Eur. Pat. Appl. 420,436, 1991.

(17) Canich, J. A. M. (Exxon) U.S. Patent 5,096,867, 1992.

(18) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Eng.* **1995**, *34*, 1143−1170.

(19) Knight, K.; Wang, D.; Waymouth, R. M.; Ziller, J. *J. Am. Chem. Soc.* **1994**, *116*, 1845.

10.1021/om990707y CCC: $19.00



1 **2** **3** **4**

Figure 1. Cyclopentadienyl−Amido Titanocenes **1**−**4**.

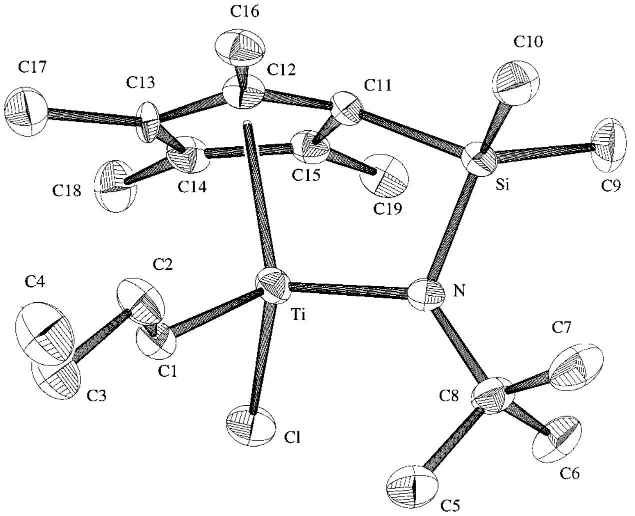
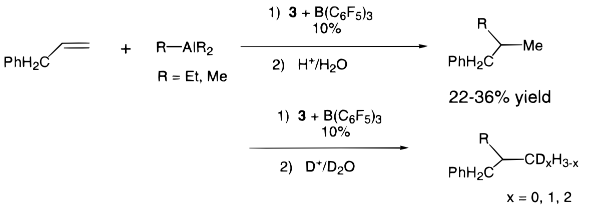


Figure 2. ORTEP diagram of the molecular structure of η^5-$(C_5Me_4)SiMe_2N(t\text{-}Bu)Ti(Bu)Cl$ (**2**). Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Ti−C1, 2.101; Ti−C2, 3.296; Ti−C1−C2, 129.7.

as (+)-Ti(η^5:η^1-$C_5H_4SiMe_2NCHMePh)Cl_2$ and Hf(η^5:η^1:η^1-$C_5H_4SiMe_2NCH_2CH_2OMe)Bu_2$.[20,21] The Ti−Cl bond length is nearly identical to those in the dichloride, whereas the Ti−C bond length is shorter by 0.1 Å than the Hf−C bond distances. The Ti−C bond length is only 0.01 Å shorter than the Ti−sp^3 C bond length of titanacyclopentene **25** (Ti−C7, vide infra). The conformation of the butyl ligand is unremarkable and provides no evidence of α- or β-hydride agostic interactions with the metal center, as determined by metal−carbon bond lengths and metal−carbon−carbon bond angles.[22] Complex **2** is thermally stable in solution; no decomposition was observed by ^{1}H NMR even after heating several hours at 80 °C. Moreover, no reactivity was observed after heating the complex at 80 °C for several days in the presence of allylbenzene.

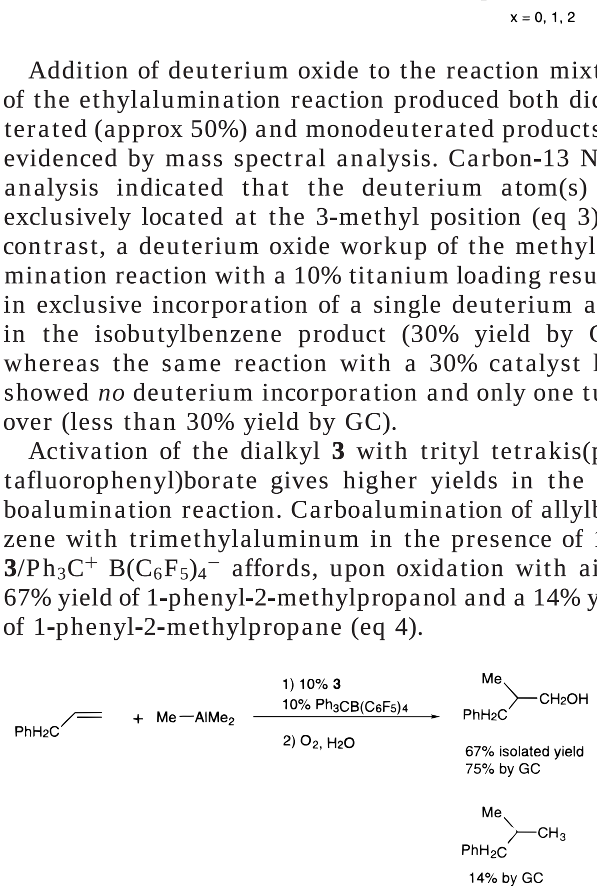
Alkylation of the dichloride **1** with 2 equiv of methyllithium yields the dialkyl **3**.[23] This complex, when activated with the potent Lewis acid $B(C_6F_5)_3$, is a catalyst for the carboalumination of olefins. Treatment of allylbenzene with 1 equiv of either triethylaluminum or trimethylaluminum using 10 mol % **3**/$B(C_6F_5)_3$ in 1,1-dichloroethane results in the alkylalumination of the olefin in low to moderate yields (eq 3).[8,9] No conversion of allylbenzene was observed if either trimethylaluminum or $B(C_6F_5)_3$ was omitted from the reaction solution.



(3)

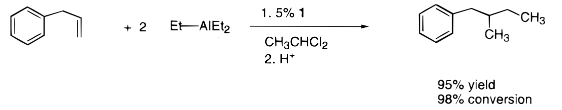
Addition of deuterium oxide to the reaction mixture of the ethylalumination reaction produced both dideuterated (approx 50%) and monodeuterated products, as evidenced by mass spectral analysis. Carbon-13 NMR analysis indicated that the deuterium atom(s) are exclusively located at the 3-methyl position (eq 3). In contrast, a deuterium oxide workup of the methylalumination reaction with a 10% titanium loading resulted in exclusive incorporation of a single deuterium atom in the isobutylbenzene product (30% yield by GC), whereas the same reaction with a 30% catalyst load showed *no* deuterium incorporation and only one turnover (less than 30% yield by GC).

Activation of the dialkyl **3** with trityl tetrakis(pentafluorophenyl)borate gives higher yields in the carboalumination reaction. Carboalumination of allylbenzene with trimethylaluminum in the presence of 10% **3**/Ph_3C^+ $B(C_6F_5)_4^-$ affords, upon oxidation with air, a 67% yield of 1-phenyl-2-methylpropanol and a 14% yield of 1-phenyl-2-methylpropane (eq 4).

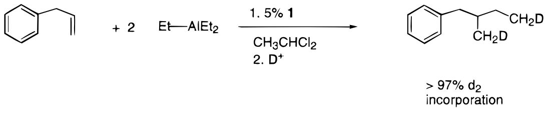


(4)

The carboalumination of olefins can also be carried out using the dichloride **1** and triethylaluminum. Carboalumination of allylbenzene proceeds smoothly to >98% conversion in the presence of a catalytic amount of the dichloride **1** and triethylaluminum, giving >95% yield of 2-methyl-1-phenylbutane upon hydrolysis (eq 5). Deuteriolysis of the reaction mixture gave the corresponding 1,4-dideuterio-2-benzylbutane in 97% yield (eq 6). No conversion is seen when trimethylaluminum is the reagent under these conditions.



(5)



(6)

To investigate the scope and selectivity of this reaction, a variety of α-olefin substrates were examined.[24] In each case, exposure of the reaction products to dry oxygen for several hours afforded alcohols upon aqueous

---

(20) Okuda, J.; Verch, S.; Spaniol, T. P.; Sturmer, R. *Chem. Ber.* **1996**, *129*, 1429−1431.

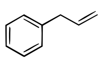
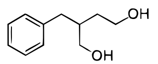
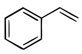
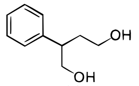
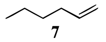
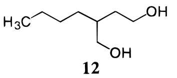
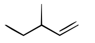
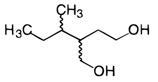
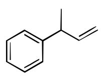
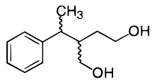
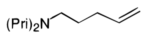
(21) Amor, F.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 47765-4767.

(22) Green, M. L. H.; Brookhart, M. *J. Organomet. Chem.* **1983**, *250*, 395−408.

(23) McKnight, A. L.; Masood, M. A.; Waymouth, R. M. *Organometallics* **1997**, *16*, 2879−2885.

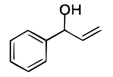
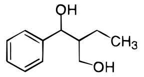
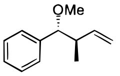
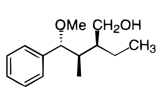
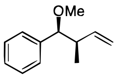
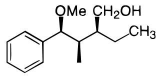
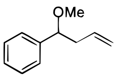
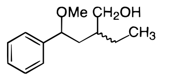
(24) Following Dzhemilev's observations on reaction sensitivity to solvent, it was found that the reaction proceeded faster with hexanes as solvent.

Table 1. Scope and Diastereoselectivity of Ethylalumination of Simple α-Olefins[a]

Substrate	Time	Conv. [%][b]	Product	Yield [%][c]
 **5**	16 h	98	 **10**	47
 **6**	92	89	 **11**	12
 **7**	48[d]	ND	 **12**	41
 **8**	16 h	ND	 **13**,1:1 dr[e]	47
 **9**	16 h	ND	 **14**, 2:1 dr[e]	64.5
		100		0

[a] Conditions: 2 equiv of Et$_3$Al, 5 mol % of catalyst, hexanes, 22 °C; O$_2$ at 0 °C, 2−3 h. [b] Conversion determined by GC relative to an internal standard. [c] Isolated yields of purified products after silica gel chromatography. [d] 1 mol % catalyst, CH$_3$CHCl$_2$ solvent. [e] Diastereomer ratio (dr) determined by quantitative 50 MHz ^{13}C NMR.

Table 2. Diastereocontrol in Ethylalumination of Oxygen-Containing α-Olefins.[a]

Substrate	Time	Conv. [%][b]	Product	Yield [%][c]
 **15**	18 h	97	 **19**, 1:1 dr[d]	6
 **16**	42 h	85	 single diastereomer **20**	55
 **17**	18 h	ND	 **21maj**, 10:1 dr[d]	53
 **18**	18 h	100	 **22**, 1.26:1 dr[d]	82

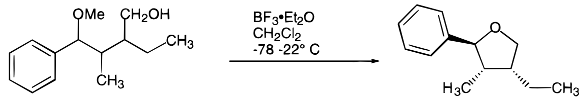
[a] Conditions: 2 equiv of Et$_3$Al, 5 mol % of catalyst, hexanes, 22 °C; O$_2$ at 0 °C, 2−3 h. [b] Conversion determined by GC relative to an internal standard. [c] Isolated yields of purified products after silica gel chromatography. [d] Diastereomer ratio (dr) determined by 200 MHz ^{1}H NMR.

workup (Table 1). In all cases but styrene a mixture of 1,4-butanediol and the corresponding mono-ols were obtained in total yields of around 80% and in a relative ratio of 3:1:1. Extensive heating failed to improve the yield of diol from 45 to 50%. Workup of the reaction with deuterium oxide instead of oxygen resulted in >97% uptake of *two* deuterium atoms, as indicated by EIMS. Styrene reacts more slowly than other α-olefins. A pseudo-first-order styrene dependence was seen, with $k_{\mathrm{obs}} = 6.12 \times 10^{-6}\ \mathrm{s}^{-1}$. Styrene also consistently afforded considerably lower yields of diol.

The reaction is tolerant of ether functionalities. The amino substrate *N*,*N*-diisopropylamino-5-pentene was consumed but not converted to an identifiable product. Other olefins such as 2-methylpentene, cyclopentene, cyclohexene, and 2,5-dihydrofuran were unreactive under these conditions. A diastereoselectivity of 2:1 was seen using 3-phenyl-1-butene, whereas 3-methylpentene showed no selectivity (Table 1).

Investigations of a series of oxygen-containing α-olefins revealed a highly selective oxidation of only the terminal carbon of the substrate to give the alcohol (Table 2). The allylic alcohol **15** gave very poor yields; no efforts were made to optimize the yield.[25] Both syn and anti isomers of 1-phenyl-1-methoxy-2-methyl-3-butene **16** and **17** react with high diastereoselectivity (10:1 dr or greater), whereas 1-phenyl-1-methoxy-3-butene **18** shows no diastereoselectivity. To determine the relative stereochemistry of the ethyl and methyl moieties, the alcohol products **20** and **21** were cyclized to the corresponding 2-phenyltetrahydrofuran **23** with BF$_3$·Et$_2$O (eq 7).

Both alcohol diastereomers converge to the same tetrahydrofuran diastereomer **23**, through epimerization at the α-carbon. ^{1}H NOE experiments were performed and the results correlated to a trans relationship between the phenyl and methyl groups and a cis relationship between the ethyl and methyl groups.[26]



20, 21 **23** (7)

The enantioselective carboalumination of allylbenzene and styrene with triethylaluminum proceeded with modest yields and low enantioselectivities using the chiral complex **4** (Table 3). The absolute stereochemistry was not determined. No diastereoselectivity was seen in the reaction with 3-phenyl-1-butene.

Discussion

Many group 4 metallocenes are reduced by main group metal alkyls containing *β*-hydrogens. For example, a common route to reduced zirconocene is treatment of Cp$_2$ZrCl$_2$ with butyllithium;[27] numerous catalytic reactions with group 4 metals rely upon this procedure to generate catalytically active species.[6,19,28,29] As a consequence of their tendency to undergo *β*-H elimination, group 4 metal dialkyl complexes containing *β*-hydrogens are relatively rare and thermally unstable.[29] Thermally stable group 4 metal dialkyls commonly possess dative *σ* donors such as phosphines or tetrahydrofuran on the metal as ancillary ligands.[21,22]

---

(25) The corresponding allyl methyl ether substrate reacts to less that 50% conversion and affords several products when analyzed by GC. GC/MS of the reaction mixture indicates products with *m*/*z* values corresponding to ethyl addition and methoxy elimination.

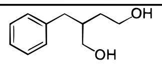
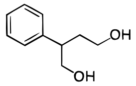
(26) A description of the NOE interactions is given in the Experimental Section.

(27) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829−2832.

(28) Suzuki, N.; Kondakov, D. Y.; Takahashi, T. *J. Am. Chem. Soc.* **1993**, *115*, 8485−8486.

(29) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1997**, *16*, 1452−1464.

Table 3. Enantioselective Ethylalumination of α-Olefins with Catalyst 4[a]

Substrate	Product	Yield[b] [%]	conc. (mg/mL)	[α]D	ee [%]
5	 **10**	53	18.4	-1.03°	28
6	 **11**	14	12.8	-10.16°	19

[a] Conditions: 2 equiv of Et_3Al, 5 mol % of catalyst, hexanes, 22 °C; O_2 at 0 °C, 2−3 h. [b] Isolated yields of purified products after silica gel chromatography.

Okuda recently reported the synthesis of stable, coordinatively saturated β-hydrogen-containing dialkyl zirconium and hafnium complexes with a tridentate CpA ligand; however, the analogous titanium complexes were unstable.[30]

The related group 4 metal monoalkyl monochloro compounds are more stable. $Cp_2Ti(Cl)(R)$ species can be formed either from Cp_2TiCl_2 and RMgCl or by $PbCl_2$ oxidation of the corresponding Ti(III) alkyl.[31,32] Stable at room temperatures, these compounds decompose in the solid state when heated. The zirconocene analogues can be formed from the reaction of an olefin and zirconocene hydride chloride, but olefin exchange and "chain walking" processes indicate that the β-hydrogens can be activated in these species as well.[33] These compounds are typically coordinatively unsaturated, which facilitates β-hydride elimination.

Group 4 metal complexes with amido ligands appear less prone to β-hydride eliminations, as evidenced by the formation of stable metal alkyls with β-hydrogens[34,35] and the report of "living" 1-hexene polymerization catalysts.[36−38] Complex **2** is a noteworthy example of a stable monoalkyl monochloro titanium species lacking an ancillary dative ligand. (Okuda has reported the in situ trapping of a coordinatively saturated analogue to **2** with *tert*-butyl cyanide.[39])

No evidence for a β-hydride agostic interaction is seen, and complex **2** is stable when heated in solution. Moreover, no olefin exchange is observed upon heating **2** with excess allylbenzene, indicating that the alkyl chloride **2** is unusually resistant to β-hydride elimination or that the resultant olefin hydride complex is resistant to olefin exchange. The resistance of **2** to β-hydride elimination is presumably a consequence of the amido ligand. Amido-ligated titanium compounds appear more resistant to both reduction to Ti(III)[40] and β-hydride elimination, but the origin of these ligand effects is unknown.

Catalytic Carboalumination. Catalysts derived from the reaction of the dialkyl **3** and either $Ph_3C^+B(C_6F_5)_4^-$ or $B(C_6F_5)_3$ are active for the carboalumination of olefins with either $AlMe_3$ or $AlEt_3$, but yields are higher with $Ph_3C^+B(C_6F_5)_4^-$ (eq 3, 4). Catalysts derived from the tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) generate no more than 2−3 turnovers per metal center (eq 3). That carboalumination proceeds readily with $AlMe_3$ and deuteriolysis and/or oxidation of the products selectively functionalizes the carbon derived from the terminal carbon of the α olefin provide strong support for a mechanism involving olefin insertion into a transition metal alkyl bond followed by transmetalation (Scheme 1).[4,9] The partial incorporation of two deuterium atoms on the 3-methyl group of 3-methyl-4-phenylbutane (eq 3) upon deuteriolysis of the ethylalumination reaction implicates the formation of a metal carbene. Carbene formation might occur by an α-elimination reaction analogous to that proposed for the formation of the Tebbe reagent (Scheme 1).[41] The formation of a carbene is likely an unproductive path for the carboalumination reaction, which would account for the low yields observed with $AlEt_3$ and $B(C_6F_5)_3$. This process might also account for the lack of label incorporated into the product of the methylalumination reaction at high catalyst load if the product were eliminated at the α-elimination step.

The catalytic carboalumination of olefins can also be carried out with the dichloride precursor **1** and Et_3Al; under these conditions $AlMe_3$ is ineffective as an alkylating agent. Carboalumination of olefins with $AlEt_3$ using 10 mol % of **1** or **4** yields 1,4-butanediols in modest yields upon oxidation. The reaction is tolerant of ethers, but no product was obtained with a tertiary amine substrate. The diastereoselectivity of catalyst **1** is limited in substrates without heteroatoms. The homoallyl ethers **16** and **17** are carbometalated with high diastereoselectivity, whereas little selectivity is observed with the allyl alcohol **15** or the homoallyl ether **18.** Similar selectivities reported by Hoveyda for the ethylmagnesiation of olefins were interpreted to be a consequence of chelation of the ether to the metal.[7]

The formation of 1,4-dideuteriobutanes upon deuteriolysis and 1,4-butanediols upon oxidation of the reaction mixtures is inconsistent with an olefin insertion mechanism as proposed in Scheme 1 and strongly implicates a metallacycle mechanism for carboalumination reactions carried out with the titanocene dichlorides and $AlEt_3$. As proposed in Scheme 2, reduction of the Cp^*ATiCl_2 by Et_3Al yields a titanium ethylene adduct, which can couple with the olefin to form a metallacycle. Transmetalation of the metallacycle provides aluminacyclopentanes, which can be oxidized or deuteriolyzed to the observed products.[42] A similar mechanism was proposed for the ethylalumination of olefins with zirconocenes;[6,43] Dzhemilev reports that

---

(30) Amor, F.; Butt, A.; duPlooy, K.; Spaniol, T.; Okuda, J. *Organometallics* **1998**, *17*, 5836−5849.

(31) Luinstra, G. A.; Teuben, J. H. *Organometallics* **1992**, *11*, 1793−1801.

(32) Waters, J. A.; Mortimer, G. A. *J. Organomet. Chem.* **1970**, *22*, 417−424.

(33) Schwartz, J. *J. Organomet. Chem. Libr.* **1976**, *1*, 461.

(34) Buerger, H.; Neese, H.-J. *J. Organomet. Chem.* **1969**, *20*, 129−137.

(35) Buerger, H.; Neese, H.-J. *J. Organomet. Chem.* **1970**, *21*, 381−390.

(36) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830−3831.

(37) Baumann, R.; Schrock, R. R. *J. Organomet. Chem.* **1998**, *557*, 69−75.

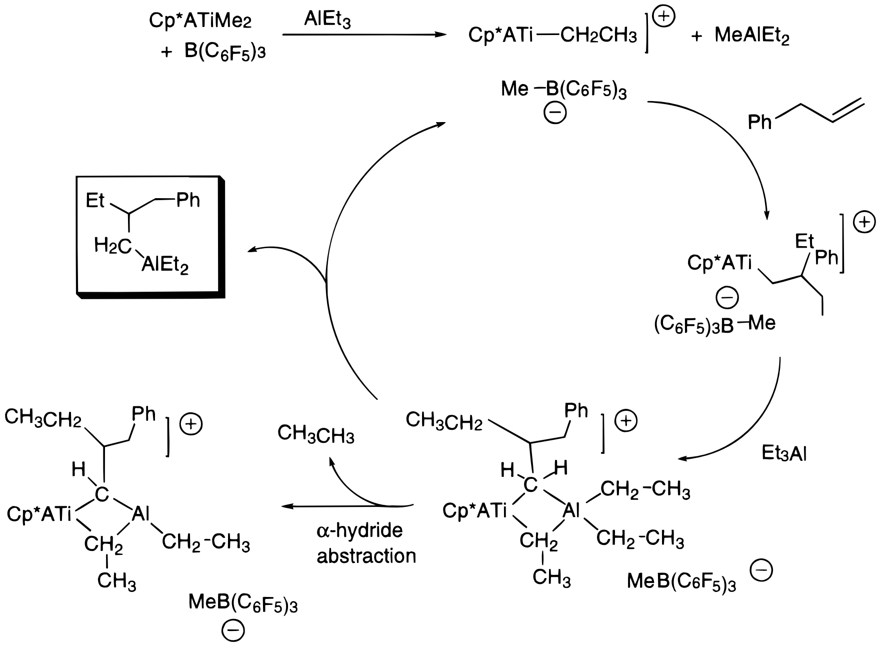
(38) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008−10009.

(39) Amor, F.; Butt, A.; duPlooy, K.; Spaniol, T.; Okuda, J. *J. Organomet. Chem.* **1998**, *558*, 139−146.

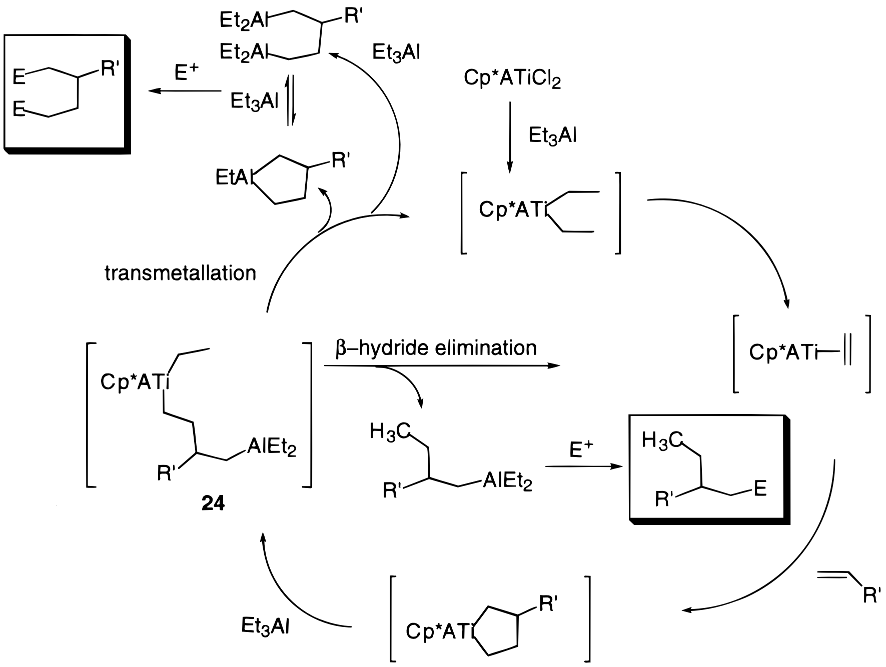
(40) Bis-cyclopentadienyl titanocenes are reduced readily to Ti(III) by alkylaluminum reagents such as MAO; complex **1** is not as readily reduced.

(41) Ott, K. C.; Deboer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223−230.

Scheme 1. Proposed Mechanism for $(C_6F_5)_3B$-Mediated Carboalumination Reaction



Scheme 2. Proposed Mechanism of Ethylalumination Reaction Catalyzed by 1



Cp_2TiCl_2 and other titanium salts were ineffective for the ethylalumination of olefins.[6]

In contrast to simple olefins, the oxygenated substrates **15**–**18** show high chemo- and regioselectivity for formation of a monoalcohol rather than the butanediol upon oxidation of the reaction mixture with air. This selectivity would arise if β-H elimination from the dialkyl **24** (Scheme 2) were faster than the second transmetalation to the aluminacyclopentane. The oxygen functionality of the substrate might be responsible for this difference in selectivity; similar effects have been observed in the ethylmagnesiation of olefins.[7]

The enantioselectivity of olefin carboaluminations using catalyst **4** is modest but similar to that seen with chiral zirconium catalysts and alkyl aluminums in other reductive coupling reactions.[43] In contrast, the enantioselectivity in olefin insertion carboaluminations with chiral zirconium catalysts can be excellent.[4,5,43] Okuda has prepared similar CpA titanium compounds from (+)α-methylbenzylamine;[20] these complexes exhibit only modest enantioselectivity in the hydrogenation of imines.[20]

Further evidence for the plausibility of the reductive coupling mechanism is provided by the observation that **1** reacts with magnesium metal and *N*-allyl-*N*-2-butynylaniline to give titanacyclopentene **25** (eq 8, Figure 3).

Magnesium reduces **1** in the presence of the alkyne to produce an alkyne adduct (analogous to the titanium–ethylene adduct of Scheme 2), which then reductively

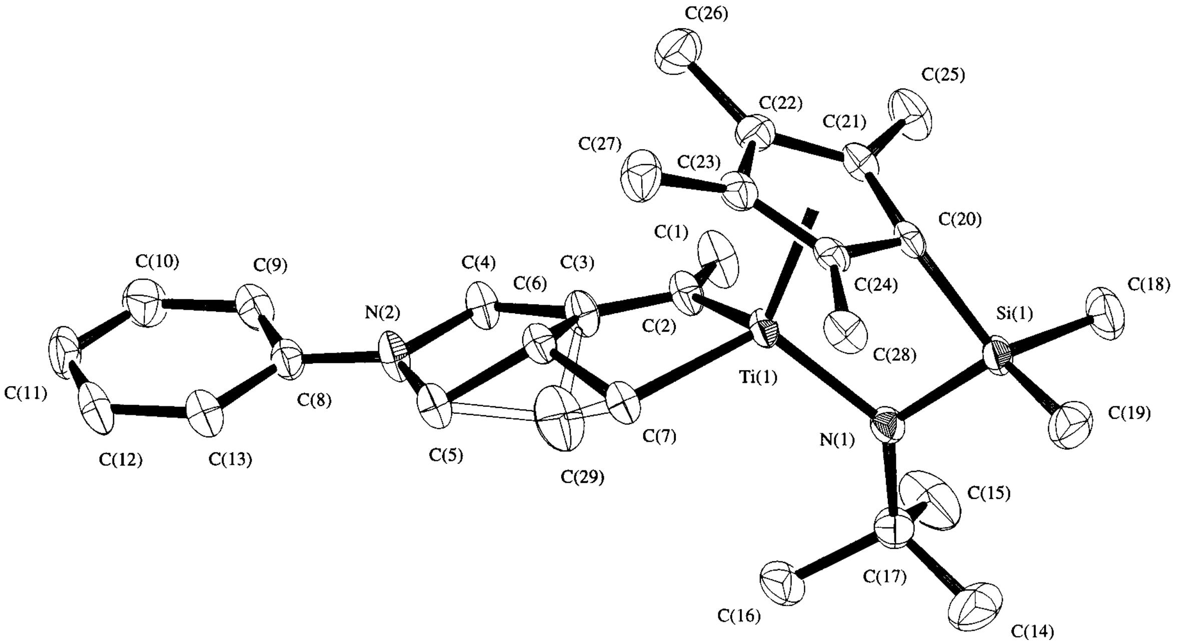
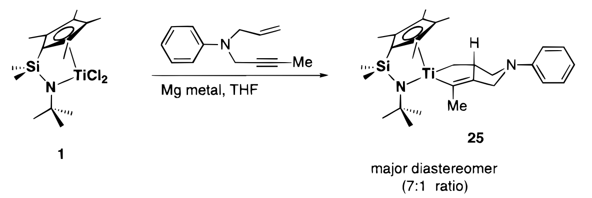


Figure 3. ORTEP of CpA titanacyclopentene **25**. The compound crystallizes as a 7:1 mixture of diastereomers. Selected bond lengths (Å) and bond angles (deg): Ti−C7, 2.115; Ti−C2, 2.076; N−Ti−Cent, 108.58; C2−Ti−C7, 93.5.



(8)

couples with the pendant olefin. Two diastereomers of metallacycle **25** are generated in an initial ratio of 2:1. Upon prolonged heating, this ratio changes to 7:1. Analysis of the X-ray data reveals a similar mixture in the crystal, where the β-H of the major isomer is *cis* to the cyclopentadienyl ligand.

Summary

Cyclopentadienyl amido titanium complexes catalyze the carboalumination of olefins. The dichloride **1** reacts with dibutylmagnesium to give an unusually stable monoalkyl monochloro titanium species **2**. When activated by $B(C_6F_5)_3$ or $[Ph_3C]^+[B(C_6F_5)_4]^-$, the dimethyl complex **3** catalyzes the carboalumination of α-olefins by an olefin insertion mechanism. The analogous titanium dihalides are competent catalysts for the ethylalumination of α-olefins to give 1,4-butanediols upon oxidation. Labeling studies implicate metallacycles as reactive intermediates. The enantioselective carboalumination of allylbenzene using the chiral metallocene **4** affords 2-benzyl-1,4-butanediol in 53% yield and 28% enantiomeric excess.

Experimental Section

General Methods. All manipulations involving air-sensitive compounds were carried out under nitrogen in a glovebox or using standard Schlenk line techniques. GC analyses were obtained on a Hewlett-Packard 5890 chromatograph equipped with an SE-30 column. NMR experiments were performed on Varian Gemini 200 and Unity Inova 500 spectrometers. GC/MS data were taken on a Hewlett-Packard 5890 chromatograph equipped with an SE-54 column attached to a Hewlett-Packard 5970 mass spectrometer. All solvents were distilled from calcium hydride, lithium aluminum hydride, or Na/benzophenone prior to use. Preparative chromatography was performed on silica gel 60, 0.02−0.04 mm.

Allylbenzene, styrene, 1-hexene, 3-methylpentene, and *N*,*N*-diisopropylamino-5-pentene were purchased from Aldrich and dried and distilled prior to use. 3-Phenylbutene was prepared from 2-phenylpropanal via a Wittig methylenation. 1-Phenyl-2-propen-1-ol was synthesized from benzaldehyde and vinylmagnesium bromide. Similarly, 1-methoxy-1-phenyl-3-butene was produced from benzaldehyde and allylmagnesium bromide. *anti*(threo)-1-methoxy-1-phenyl-2-methyl-3-butene was selectively prepared via a Hiyama addition of crotyl chromium dichloride to benzaldehyde followed by methylation of the alcohol product.[44] Boron trifluoride−diethyl etherate-catalyzed addition of crotyl tributyl stannane to benzaldehyde afforded an inseparable 4:1 mixture of syn (erythro) and anti (threo) 1-hydroxy-1-phenyl-2-methyl-3-butene. Methylation afforded the same ratio of *syn*- (erythro) and *anti*-1-methoxy-1-phenyl-2-methyl-3-butene, which were distinguishable by ^1H NMR and utilized in this mixture. Dibutylmagnesium was prepared by treatment of butylmagnesium chloride with diglyme, followed by filtration of magnesium dichloride precipitate and concentration in vacuo. η^5-$(C_5Me_4)SiMe_2N(tBu)TiCl_2$ (**1**),η^5-$(C_5Me_4)SiMe_2N(tBu)TiMe_2$ (**3**), and η^5-(indenyl)$SiMe_2N(CH(CH_3)Ph)TiCl_2$ (**4**) were prepared as described previously.[23]

Synthesis of η^5-$(C_5Me_4)SiMe_2N(tBu)Ti(Bu)Cl$ (2). A 50 mL Schlenk flask was charged with 0.095 g of dibutylmagnesium (0.687 mmol, 1.0 equiv) and 0.255 g of η^5-$(C_5Me_4)SiMe_2N(tBu)TiCl_2$ (0.692 mmol, 1.01 equiv) in the drybox. After adapting the flask to a vacuum line, 10 mL of tetrahydrofuran was added via cannula, and the resulting solution was stirred for 40 min. The solvent was then removed in vacuo, and the residue was extracted through a cannula filter with 3 × 10 mL of dry pentane. The pentane solution was concentrated in vacuo and recrystallized from pentane at −50 °C. Red-orange

---

(42) The low yield of diol product can be attributed to incomplete oxidation of the aluminocyclopentanes.

(43) Dawson, G.; Durrant, C. A.; Kirk, G. G.; Whitby, R. J. *Tetrahedron Lett.* **1997**, *38*, 2335−2338.

(44) Mulzer, J.; Kattner, L.; Strecker, A. R.; Schroder, C.; Buschmann, J.; Lehmann, C.; Luger, P. *J. Am. Chem. Soc.* **1991**, *113*, 4218−4229.

needlelike crystals were isolated (186 mg, 70% yield). X-ray quality crystals were grown from pentane at −30 °C in a drybox. ^{1}H NMR: (C_6D_6) δ 0.379 (s, 3H); 0.446 (s, 3H); 0.55 (d, J = 10 Hz, 1H); 0.908 (t, J = 7.2 Hz, 3H); 1.24 (m, 4H); 1.552 (s, 9H); 1.931 (s, 6H); 1.981 (s, 3H); 2.039 (s, 3H); ^{13}C NMR: (THF-d_8) δ 5.9, 6.0, 12.1, 12.6, 13.8, 15.2, 15.4, 28.7, 34.0, 36.8, 60.3, 78.9, 102.4, 133.37, 133.43, 134.8, 136.5. Anal. Calcd: C, 58.52; H, 9.31; Ti, 12.28. Found: C, 58.38; H, 9.06; Ti, 12.32

$B(C_6F_5)_3$-Mediated Carboalumination Reactions, Representative Procedure. A 25 mL Schlenk flask was charged with 17 mg of η^5-(C_5Me_4)$SiMe_2$N(tBu)$TiMe_2$ (0.05 mmol, 0.1 equiv), 29 mg of $B(C_6F_5)_3$ (0.05 mmol, 0.1 equiv), 64 mg of decane as internal standard, and 2 mL of 1,1-dichloroethane. Trimethylaluminum (0.05 mL) was added to the reaction solution, followed by dropwise addition of 59 mg of allylbenzene in 8 mL of 1,1-dichloroethane. The reaction was monitored by GC analysis of the organic fraction of aliquots quenched in water/diethyl ether. The single product peak was identified as isobutylbenzene by co-GC with authentic material. A 36.5% yield is realized after 2 h; no further conversion or product formation is seen after this time.

The corresponding reaction with triethylaluminum was quenched with either H_2O or D_2O. The deuterated isobutylbenzene product was isolated by preparatory GC techniques after passing the crude reaction mixture through silica and removing the solvent. GC/MS showed peaks at m/z = 150 and 149, indicating both mono- and dideuteration. Proton-decoupled ^{13}C NMR: ($CDCl_3$) δ 11.4 (s), 18.6 (m), 29.1 (s), 35.5 (s), 43.3 (s), 125.5 (s), 128.0 (s), 129.2 (s). *ipso*-Carbon signal in the baseline.

Representative Procedure for Ethylalumination Reaction. Synthesis of 2-Benzyl-1,4-butanediol (10). In a drybox, a 25 mL Schlenk flask was charged with 18 mg of η^5-(C_5Me_4)$SiMe_2$N(tBu)$TiCl_2$ (0.05 mmol,), 118 mg of allylbenzene (1 mmol), and 2 mL of hexanes. To this clear yellow solution was added 0.28 mL of neat triethylaluminum (2 mmol), generating a dark brown solution. The reaction was monitored by quenching aliquots in water/diethyl ether and analyzing the organic phase by GC/MS. The GC/MS showed clean conversion to a single product of m/z = 148 amu, consistent with the molecular formula $C_{11}H_{16}$. Aliquots quenched with deuterium oxide also showed a single product by GC, with m/z values of 150 and 149 amu in a ratio of 98:2, indicating almost exclusive dideuteration. The reaction solution was stirred for 16 h, diluted to 20 mL with hexanes, and cooled to 0 °C. Dry O_2 was bubbled through the solution for 2 h, after which the oxygen-saturated solution was warmed to ambient temperature and stirred for several hours. The reaction was worked up by addition of 25 mL of 10% HCl and extraction with 3 × 25 mL of diethyl ether. The combined organics were washed with brine, dried over magnesium sulfate, and concentrated on a rotary evaporator. Chromatography on silica gel with 20% hexanes in ethyl acetate as solvent allowed facile purification of 83 mg of 2-benzyl-1,4-butanediol (47% yield) from 61 mg of side products 2-benzylbutanol and 3-benzylbutanol (19% yield each). The mono-ol products can be separated using 15% ethyl acetate in hexanes and distinguished by the ^{13}C chemical shifts of the methylene carbons adjacent to oxygen. 2-Benzyl-1,4-butanediol: ^{1}H NMR ($CDCl_3$) δ 1.5−1.8 (m, 2H); 1.8−2.0 (m, 1H); 2.5−2.7 (m, 2H); 3.4−3.8 (m, 4H); 7.2−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 35.200, 38.128, 41.178, 60.887, 65.454, 126.037, 128.389, 129.132, 140.345.[6] 2-Benzylbutanol: ^{1}H NMR ($CDCl_3$) δ 0.949 (t, J = 7.6 Hz, 3H) 1.2−1.8 (m, 3H); 2.647 (d, J = 7 Hz, 2H); 3.55 (d, J = 5 Hz,2H); 7.2−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 11.2, 23.2, 37.2, 44.1, 64.5, 125.9, 128.3, 129.2, 140.9.[45] 3-Benzylbutanol: ^{1}H NMR ($CDCl_3$) δ 0.897 (t, J = 6.6 Hz, 3H) 1.2−2.0 (m, 3H); 2.638 (dd, J = 7, 13 Hz, 2H); 3.68 (m, J = 7 Hz,2H); 7.2−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.4, 31.6, 39.4, 43.7, 61.1, 125.8, 128.2, 129.2, 141.1.[46]

2-Phenyl-1,4-butanediol (11). The reaction was carried out as described above for compound **10**. This compound has previously been characterized.[47,48] ^{1}H NMR: ($CDCl_3$) δ 1.8−2.0 (m, 2H); 2.975 (dt, J = 15.2, 6.6 Hz, 1H); 3.5−3.7 (m, 2H); 3.971 (t, J = 6.4 Hz, 2H), 7.2−7.4 (m, 5H). ^{13}C NMR: ($CDCl_3$) δ 35.7, 45.9, 61.0, 67.4, 126.8, 127.8, 128.7, 140.

3-Hydroxymethyl-1-octanol (12). The reaction was carried out as described above for compound **10**. This compound has previously been characterized.[5] ^{1}H NMR: ($CDCl_3$) δ 0.8823 (t, J = 6.6 Hz, 3H); 1.216−1.286 (m, 6H); 1.56−1.62 (m, 2H); 1.65−1.72 (m, 1H); 3.4553 (dd, J = 7,7 Hz, 1H); 3.6309 (m, 2H); 3.7637 (m, 1H). ^{13}C NMR: ($CDCl_3$) δ 14.0, 22.9, 29.2, 31.4, 35.8, 39.3, 61.1, 66.3.

1:1 *syn*/*anti*-3-Hydroxymethyl-4-methyl-1-hexanol (13). The reaction was carried out as described above for compound **10**. This compound has previously been characterized.[49] ^{1}H NMR: ($CDCl_3$) δ 0.79−0.92 (m, 6H); 1.1−1.7 (m, 6H); 3.188 (bs, O*H*); 3.38−3.85 (m, 4H). ^{13}C NMR: ($CDCl_3$) δ 12.0, 15.4, 15.7, 26.6, 26.9, 32.0, 34.3, 36.7, 37.3, 43.9, 44.2, 62.1, 62.2, 64.5, 66.0.

3-Hydroxymethyl-4-phenyl-1-pentanol (2:1 dr) (14). The reaction was carried out as described above for compound **10**. ^{1}H NMR: ($CDCl_3$) δ 1.287 (dd, J = 7, 2 Hz, 3H); 1.4−1.8 (m, 2H); 1.8−2.0 (m, 1H); 2.839 (q, J = Hz, 1H); 3.3−3.9 (m, 4H); 7.1−7.4 (m, 5H). ^{13}C NMR: ($CDCl_3$) δ 13.9, 17.8, 18.9, 20.8, 32.2, 33.3, 40.4, 40.5, 44.9, 45.3, 60.6 (min), 60.7 (maj), 63.2 (min), 64.3 (maj), 125.9, 127.4, 127.5, 128.2, 145.8. Anal. Calcd: C, 74.19; H, 9.34. Found: C, 74.22; H, 9.30.

1:1 *syn*/*anti*-1-Phenyl-2-ethyl-1,3-propanediol (19). The reaction was carried out as described above for compound **10**. This compound has previously been characterized.[7] ^{1}H NMR: ($CDCl_3$) δ 0.871 (t, J = 7.4 Hz, 3H); 0.883 (t, J = 7.4 Hz, 3H); 1.2−1.35 (m, 4H); 1.6−1.9 (m, 2H); 2.959 (bs, 2H); 3.739 (d, J = 4.6 Hz, 4H); 4.711 (d, J = 7.2 Hz, 1H); 5.010 (d, J = 2 Hz, 1H). ^{13}C NMR: ($CDCl_3$) δ 11.5, 11.9, 17.8, 21.0, 47.9, 48.1, 63.6, 64.2, 77.1, 79.0,126.5,126.5, 127.5, 127.7, 128.2, 128.5.

***anti*,*syn*-4-Phenyl-4-methoxy-3-methyl-2-ethyl-1-butanol (20).** The reaction was carried out as described above for compound **10**. ^{1}H NMR: ($CDCl_3$) δ 0.798, (t, J = 7 Hz, 3H); 0.885 (d, J = 7 Hz, 3H); 1.1−1.3 (m, 4H); 3.219 (s, 3H); 3.2−3.6 (m, 2H); 4.058 (d, J = 7.4 Hz, 1H); 7.2−7.4 (m, 5H). ^{13}C NMR: ($CDCl_3$) δ 12.2; 14.3, 21.3, 42.5, 43.5, 56.7, 63.4, 86.7, 127.4, 127.6, 128.3, 140.8. Anal. Calcd: C, 75.63; H, 9.98; Found C, 75.63; H, 9.96.

***syn*,*anti*-4-Phenyl-4-methoxy-3-methyl-2-ethyl-1-butanol (21 maj).**The reaction was carried out as described above for compound **10**. ^{1}H NMR: ($CDCl_3$) δ 0.822, (d, J = 7.4 Hz, 3H); 0.915 (d, J = 7.4 Hz, 3H); 1.2−1.4 (m, 2H); 1.8−1.9 (m,1H); 3.282 (s, 3H); 3.4−3.7 (m, 2H); 4.2735 (d, J = 3.4 Hz, 1H); 7.2−7.4 (m, 5H). ^{13}C NMR: ($CDCl_3$) δ 6.9, 12.3, 24.0, 42.7, 47.3, 57.1, 63.0, 81.1, 126.8, 127.3, 128.3, 141. Anal. Calcd: C, 75.63; H, 9.98. Found: C, 75.63; H, 9.96.

***syn*,*syn*-4-Phenyl-4-methoxy-3-methyl-2-ethyl-1-butanol (21min).**The reaction was carried out as described above for compound **10**. ^{1}H NMR: ($CDCl_3$) δ 0.788, (t, J = 6.4 Hz, 3H); 0.957 (d, J = 6.8 Hz, 3H); 1.3−1.6 (m, 3H); 1.85−1.95 (m,1H); 3.163 (s, 3H); 3.545 (dd, J = 6,6 Hz, 2H); 3.937 (d, J = 7.8 Hz, 1H); 7.2−7.4 (m, 5H). ^{13}C NMR: ($CDCl_3$) δ 10.0; 14.6, 29.8, 38.3, 43.1, 56.5, 61.1, 82.2, 127.4, 127.6, 128.3, 141.

1.26:1 (dr) 4-Phenyl-4-methoxy-2-ethyl-1-butanol (22). The reaction was carried out as described above for compound **10**. ^{1}H NMR: ($CDCl_3$) δ 0.888, (t, J = 7.6 Hz, 3H); 0.893 (t, J = 7.4 Hz, 3H); 1.2−1.5 (m, 4H); 1.5−2.0 (m,6H); 3.214 (s, 3H);

---

[45] Crandall *J. Org. Chem.* **1972**, *37*, 6.

[46] McQuillin *J. Chem. Soc., Dalton Trans.* **1971**, 931.

[47] Bailey, W. F.; Cioffi, E. A. *J. Chem. Soc., Chem. Commun.* **1981**, *4*, 155−156.

[48] Hiyama, T.; Kubayashi, K.; Fujita, M. *Tetrahedron Lett.* **1984**, *25*, 4959.

[49] Botteghi, C. *J. Prakt. Chem.* **1972**, *314*, 840−850.

3.225 (s, 3H); 3.2−3.8 (m, 4H); 4.178 (dd, $J = 9.6$, 3 Hz, 1H); 4.295 (dd, $J = 8.6$, 3.4 Hz, 1H); 7.2−7.4 (m, 5H). ^{13}C NMR: (CDCl$_3$) δ 11.3; 23.6, 25.2, 38.9, 40.0, 41.5, 56.5, 65.3, 65.9, 81.3, 83.9, 126.4, 127.6, 128.5, 141. Anal. Calcd: C, 74.96; H, 9.68. Found: C, 74.87; H, 9.96.

***trans,cis*-2-Phenyl-3-methyl-4-ethyltetrahydrofuran (23).** An oven-dried 25 mL Schlenk flask was charged with 64.3 mg (0.287 mmol) of compound **20** and 3 mL of dry methylene chloride. The flask was purged for 10 min with N_2, then cooled to −78 °C. An 80 μL aliquot of $BF_3 \cdot Et_2O$ was added via syringe, and the solution was warmed to RT and stirred for 3 days. When TLC analysis indicated the reaction was complete, the reaction was quenched with 5 mL H_2O/10 mL methylene chloride. Separation of the organic phase, evaporation of solvent, and SiO_2 chromatography (9:1 hexanes/EtOAc) afforded 30 mg of product (55% yield), a yellow oil. Compound **21maj** was transformed to **23** utilizing the same procedure. ^{1}H NMR: (CDCl$_3$) δ 0.914 (t, $J = 7.4$ Hz, 3H, CH$_2$*CH$_3$)*, 1.018 (d, $J = 6.8$ Hz, 3H, CH$_3$), 1.2−1.4 (m, 1H, −C*Ha*$_2$−), 1.4−1.6 (m, 1H −C*Hb*$_2$−), 2.1−2.2 (m, 2H, −C*H*−), 3.709 (dd, $J = 5.6$, 8.5 Hz, 1H, ROC*H*−), 4.219 (dd, $J = 5.6$, 8.5 Hz, 1H, ROC*H*−), 4.504 (d, $J = 5.8$ Hz, 1H, Ph(OR)C*H*−). ^{13}C NMR: (CDCl$_3$) δ 12.6, 12.7, 20.3, 43.6, 44.7, 72.7, 87.3, 125.7, 127.1, 128.2, 143.5. HRMS: calc $C_{13}H_{18}O$ 190.135765; obsvd 190.135285.

[η-5:η-1-Tetramethylcyclopentadienyldimethylsilyl(*tert*-butyl)amido] 2-methyl-7-phenylaza-3-titanabicyclo[3.3.0]oct-1-ene (25). An oven-dried 25 mL Schlenk flask was charged with 6.7 mmol of magnesium powder (∼50 mesh, 166 mg). After pump/purging three times with nitrogen, the flask was taken into the drybox, where it was charged with 1.3 mmol of **1** (500 mg). This flask was then reattached to the vacuum manifold. A second oven-dried 25 mL Schlenk flask was charged with 1.3 mmol of the *N*-allyl-*N*-2-butynylaniline (254 mg). The enyne was dissolved in 20 mL of THF, and the resulting solution was transferred to the reaction flask via cannula. The resulting solution quickly changes from clear yellow to a translucent, dark red color. The reaction was stirred for 12 h, then the THF was removed in vacuo. The dark solid was extracted with toluene, which was filtered through a cannula to a separate Schlenk flask. The toluene was concentrated to 4 mL to give a yellow precipitate. Warming the solution redissolved the precipitate, and product was recrystallized at −50 °C. A yellow semicrystalline precipitate (318 mg, 49% yield) was isolated by cannula filtration. ^{1}H NMR indicates the formation of two diastereomers in a ratio of 3:1. When heated in toluene, THF, or benzene, the diastereomer ratio changes to 6.5:1. ^{1}H NMR major diastereomer: (toluene-d_8) δ 0.5073 (s, 3H), 0.5622 (s, 3H), 1.22 (m, 1H), 1.303 (s, 9H), 1.36 (m, 1H), 1.673 (s, 3H), 1.8064 (s, 3H), 1.83(m, 1H), 1.866 (s, 3H), 1.969 (s, 3H), 2.100 (s, 3H), 2.74 (t, 1H), 3.83 (d, 1H), 3.88 (t, 1H), 4.08 (d, 1H), 6.62 (d, 2H), 6.8 (m,1H), 7.263 (t, 2H). ^{13}C NMR: (CDCl$_3$) δ 6.32, 6.58, 11.13, 11.13, 14.57, 14.69, 22.34, 27.92, 34.45, 35.10, 53.27, 58.2, 61.02, 111.95, 112.04, 112.45, 115.85, 116.19, 129.00, 129.08, 129.13, 142.47. Anal. Calcd: C, 71.76; H, 9.04. Found: C, 71.63; H, 9.02.

Crystal Structure of [η-5:η-1-Tetramethylcyclopentadienyldimethylsilyl(*tert*-butyl)amido]titanium(butyl)chloride. Data Collection. An air-sensitive crystal of $C_{19}H_{36}NClSiTi$ with approximate dimensions of 0.10 × 0.15 × 0.18 mm^3 grown from a solution of pentane was mounted on a glass fiber in paratone oil at −80 °C using an improvised cold stage. All measurements were made on a Siemens SMART[50] diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection obtained from a least-squares refinement using the setting angles of 2993 carefully centered reflections with $I > 10\sigma(I)$ in the range 3.59° < 2θ < 49.40° corresponded to a primitive triclinic cell with dimensions $a = 9.6031(5)$ Å; $b = 10.1246(5)$ Å; $c = 12.4133(5)$ Å; $V = 1084.92(8)$ Å^3; $\alpha = 66.499(1)$; $\beta = 82.050(1)°$; $\gamma = 79.344(1)°$. For $Z = 2$ and fw = 389.94, the calculated density is 1.19 g/cm^3. Wilson statistics supported a centric space group which is $P1$ (No. 2). The data were collected at a temperature of −110 ± 1 °C using the ω scan technique to a maximum 2θ value of 49.4°.

Data Reduction. Data were integrated using the program SAINT[51] with a 1.6 × 1.6 × 0.6° box. A total of 5853 reflections were collected. A correction for decay was deemed unnecessary. An empirical absorption correction, XPREP, was applied which resulted in transmission factors ranging from 0.924 to 0.937. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ, for Mo Kα radiation is 5.73 cm^{-1}. Symmetry-equivalent, non-Friedel, reflections were averaged to produce 3560 unique reflections ($R_{int} = 0.04$).

Structure Solution and Refinement. The structure was solved by direct methods[52] and expanded using Fourier techniques.[53] All non-hydrogen atoms were refined anisotropically. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.53 and −0.69 e/Å,[54] respectively. Hydrogen atoms were included at idealized positions, 0.95 Å from their parent atoms. The final cycle of full-matrix least-squares refinement[54] was based on 2452 observed reflections ($I > 3\sigma(I)$) and 208 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.057$; $R_w = [(\sum_w(|F_o| - |F_c|)^2/\sum_w F_o{}^2)]^{1/2} = 0.068$. The standard deviation of an observation of unit weight[55] was 2.10. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\sum_w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. Neutral atom scattering factors were taken from Cromer and Waber.[56] Anomalous dispersion effects were included in F_{calc};[57] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[58] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[59] All calculations were performed using the teXsan[60] crystallographic software package of Molecular Structure Corporation.

X-ray Crystal Structure of [η-5:η-1-Tetramethylcyclopentadienyldimethylsilyl(*tert*-butyl)amido]-2-methyl-7-phenylaza-3-titanabicyclo[3.3.0]oct-1-ene (25). Data Collection. A colorless block crystal of $C_{28}H_{42}N_2SiTi$ having approximate dimensions of 0.15 × 0.28 × 0.7 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a SMART[50] CCD area detector with graphite-monochromated Mo Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured

---

(50) *SMART*, Area-Detector Software Package; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

(51) *SAINT*, SAX Area-Detector Integration Program, V4.024; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

(52) Sheldrick, G. *SHELXS-86*; 1986. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

(53) DIRDIF92: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system, Technical Report of the Crystallography Laboratory; University of Nijmegen, The Netherlands, 1992.

(54) Least-squares function minimized: $\sum w(F_o{}^2 - F_c{}^2)^2$ where $w = 1/[\sigma^2(F_o)] = [\sigma^2_c(F_o) + p^2F_o{}^2/4]^{-1}$; $\sigma_c(F_o)$ = esd based on counting statistics; p = p-factor

(55) Standard deviation of an observation of unit weight: $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o = number of observations and N_v = number of variables.

(56) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. 4.

(57) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(58) Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Kluwer Academic Publishers: Boston, 1992; Vol. C, pp 219−222.

(59) Creagh, D. C.; Hubbell, J. H. *Tables for Crystallography*; Kluwer Academic Publishers: Boston, 1992; Vol. C.

(60) *teXsan*; Crystal Structure Analysis Package; Molecular Structure Corporation: The Woodlands, TX, 1985 & 1992.

positions of 4933 reflections in the range 3.52° < 2θ < 52.3° corresponded to a primitive triclinic cell with dimensions $a = 10.0852(5)$ Å; $b = 11.2983(6)$ Å; $c = 12.5685(7)$ Å; $V = 1305.5(1)$ Å^3; $\alpha = 107.427(1)°$; $\beta = 103.103(1)°$; $\gamma = 96.449(1)°$. For $Z = 2$ and fw = 482.64, the calculated density is 1.23 g/cm^3. Based on packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (No. 2). The data were collected at a temperature of −108 ± 1 °C using the ω scan technique to a maximum 2θ value of 52.3°. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3°, counted for a total of 10 s per frame.

Data Reduction. Data were integrated by the program SAINT[51] with box parameters of 1.6 × 0.6. Of the 7151 reflections that were collected, 4471 were unique ($R_{\mathrm{int}} = 0.034$); equivalent reflections were merged. No decay correction was applied.

The linear absorption coefficient, μ, for Mo Kα radiation is 3.9 cm^{-1}. Data were analyzed for agreement and possible absorption using XPREP.[61] A semiempirical absorption correction based on 3509 reflections with $I > 10\sigma(I)$ was applied that resulted in transmission factors ranging from 0.811 to 0.969. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement. The structure was solved by direct methods[52] and expanded using Fourier techniques.[62] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement[54] on F^2 was based on all 4471 observed reflections and 424 variable parameters and converged (largest parameter shift was 0.08 times its esd) with unweighted and weighted agreement factors of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.073$; $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.046$ (for 3711 reflns $I(\sigma) > 3\sigma(I)$); and $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2} = 0.118$. The standard deviation of an observation of unit weight[55] was 1.94. The weighting scheme was based on counting statistics and included a factor ($p = 0.030$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The methine carbon of the five-membered nitrogen heterocycle was modeled as a site-disordered pair at 9:1 occupancy ratio. This reflects the contribution of two separate diastereomers to the asymmetric unit. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.50 and −0.45 e/Å^3, respectively, and were located near the metal atom.

Neutral atom scattering factors were taken from Cromer and Waber.[56] Anomalous dispersion effects were included in F_{calc};[54] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[58] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[59] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[63]

Acknowledgment. We thank the NSF for support of this work (NSF CHE-9522881). We also thank Dr. Andrew McKnight for providing (+)-[η^5:η^1-indenyldimethylsilyl(α-methylbenzyl)amido]titanium dichloride, and Ms. Shirley Lin for help in manuscript preparation.

Supporting Information Available: A listing of bond lengths, bond angles, and dihedral angles for the two crystal structures reported. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990707Y

---

(61) *XPREP* (v 5.03); Part of the SHELXTL Crystal Structure Determination, Siemens Industrial Automation, Inc.: Madison, WI, 1995.

(62) *DIRDIF94*: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.

(63) *teXsan for Windows*, Crystal Structure Analysis Package; Molecular Structure Corporation: The Woodlands, TX, 1997.