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Remarkable Reactions and Intermediates in Titanocene(IV) Chemistry: Migratory Insertion Reactions of 2,2-Disubstituted-1-alkenes, Intramolecular 1,5-σ Bond Metathesis via ε-Agostic Interactions, and a Rare Example of a β-Agostic Alkyltitanocene Complex

Francoise Sauriol,† Jessica F. Sonnenberg,† Sarah J. Chadder,†
Alexandre F. Dunlop-Brière,† Michael C. Baird,*,† and Peter H. M. Budzelaar*,‡

Departments of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada, and University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

Received June 11, 2010; E-mail: bairdmc@chem.queensu.ca

Abstract: The compound Cp_2TiMe_2 reacts with $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 at 205 K to give, *inter alia*, $[Cp_2TiMe(CD_2Cl_2)][B(C_6F_5)_4]$. This solvent-separated ion pair reacts in turn with 2,4-dimethyl-1-pentene (DMP) to give a series of cationic species, the first being the alkene complex $[Cp_2TiMe(DMP)]^+$, which undergoes ready migratory insertion to form the σ-alkyl complex $[Cp_2Ti(CH_2CMe_2CH_2CHMe_2)]^+$. The latter, which does not contain a β-hydrogen atom, rearranges rapidly via an unprecedented 1,5-σ bond metathesis reaction involving two isomeric ε-agostic species to give the σ-alkyl species $[Cp_2Ti(CH_2CHMeCH_2CMe_3)]^+$; this does contain a β-hydrogen atom and, in concurrent processes, eliminates H_2 or 2,4,4-trimethyl-1-pentene (a major product) to form respectively the allylic complex $[Cp_2Ti\{\eta^3\text{-}(CH_2)_2CCH_2CMe_3\}]^+$ (a major product) or the hydride complex $[Cp_2TiH]^+$. The latter reacts reversibly with free DMP to give the insertion product $[Cp_2Ti(CH_2C\mathit{H}MeCH_2CHMe_2)]^+$ (**V**, a major product), in which the italicized hydrogen atom engages in a β-agostic interaction with the metal atom. Compound **V** is a rare example of both a β-agostic derivative of a group 4 metallocene and a β-agostic compound of any metal in which the ^1H resonance of the agostic hydrogen can be identified in the ^1H NMR spectrum (δ −3.43). Interestingly, a NOESY experiment on **V** indicates slow mutual exchange between the agostic hydrogen atom, the hydrogen atoms on C(1), and those of Me(2). These observations are consistent with the intermediacy of the allylic dihydrogen species $[Cp_2Ti(H_2)\{\eta^3\text{-}(CH_2)_2CCH_2CHMe_2\}]^+$, which loses H_2 to form $[Cp_2Ti\{\eta^3\text{-}(CH_2)_2CCH_2CHMe_2\}]^+$ (a minor product). Support for all steps of the proposed reaction scheme comes from product distributions, from labeling studies utilizing $[Cp_2Ti(CD_3)(CD_2Cl_2)]^+$, and from extensive DFT calculations. The observed titanocene-based chemistry stands in stark contrast to that of the analogous zirconium system, in which the unusual but well-characterized cationic methyl alkene complex $[Cp_2ZrMe(DMP)]^+$ does not undergo migratory insertion and subsequent reactions.

In recent years, there has been considerable interest in the utilization of metallocene complexes of the type $Cp'_2M(Me)(WCA)$ (**A**, where Cp′ = substituted cyclopentadienyl; M = Ti, Zr, Hf; Me = methyl; WCA = weakly coordinating anion such as $B(C_6F_5)_4^-$) as catalysts for the polymerization of alkenes $CH_2{=}CHR$ (R = H, alkyl, aryl).[1] It is universally accepted that polymerization involves initial substitution of the WCA by the alkene to generate a cationic alkene intermediate, $[Cp_2M(Me)(\eta^2\text{-}CH_2{=}CHR)]^+$ (**B**), as in Scheme 1, and that the latter then undergoes migratory insertion, involving 1,2-methyl migration via a four-centered transition state **C**, to give an alkyl intermediate (**D**).

Subsequent steps involve a series of similar insertion reactions via intermediates of the type **E**, which may be stabilized by β-agostic interactions as in **F**. The β-agostic mode of bonding, denoted by the half-arrow in **F**, involves donation of the electron pair in a delocalized H−C(2)−C(1) σ-bonding molecular orbital to a vacant orbital on the highly Lewis acidic metal ion. Although β-agostic species of type **F** have never been directly observed in active group 4 metallocene catalyst systems, there is considerable theoretical evidence for them as resting states during polymerization processes, and β-agostic structures have

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† Queen's University.
‡ University of Manitoba.

(1) For useful reviews see: (a) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (b) Resconi, L.; Camurati, I.; Sudmeijrt, O. *Top. Catal.* **1999**, *7*, 145. (c) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (d) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (e) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (f) Rappé, A. K.; Skiff, W. M.; Casewit, C. J. *Chem. Rev.* **2000**, *100*, 1435. (g) Bochmann, M. *J. Organomet. Chem.* **2004**, *689*, 3982. (h) Fujita, T.; Makio, H. *Comprehensive Organometallic Chemistry*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Amsterdam, 2007; Vol. III, Chapter 11.20. (i) Froese, R. D. J. In *Computational Modeling for Homogeneous and Enzymatic Catalysis*; Morokuma, K., Musaev, D. G., Eds.; Wiley-VCH: Weinheim, Germany, 2008; p 149. (j) Busico, V. *Macromol. Chem. Phys.* **2007**, *208*, 26. (k) Wilson, P. A.; Hannant, M. H.; Wright, J. A.; Cannon, R. D.; Bochmann, M. *Macromol. Symp.* **2006**, *236* (Olefin Polymerization), 100. (l) Alt, H. G.; Licht, E. H.; Licht, A. I.; Schneider, K. J. *Coord. Chem. Rev.* **2006**, *250*, 2.

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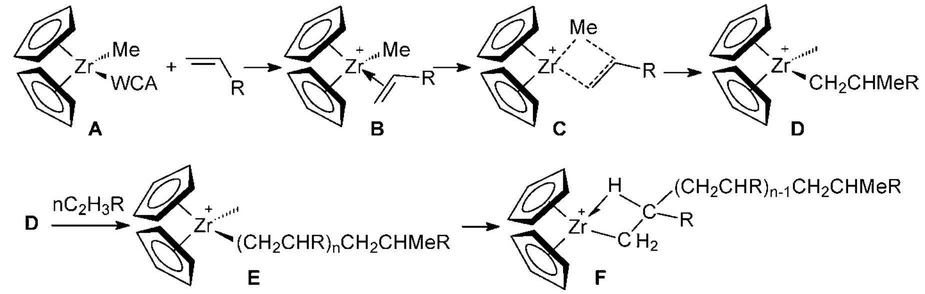
Scheme 1

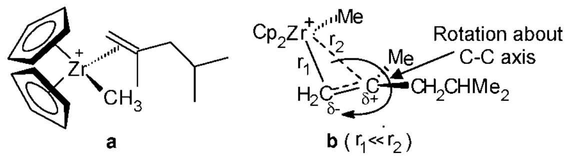


been reported for early transition metal alkyls that are not active in catalysis[2d] (see also below). In addition, examples are also known for late transition metal compounds.[2]

Until our recent reports,[3] simple alkyl alkene complexes of type **B** had also never been observed, apparently because a lack of π back-donation from the d^0 metal ions results in weak alkene−metal bonding, while the activation energies for the type of migratory insertion processes shown in Scheme 1 are very low for ethylene, propylene, and 1-alkenes. That said, using the 2,2-disubstituted alkenes 2,4-dimethyl-1-pentene (DMP) and 2,4-dimethyl-1-heptene (DMH), both examples of a type of alkene that *does not* readily undergo migratory insertion reactions, we were able to characterize in solution at low temperatures the novel cationic complexes $[Cp_2Zr(Me)(DMP)]^+$ and $[Cp_2Zr(Me)(DMH)]^+$ with the $B(C_6F_5)_4^-$ counteranion.[3]

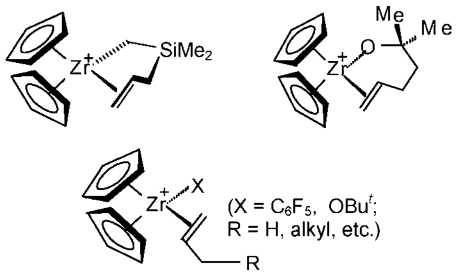
Density functional theory (DFT) calculations on $[Cp_2Zr(Me)(DMP)]^+$ suggested a structure much as in Scheme 2, **a**, albeit with a Zr−C(1) distance (2.61 Å) much less than the Zr−C(2) distance (3.36 Å).[3b] Consistent with an apparently very weak Zr−C(2) interaction, variable-temperature NMR studies demonstrated rotation of the $[-C(Me)CH_2CHMe_2]$ moiety relative to the terminal methylene hydrogens $=CH_2$, as indicated in Scheme 2, **b**.[3b] These two lines of evidence are consistent with the relevance of a near-η^1 structure as in Scheme 2, **b**, of a type believed to be involved in carbocationic polymerization of, e.g., isobutene by cationic metallocene complexes.[4]

Scheme 2



In contrast, although there are reports of a few d^0 alkene zirconocene complexes that are stabilized by chelation and/or contain no ligand that can participate in migratory insertion (Scheme 3),[5] these compounds exhibit considerably less asymmetry in the Zr−C bonding and do not undergo rotation of the substituents on C(2) relative to the terminal $=CH_2$ group.

Scheme 3



Thus, the mode of alkene coordination in the 2,2-disubstituted alkene complexes $[Cp_2Zr(Me)(DMP)]^+$ and $[Cp_2Zr(Me)(DMH)]^+$ is without question unusual, and we decided to study further this class of compounds. In addition to ongoing work on substituted dicyclopentadienyl zirconium complexes of a series of 2,2-disubstituted alkenes, we have also briefly investigated the chemistry of the $Cp_2HfMe_2/[Ph_3C][B(C_6F_5)_4]$ system. Unfortunately, the hafnium precursor is much less reactive than is its zirconium analogue, and while the desired $[Cp_2HfMe(DMP)][B(C_6F_5)_4]$ can be detected, it forms very slowly and cannot be obtained in sufficiently high concentrations to be fully characterized by NMR spectroscopy.

We have turned, therefore, to the chemistry of the analogous $Cp_2TiMe_2/[Ph_3C][B(C_6F_5)_4]$ system, noting that reaction of Cp_2TiMe_2 with [triphenylcyclopropenium]$[B(C_6F_5)_4]$ (1:1.1 mol ratio) in CD_2Cl_2 has been reported to give a red solution of $[Cp_2TiMe][B(C_6F_5)_4]$, with Cp and methyl chemical shifts of δ 6.38 and 1.30, respectively (273 K).[6a] In contrast, we find that reactions of Cp_2TiMe_2 *with varying ratios* of $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 give mixtures of compounds, identified tentatively

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as $[Cp_2TiMe(CD_2Cl_2)][B(C_6F_5)_4]$, $[Cp_2TiMeB(C_6F_5)_4]$, and $\{[Cp_2TiMe]_2(\mu\text{-}Me)\}[B(C_6F_5)_4]$, analogous to those of the previously reported zirconium system,[3b] but that treatment of these with 2,4-dimethyl-1-pentene does not result in formation of an identifiable complex $[Cp_2TiMe(DMP)][B(C_6F_5)_4]$. The latter apparently forms but undergoes migratory insertion to give the σ-alkyl complex $[Cp_2Ti(CH_2CMe_2CH_2CHMe_2)][B(C_6F_5)_4]$, which rearranges rapidly via a σ-bond metathesis reaction involving two ε-agostic species to give the isomeric σ-alkyl complex $[Cp_2Ti(CH_2CHMeCH_2CMe_3)][B(C_6F_5)_4]$. The latter undergoes both rearrangement and loss of H_2 to give the allylic species $[Cp_2Ti\{\eta^3\text{-}(CH_2)_2CCH_2CMe_3\}][B(C_6F_5)_4]$ and also β-elimination to give the C_8 alkene 2,4,4-trimethyl-1-pentene and the hydride complex $[Cp_2TiH]^+$. The latter reacts in turn with free 2,4-dimethyl-1-pentene to give the insertion complex $[Cp_2Ti(CH_2C\mathit{H}MeCH_2CHMe_2)]^+$, in which the italicized hydrogen atom engages in a β-agostic interaction with the metal atom, analogous to the complex shown as **F** in Scheme 1 but in this case sufficiently stable to be characterized. We report herein the experimental and computational evidence for this quite unanticipated series of results.

Experimental Section

All syntheses were carried out under dry, deoxygenated argon using standard Schlenk line techniques. Argon was deoxygenated by passage through a heated column of BASF copper catalyst and then dried by passing through a column of activated 4-Å molecular sieves. Handling and storage of air-sensitive organometallic compounds were done in an MBraun Labmaster glovebox, and NMR spectra were recorded using a Bruker AV600 spectrometer. ^1H and ^{13}C NMR data are referenced to TMS via the residual protons signals of the deuterated solvents. 2,4-Dimethyl-1-pentene was purchased from ChemSampCo, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene from Aldrich, and 2,4-dimethyl-2-pentene from Pfaltz & Bauer; all were stored over activated 4-Å molecular sieves. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Asahi Glass Co. and used as obtained, and CH_3Li and CD_3Li were purchased from Aldrich. Cp_2TiMe_2 was synthesized from Cp_2TiCl_2 and methyl lithium as described elsewhere.[6] As Cp_2TiMe_2 is prone to decomposition to black materials if stored in the solid state,[6] it was generally stored in toluene solution at −30 °C. Dichloromethane-d_2 was dried by storage over activated 4-Å molecular sieves.

Solutions for NMR studies were prepared in a nitrogen-filled glovebox by combining varying amounts of $[Ph_3C][B(C_6F_5)_4]$ (in 0.3 mL CD_2Cl_2) with 10 mg of Cp_2TiMe_2 (in 0.3 mL of CD_2Cl_2) at room temperature to give bright yellow solutions. The NMR tubes were sealed with rubber septa, taken quickly out of the glovebox, and immersed within 2−4 min in a dry ice/acetone bath (195 K). In a typical experiment, a sample was then placed in the precooled (205 K) probe of the NMR spectrometer, a ^1H NMR spectrum was run, and 10 mol equiv of 2,4-dimethyl-1-pentene was layered onto the cold solution (195 K). The tube was tapped gently to induce slight mixing and spectra were obtained at various temperatures as more DMP diffused into the sample, but samples were not shaken, as thorough mixing induced oligomerization.

All geometry optimizations were carried out with Turbomole[7a,b] using the TZVP basis[7c] (small-core pseudopotential for Zr,[7d] all-electron for Ti) and the functionals b-p[7e−g] and b3-lyp[7g−j] (the latter with the RI approximation) in combination with an external optimizer (PQS OPTIMIZE).[7k,l] Vibrational analyses were carried out for all stationary points to confirm their nature (one imaginary frequency for transition states, none for minima). Final energies were obtained using the TZVPP basis[8a] (no RI approximation for b-p results) and a COSMO solvent correction: $\epsilon = 9.1$ (CH_2Cl_2) and 2.4 (for comparison with the reactions of the Zr analogues in toluene).[8b] These were combined with thermal corrections (enthalpy and entropy, 205 K, 1 bar) from the TZVP vibrational analyses to arrive at the final free energies. To account for the reduced freedom of movement in solution, entropy contributions to the free energies were scaled to two-thirds of their gas-phase values.[8c,d] The results for the two functionals are roughly similar, except that calculated barriers are systematically somewhat higher with the b3-lyp functional. In the text we will only refer to the b-p energies in CH_2Cl_2, relative to $[Cp_2TiMe(CH_2Cl_2)]^+$; for full results and corresponding b3-lyp energies, see Table S1 in the Supporting Information.

NMR chemical shifts and spin−spin coupling constants were calculated with Gaussian 03,[8e] performed with Turbomole b3-lyp optimized geometries using the TZVP basis set on Ti (SDD basis and pseudopotential on Zr[8f,g]) and the TZVP, IGLO-II, and IGLO-III[8h] basis sets on C and H, in combination with the functionals B3LYP[7h,j,m] and BP86.[7e,f] Calculated H−H and C−H couplings were found to be insensitive to the choice of the C/H basis, but the performance of BP86 was noticeably poorer than that of B3LYP for simple reference compounds (alkanes and alkenes), so in the text we mention only the B3LYP/IGLO-III NMR results. For full results of the calculations, see Tables S2−S5 in the Supporting Information.

Results and Discussion

Formation of Methyltitanium Species from Reactions of Cp_2TiMe_2 with $[Ph_3C][B(C_6F_5)_4]$. Reactions of the Cp_2TiMe_2/$[Ph_3C][B(C_6F_5)_4]$ system were carried out several times and with

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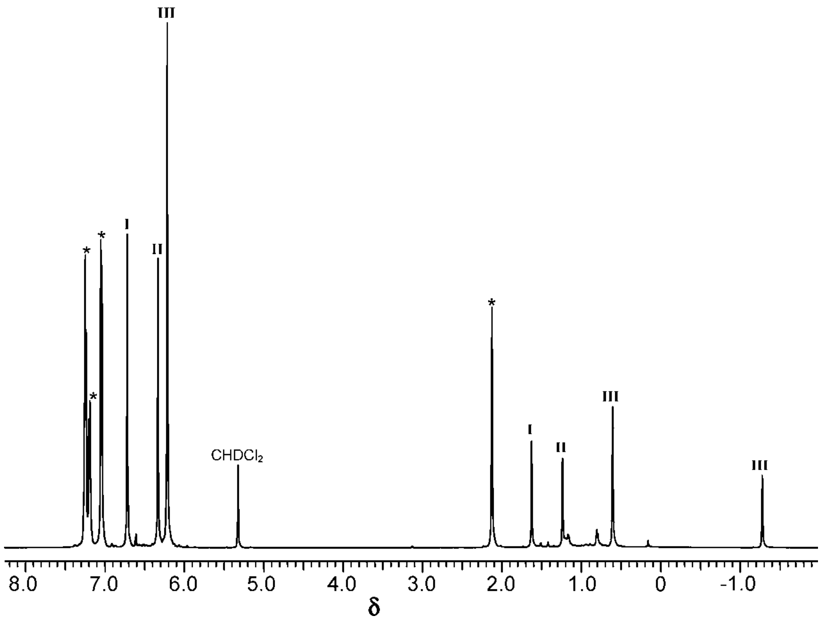

Figure 1. ^{1}H NMR spectrum (205 K) of a reaction mixture obtained from reaction of $[Ph_3C][B(C_6F_5)_4]$ with approximately 2 equiv of Cp_2TiMe_2 and showing the presence of $[Cp_2TiMe(CD_2Cl_2)][B(C_6F_5)_4]$ (**I**), $[Cp_2TiMeB(C_6F_5)_4]$ (**II**), and $\{[Cp_2TiMe]_2(\mu\text{-Me})\}[B(C_6F_5)_4]$ (**III**); * denotes the resonances of $MeCPh_3$.

reactant ratios in the range ~0.5:1 to ~2:1. Bright yellow NMR samples were prepared as described in the Experimental Section and were placed in the probe of a 600 MHz NMR spectrometer preset to 205 K. The NMR spectra were found to exhibit resonances of the product of methyl abstraction by trityl ion, $CMePh_3$ (δ 7.0−7.3 (m), 2.13 (s)), and of up to three new titanium complexes. As an example, the ^{1}H NMR spectrum of a typical reaction mixture ($[Cp_2TiMe_2] \approx 2[Ph_3C^+]$, Figure 1) exhibited singlet Cp resonances at δ 6.72, 6.33, and 6.21 and singlet Ti−Me resonances at δ 1.63, 1.24, 0.61, and −1.28. On the basis of relative intensities and NOESY correlations in this and several similar spectra run at 205 K, the resonances at δ 6.72 and 1.63 are to be assigned to the same molecule, as are those at δ 6.33 and 1.24 and those at δ 6.21, 0.61, and −1.28. Conversions to each of the species varied somewhat, depending in part of the Cp_2TiMe_2:$[Ph_3C][B(C_6F_5)_4]$ ratio, but the species with resonances at δ 6.72 and 1.63 was generally formed in 68−95% yield, that with resonances at δ 6.33 and 1.24 in 5−20% yield, and that with resonances at δ 6.21, 0.61, and −1.28 in 0−17% yield.

By analogy with similar corresponding zirconocene systems,[3a,b] one anticipates formation of the compounds $[Cp_2TiMe(CD_2Cl_2)][B(C_6F_5)_4]$ (**I**), $[Cp_2TiMeB(C_6F_5)_4]$ (**II**), and $[\{Cp_2TiMe\}_2(\mu\text{-Me})][B(C_6F_5)_4]$ (**III**), and assignment of the trio of resonances at δ 6.21, 0.61, and −1.28 to the methyl-bridged dinuclear species **III** is apparent on the basis of the number of methyl resonances and comparison with the spectrum of the zirconium analogue.[3b] To distinguish between the two mononuclear species, we note that Cp chemical shifts in metallocene compounds are generally strongly influenced by inductive effects,[3i,9] and it thus seems reasonable to assign the less shielded Cp resonance at δ 6.72 to the cationic species **I** and the more shielded Cp resonance at δ 6.33 to the neutral species **II**. Similar assignments have been suggested for the analogous zirconium compounds $[Cp_2ZrMe(\text{solvent})][B(C_6F_5)_4]$ (solvent = CD_2Cl_2, C_6D_5Cl) and $Cp_2ZrMeB(C_6F_5)_4$,[3a,b] and thus **I** is believed to contain a solvent-separated or outer-sphere ion pair, while **II** is believed to contain a contact or inner-sphere ion pair in which, presumably, the anion coordinates via one or more fluorine atoms.[1a] HSQC and HMBC experiments carried out on a mixture containing **I**, **II**, and **III** showed that the methyl and Cp ^{13}C chemical shifts of **I** are δ 75.7 ($^1J_{CH}$ = 129 Hz) and 128.1 ($^1J_{CH}$ = 176 Hz), respectively, and that those of **II** are δ 62.8 ($^1J_{CH}$ = 126 Hz) and 117.4 ($^1J_{CH}$ = 176 Hz), respectively. The ^{13}C chemical shifts of the terminal methyl, bridging methyl, and Cp groups of **III** are δ 55.8 ($^1J_{CH}$ = 127 Hz), 44.2 ($^1J_{CH}$ = 138 Hz), and 115.6, respectively. The methyl $^1J_{CH}$ values are typical of literature data.[10]

As indicated above, utilization of a significant deficiency of $[Ph_3C][B(C_6F_5)_4]$ resulted in the observation of larger proportions of **III** and even of unreacted Cp_2TiMe_2 (δ 6.03, −0.28) in reaction mixtures, while reaction of excess $[Ph_3C][B(C_6F_5)_4]$ resulted only in the formation of **I** and **II**. In cases where comparable amounts of Cp_2TiMe_2 and $[Ph_3C][B(C_6F_5)_4]$ were used, the relative proportions of **I** and **II** varied unpredictably. The number of titanium-containing products observed here, up to three, is at variance with the single product, **II**, reported from the reaction of Cp_2TiMe_2 with [triphenylcyclopropenium]-$[B(C_6F_5)_4]$ (1:1.1 mol ratio).[6a] The differences are attributable to the varying Cp_2TiMe_2:$[Ph_3C][B(C_6F_5)_4]$ ratios used here and also, probably, to the differing degrees of warming of the samples.

Reactions of Mixtures of I, II, and III with 2,4-Dimethyl-1-pentene: An Overview. We earlier showed that reactions of 2,4-dimethyl-1-pentene (DMP) with the Cp_2ZrMe_2/$[Ph_3C][B(C_6F_5)_4]$ system in both C_6D_5Cl and CD_2Cl_2 produce the novel, cationic methyl-alkene species $[Cp_2ZrMe(DMP)]^+$. NMR spectra of the latter were found to exhibit evidence (NOESY) for exchange between the two terminal methylene hydrogen atoms, arising from a most unusual rotation of the ${=}CMeCH_2CHMe_2$ group relative to the terminal $=CH_2$ (Scheme 2, **b**), for intramolecular

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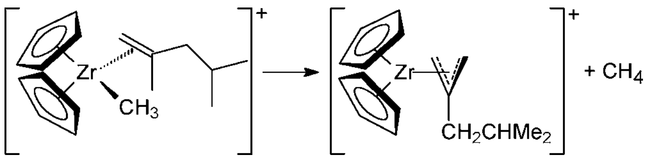
(9) Gray, D. R.; Brubaker, C. H. *Inorg. Chem.* **1971**, *10*, 2143.

(10) Courtot, P.; Pichon, R.; Salaun, J. Y.; Toupet, L. *Can. J. Chem.* **1991**, *69*, 661.

"flipping" between faces and for intermolecular exchange between free and coordinated DMP. The DMP complex was also found to decompose to methane and the allylic species, as shown in Scheme 4.[3a,b]

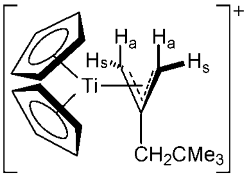
Scheme 4



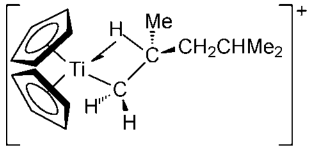
Anticipating analogous chemistry with the Cp_2TiMe_2/$[Ph_3C][B(C_6F_5)_4]$/DMP system, we opted to begin by searching for exchange cross peaks between the resonances of the terminal methylene hydrogen atoms of free DMP with resonances which could then be assigned to the terminal methylene hydrogen atoms of coordinated DMP in $[Cp_2Ti(Me)(DMP)]^+$. To this end, and as a general procedure, 10 mol equiv of 2,4-dimethyl-1-pentene was added to NMR tubes containing CD_2Cl_2 solutions of various combinations of the titanium precursors **I**, **II**, and **III**, prepared as above at 205 K and maintained at that temperature. Each tube was tapped gently to induce slow diffusion of the DMP toward the bottom of the NMR tube, but samples were not shaken, as more thorough mixing resulted in significant oligomerization, as indicated by broadened resonances at δ ~2.4 and 4.0−5.0. Indeed, minor resonances of apparent oligomerization products (δ 2.44 (br), 4.86 (br)) were observed in the NMR spectra of several reaction mixtures, but oligomer formation was generally kept to a minimum. A control experiment showed that $[Ph_3C][B(C_6F_5)_4]$ alone does not induce oligomerization of DMP at the temperatures used in this study.

Reaction mixtures were monitored at 205 K and above by a series of 1D ^1H NMR and 2D NOESY experiments extending over 1−4 h. To our initial chagrin, under no conditions of temperature or combinations of **I**, **II**, and **III** did we observe cross peaks that would provide evidence of exchange between free and coordinated DMP. Instead, as shown below, we typically observed the formation of 2,4,4-trimethyl-1-pentene (TMP) and the β-agostic species **V** in yields of ~2% within 10 min and 4−5% within 30 min. The amount of **V** generally decreased after 1−2 h as the resonances of allylic species **IV** and, to a lesser extent, **VI**, appeared and grew in. When the reaction was carried out at 225 K, the agostic species **V** was not observed, but the allyl compounds **IV** and **VI** formed relatively rapidly. On one occasion, a sample containing 4−5% of agostic species **V** was warmed slowly to 225 K. The resonances of **V** broadened and decreased to 1−2% at 225 K, but cooling to 205 K did not result in its re-forming. Compound **V** thus decomposes at temperatures above 205 K. No other identifiable titanocene compounds formed in significant quantities over 1−3 h time periods in the temperature range 205−225 K.

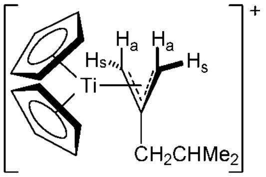
Interestingly, these products resulted only from reactions of the solvent-separated, cationic complex **I**, as the contact ion pair **II** was essentially inert to reaction with DMP at the temperatures used in this study. While the greater reactivity of **I** than of **II** may be rationalized on the basis of both electrostatic and steric factors, the apparent disinclination of **II** to convert to and thus replenish **I** seems surprising. However, NOESY experiments at temperatures as high as 225 K and with mixing times of 3 and 0.4 s revealed no indication of intermolecular exchange of either methyl or Cp ligands of these compounds; thus, under the conditions of the experiments described here, any equilibration between **I** and **II** must be very slow, and neither converts to the other at a significant rate.



IV



V



VI

Note that TMP is an eight-carbon compound and that **IV** contains an eight-carbon allylic ligand; both presumably arise from a combination of DMP and the Ti−Me group of **I**. In contrast, **V** contains a seven-carbon fragment that appears to arise from combination of a coordinated DMP with an as-yet undetected titanium hydride, and it is also a β-agostic species of the type noted above as never having been previously observed in a group 4 metal metallocene complex of this type. In addition, while **VI** is the titanium analogue of the allylzirconium species shown in Scheme 4, it forms in relatively small amounts and appears to be a secondary product; thus, its mode of formation is not as shown in Scheme 4.

Identification of 2,4,4-Trimethyl-1-pentene (TMP, $CH_2{=}C(Me)CH_2CMe_3$). Soon after addition of DMP to a solution of the titanium reactants at 205 K, there appeared singlet resonances of comparable intensity at δ 4.56 and 4.79, i.e. in the same region as the terminal methylene resonances of DMP (δ 4.59, 4.66). A COSY experiment showed that the new resonances were mutually coupled, and NOESY, HSQC, and HMBC experiments indicated that they were to be attributed to the terminal methylene hydrogen atoms of TMP. The other singlet resonances of TMP were subsequently observed at δ 1.79 (Me-2), 1.87 (CH_2), and 0.85 (CMe_3), and the assignments were then unambiguously confirmed by comparison with the ^1H NMR spectrum (CD_2Cl_2, 205 K) of an authentic sample of TMP.

Identification of the Titanium-Containing Products: Structure of IV. Concomitant with the above, we sought evidence for new titanocene species in a series of experiments monitored by ^1H NMR spectroscopy. Since the high-field regions of ^1H NMR spectra (δ 1−2) were generally complicated by plethorae of methyl, methylene, and methyne resonances arising from **I**, **II**, **III**, DMP, and the various products, we monitored initially the Cp region of the spectra (δ 5.5−7.5), which was generally relatively free of interferences. A good example is shown in Figure 2, where the resonances of **I** and **II** are observed at δ 6.72 and 6.33, respectively (Figure 2a). On the addition of DMP (Figure 2b,c), new Cp resonances appear at δ 6.86 and 6.75 and grow stronger. Another Cp resonance also appears at δ ~7.08 but is partially obscured by a stronger phenyl resonance of $CMePh_3$ and is not shown. Longer reaction times and somewhat higher temperatures result in the Cp resonance at δ 6.75 broadening somewhat because of the growth of another Cp resonance at about the same chemical shift. At temperatures >225 K, the resonance at δ 6.86 weakened drastically.

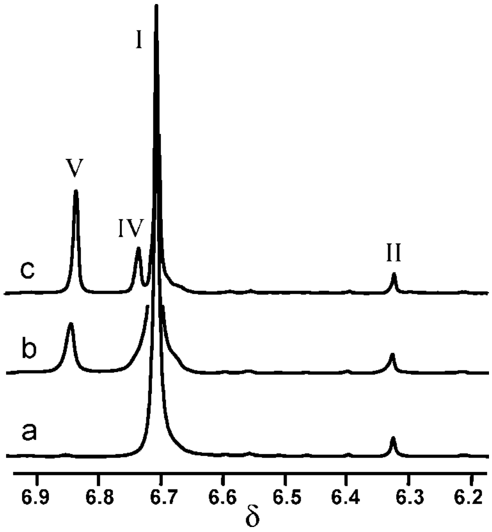


Figure 2. ^{1}H NMR spectrum (205 K, in the region δ 6.25−7.00) of a reaction mixture involving 2,4-dimethyl-1-pentene, [$Cp_2TiMe(CD_2Cl_2)$]-[$B(C_6F_5)_4$] (**I**), and [$Cp_2TiMeB(C_6F_5)_4$] (**II**) (a) before the addition of DMP, (b) 10 min after mixing, and (c) several hours after mixing.

Unfortunately, as is clear from Figure 2, conversions to the Cp-containing products were never high, and thus identification and assignment of each compound's other resonances, which would always be of lower intensities, could not be readily monitored solely by 1D ^{1}H NMR spectroscopy. However, NOESY and COSY experiments complemented by HSQC and HMBC experiments generally provided unambiguous assignments.

Thus, a NOESY experiment (Figure S1, Supporting Information) exhibited NOE correlations between the Cp resonances at δ 6.75 and ~7.08, and, as these two resonances appear to have comparable intensities, they are reasonably attributed to two nonequivalent Cp ligands of a titanocene species. NOE correlations were also observed between the Cp resonance at δ 6.75 and singlets at δ 1.80 and 3.12, between the Cp resonance at δ ~7.08 and a singlet at δ 6.02, and between the singlets at δ 1.80 and 6.02. Other NOEs were also noted between the resonances at δ 3.12 and 1.80 and a resonance at δ 0.86.

Once identified as belonging to the same molecule, the six resonances noted at δ 0.86, 1.80, 3.12, 6.02, 6.75, and 7.08 were found to integrate reasonably well (given the extent of overlap) to nine, two, two, two, five, and five hydrogens, respectively, while a DEPT-HSQC experiment indicated that the resonance at δ 3.12 was indeed attributable to a CH_2 group. A COSY experiment (Figure S2, Supporting Information) showed that the resonances at δ 1.80 and 6.02 were mutually coupled but revealed no other significant spin−spin couplings between the resonances at δ 0.86, 1.80, 3.12, 6.02, 6.75, and 7.08. An HSQC experiment (Figure S3, Supporting Information) showed that the protons at δ 3.12 and 0.86 were bonded to carbon atoms with chemical shifts of δ 60.9 ($^1J_{CH}$ = 129 Hz) and 29.3, respectively, that the Cp protons at δ 6.75 and 7.08 were bonded to carbon atoms with chemical shifts of δ 120.7 and 122.2, respectively, and that the protons with chemical shifts δ 1.80 and 6.02 were attached to the same carbon atom (δ 85.5, $^1J_{CH}$ = 160, 153 Hz, respectively), despite their large difference in chemical shift but consistent with the strong mutual NOE correlations mentioned above.

Interestingly, in view of the HSQC correlation of the ^{1}H resonance at δ 6.02 and the ^{13}C resonance at δ 85.5, an HMBC experiment (Figure S4, Supporting Information) exhibited a cross peak between the same pair of ^{1}H and ^{13}C resonances, indicating that the site attributed to the ^{13}C resonance at δ 85.5 must contain two identical terminal carbon atoms, as in a symmetrical allyl group. Thus, it was becoming increasingly clear that the new complex was to be identified as **IV**, an eight-carbon homologue to the symmetric seven-carbon complex shown in Scheme 4. Note that, on the basis of the observed NOEs, the resonance at δ 7.08 may be assigned to the Cp group of **IV** that eclipses the two H_a atoms and the resonance at δ 6.75 to the Cp ligand that eclipses the neopentyl group. Thus, the resonances at δ 1.80 and 6.02 are assigned to H_s and H_a, respectively, and their significant differences in orientation relative to the Cp ligands provides a rationale for the very large difference in chemical shift between them.

Ring current effects[11] on H_a and H_s must be very different, a conclusion supported computationally (see Experimental Section and Tables S2 and Tables S3 of the Supporting Information). The chemical shifts are also very different from those of the corresponding zirconium complex, δ ~2.9 (H_s) and 3.6 (H_a),[3a,b] the difference between the titanium and zirconium systems probably arising from the significantly different covalent radii of the two metals. Thus, it has been noted previously that differences between the chemistry of otherwise identical compounds of the two metals lie in the greater steric crowding around the smaller metal atom,[12] and it seems that shorter titanium−ligand distances force the allylic hydrogens closer to the Cp ligands, thus enhancing ring current effects. The HMBC correlations facilitated assignments of the ^{13}C chemical shifts of the center carbon of the allyl group (δ 175.9) and of the *tert*-butyl quaternary atom (δ 33.1), and further HMBC correlations were observed between the H_a resonance at δ 6.02 and the CH_2 ^{13}C resonance at δ 60.9, between the CH_2 ^{1}H resonance at δ 3.12 with both the ^{13}C allylic resonances at δ 85.5 and 175.9 and the ^{13}C *tert*-butyl resonances at 29.3 and 33.1, and between the *tert*-butyl ^{1}H resonance at δ 0.86 and the ^{13}C resonances at δ 60.9 (CH_2) and 33.1 (CMe_3).

As the series of 2D NMR experiments neared completion, it became apparent that **IV** is thermally stable to temperatures in excess of 250 K. Thus, although an attempt at recrystallization failed, it was possible to obtain a sample of crude product free of volatile reactants and byproducts. To this end, a reaction mixture (Cp_2TiMe_2/[Ph_3C][$B(C_6F_5)_4$]/DMP) prepared as above was stirred at 213 K for 1 h, the solvent was removed under reduced pressure, and the solid product was washed well with cold hexanes. All volatiles were removed under reduced pressure, and a ^{1}H NMR spectrum of the residue in CD_2Cl_2 was run at 205 K. As can be seen in Figure S5 of the Supporting Information, the resonances listed above at δ 0.86, 1.80, 3.12, 6.02, 6.75, and 7.08 were now much more apparent.

In addition to the resonances attributed above to **IV**, spectra also exhibited weak ^{1}H resonances with chemical shifts very similar to those of **IV**. Thus, as mentioned above, the Cp resonance at δ 6.75 broadened slightly with time, and, in addition to the resonances of **IV** at δ 6.02 and 1.80, 1D ^{1}H NMR spectra also exhibited a pair of much weaker resonances at δ 5.99 and 1.84. Given the near coincidence of these resonances with the H_s and H_a resonances of **IV**, we wondered if they might be attributable to the same positions of the allyl complex denoted above as **VI**.

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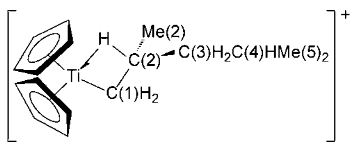
(12) Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1995**, *14*, 746.

Although **VI** was never present at a level of more than 10% of **IV**, with the result that its resonances were generally very weak and/or obscured by other resonances, we were able to identify **VI** with reasonable certainty. Allyl complex **VI** is very similar in structure to **IV**, the only difference being an isopropyl group in place of the *tert*-butyl group, and thus the analysis of **VI** was very similar to that of **IV**. The ^{1}H chemical shifts derived for **VI** are (215 K, CD_2Cl_2) δ 1.84 (s, 2H, H_s), 5.99 (s, 2H, H_a), 3.08 (d, 2H, CH_2), 1.61 (m, 1H, CH), 0.88 (d, Me), 6.75, 7.08 (s, Cp), while the ^{13}C chemical shifts are δ 85.0 (terminal carbon of the allyl group), 56.2 (CH_2), 22.2 (CH_3), 177.6 (center carbon of the allyl group), 30.7 (*C*H), 122.2, 120.7 (Cp). A COSY experiment demonstrated spin−spin coupling between H_s and H_a, between the CH_2 and CH groups, and between the CH and Me groups, and, as with **IV**, an HSQC experiment confirmed that the hydrogen atoms with resonances at δ 1.84 and 5.99 are on the same carbon atom despite their large differences in shift. An HMBC experiment was very helpful in the characterization of **VI**, yielding the ^{13}C chemical shift of the allylic center carbon at δ 177.6 and of the CH group at δ 30.7. Also supporting the structure of **V** were cross peaks between the resonance at δ 5.99 with the CH_2 ^{13}C resonance at δ 56.2 and between the CH_2 resonance at δ 3.08 with the ^{13}C resonances at δ 85.0 (terminal carbon of the allyl group), 177.6 (center carbon of the allyl group), 30.7 (*C*H), and 22.2 (CH_3). Other correlations were too weak to be observed. NOEs of **VI** were observed between the Cp resonance at δ 7.08 and the resonance of H_a at δ 5.99, as well as between the Cp resonance at δ 6.75 and both the CH_2 resonance at δ 3.08 and the H_s resonance at δ 1.84 (see Figures S1−S4, Supporting Information).

Structure of the β-Agostic Complex, $[Cp_2Ti(CH_2C(\beta\text{-H})(Me)CH_2CHMe_2)]^+$ (V). In addition to the resonances of TMP, **IV**, and **VI**, a fourth set of resonances was also found to develop when the temperature was maintained at 205 K (they are absent in Figures S1−S4, which were run at 215 K). The most immediately noticeable of these were the above-mentioned Cp singlet at δ 6.86 (~10H), two elements of an AB quartet at δ 3.89 and 3.99 (1H each, $J = 4.5$ Hz), and a broad resonance of comparable intensity (1H) at δ −3.43. The negative value of the latter is very unusual, as terminal hydrides of d^0 group 4 compounds generally exhibit positive chemical shifts.[13]

A COSY experiment (Figure S6, Supporting Information) indicated that the three resonances at δ 3.89, 3.99, and −3.43 were mutually coupled and that the resonance at δ −3.43 was also coupled to an apparent methyl resonance (intensity three) at δ 1.42 and a resonance of intensity one at δ 1.60. In addition, two apparent methyl resonances at δ 0.60 and 0.88 were coupled to an apparent CH resonance at δ 1.57. A NOESY experiment (Figure S7, Supporting Information) revealed NOEs between the Cp resonance at δ 6.86 with the resonances at δ 3.89, 3.99, 1.42, and −3.43, and integrations indicated that the resonances at δ 6.86, 3.89, 3.99, 1.42, and −3.43 correspond to ten, one, one, three, and one hydrogen, respectively. Note that the resonances at δ 3.89/3.99, 1.42, and −3.43 also exhibited negative correlations, implying mutual exchange processes. The significance of this latter observation will be discussed below. An HSQC experiment (Figure S8, Supporting Information) indicated the carbon−hydrogen connectivities shown in Table 1, while partial traces of the HSQC spectrum gave some of the spin−spin coupling constants of Table 1 (Figure S9, Supporting Information).

Table 1. NMR Data for **V**



atom positions	δ (^{1}H)	δ (^{13}C)	coupling constants
H(1,1′), C(1)	3.89, 3.99	110.8	$^2J_{HH} = 4.5$ Hz,[a] $^1J_{CH} = 145.3$ Hz
H(2), C(2)	−3.43	54.3	$^1J_{CH} = 87.2$ Hz[a]
Me(2)	1.42	25.1	
H(3), C(3)	1.60, 1.71	50.8	
H(4), C(4)	1.57	24.9	
Me(5)	0.60	20.1	
Me(5′)	0.88	22.7	
Cp	6.86	120.7	

[a] The coupling constants between the resonance at δ −3.43 and those at δ 3.91, 3.99, and 1.44 are 4.5, <3, and 4.5 Hz, respectively.

An HMBC experiment (Figure S10, Supporting Information) demonstrated correlations between the ^{1}H resonances at δ 3.89 and 3.99 with ^{13}C resonances at δ 50.8 and 25.1 (which is known from the HSQC experiment to correlate with the proton resonance at δ 1.42). The resonance at δ 1.42 also correlates with carbon resonances at δ 50.8 (aliphatic region), 54.3 (aliphatic region; known from the HSQC experiment to be attached to the proton with chemical shift δ −3.43), and 110.8. The HMBC experiment also showed that the proton at δ 0.60, which has the same amplitude as that at δ 1.42, correlates with the carbon resonances at δ 50.8, 24.9, and 22.7.

Species **V** is thus a titanocene complex containing a seven-carbon ligand, with all carbon atoms presumably derived from DMP alone rather than from a combination of DMP and a Ti−Me group. Indeed, the fact that DMP has been incorporated into **V** was demonstrated by a NOESY experiment at 220 K which showed that **V** undergoes intermolecular exchange with free DMP. Interestingly, one hydrogen atom in **V**, that which exhibits the negative chemical shift, must be in a most unusual environment, and its very small $^1J_{CH}$ of 87.2 Hz is clearly diagnostic of an agostic hydrogen atom.[2,14] Based on all of the 2D NMR evidence, the structure must be essentially as shown for **V**, as indicated above. Assignments of all of the ^{1}H and ^{13}C NMR data for **V** are collected in Table 1.

Computational Study of V. Figure 3 shows the minimized structure of **V**, based on calculations at the b-p level. Important bond lengths and angles are presented in Table 2, which also includes for purposes of comparison relevant structural information for $[Cp_2Ti(Et)]^+$ (Et = ethyl), calculated at the same level, and both crystallographic and calculated data for the extensively studied $Ti(Et)Cl_3(dmpe)$[2d,14] and the zirconocene complex, $[(\eta^5\text{-}C_5H_4Me)_2Zr(Et)(PMe_3)]^+$.[15] The structures of the latter two compounds are shown in Figure 4. Both have been shown experimentally to contain a β-agostic ethyl ligand with a small M−C(1)−C(2) bond angle and a close approach of a β-hydrogen atom to the metal, and in both cases the unique β-agostic

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(13) (a) Bickley, D. G.; Hao, N.; Bougeard, P.; Sayer, B. G.; Burns, R. C.; McGlinchey, M. J. *J. Organomet. Chem.* **1983**, *246*, 257. (b) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. (c) van den Hende, J. R.; Hessen, B.; Meetsma, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 537. (d) Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed.* **1992**, *31*, 1375. (e) de Wolf, J. M.; Blaauw, R.; Meetsma, A.; Teuben, J. H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 4977. (f) Visser, C.; van den Hende, J. R.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2001**, *20*, 1620. (g) Baldwin, S. M.; Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **2008**, *130*, 17423.

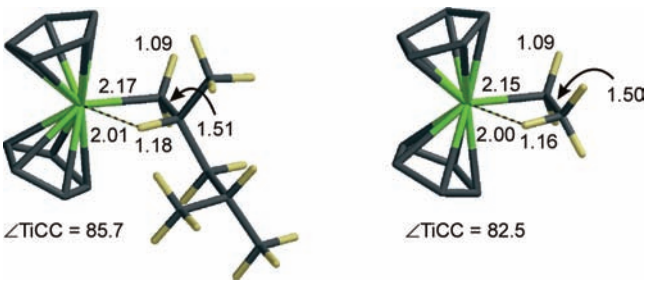

Figure 3. Calculated geometries (b-p/TZVP) for **V** and $[Cp_2Ti(Et)]^+$. Bond lengths are in angstroms, angles in degrees. Cyclopentadienyl hydrogens have been omitted for clarity.

hydrogen was located in the electron density maps and the metal−hydrogen bond distance was determined. For details of the calculations, see the Experimental Section and Tables S4 and S5 of the Supporting Information.

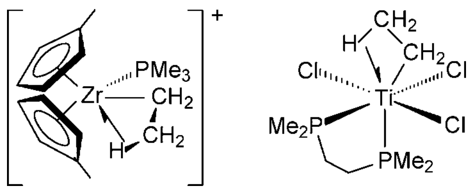

Figure 4. Structures of $[(\eta^5\text{-}C_5H_4Me)_2Zr(Et)(PMe_3)]^+$ and $Ti(Et)Cl_3(dmpe)$.

As indicated in Figure 3 and Table 2, the Ti−C(1) bond lengths calculated for **V** and $[Cp_2Ti(Et)]^+$ are well within the range of bond lengths found crystallographically for a variety of titanocene-alkyl compounds (2.00−2.239 Å),[16] and both compare well also with the calculated and crystallographic data for $Ti(Et)Cl_3(dmpe)$. Consistent with β-agostic structures, the M−C(2) bond distances are in the narrow range, 13−18% longer than the corresponding M−C(1) bond lengths, and the metal−C(1)−C(2) bond angles are all considerably smaller (<86°) than the tetrahedral bond angle. Although no literature precedent exists for titanocene-β-agostic metal−hydrogen bond distances, the Ti−H distances obtained here for **V** and $[Cp_2Ti(Et)]^+$ compare well with those of $Ti(Et)Cl_3(dmpe)$ and $[(\eta^5\text{-}C_5H_4Me)_2Zr(Et)(PMe_3)]^+$ and are appropriately shortened relative to the metal−μ-H distances of several bridging hydrides of zirconium.[13]

DFT calculations were also carried out on $Ti(Et)Cl_3(dmpe)$, and the calculated structural parameters are in good agreement with the experimental data.[14e] In any case, the data for $Ti(Et)Cl_3(dmpe)$ clearly imply an agostic interaction analogous to that observed experimentally for **V**. In general, in these agostic ethyl complexes, the methyl groups undergo rapid rotation and only average chemical shifts are observed. Thus, rotation about the C(1)−C(2) bond of $Ti(Et)Cl_3(dmpe)$ is rapid on the NMR time scale, and the agostic bonding seems weaker than in **V**,[14b] although we note that the β-methyl group can rotate without losing all agostic interactions. However, $^1J_{CH}$ and $^2J_{HH}$ for the $C(1)H_2$ group of $Ti(Et)Cl_3(dmpe)$ are 150 and 7.8 Hz,[14b] respectively, rather similar to the corresponding data for **V**.

The negative chemical shift of the agostic hydrogen of **V** seems unusual, since terminal d^0 group 4 metal hydrides exhibit positive chemical shifts.[13] However, as with the allylic resonances discussed above, calculations suggest that the negative shift is mainly caused by the ring current effects of the cyclopentadienyl rings. Supporting this conclusion, similar negative shifts are calculated for the β-agostic hydrogens of $[Cp_2Ti(Et)]^+$ and $[(\eta^5\text{-}C_5H_4Me)_2Zr(Et)(PMe_3)]^+$ but *not* for that of $Ti(Et)Cl_3(dmpe)$, which is similarly agostic but does not contain Cp ligands.

Also apparently anomalous, the C(1) chemical shift of δ 110.8 and the values of $^2J_{HH}$ (4.5 Hz) and $^1J_{CH}$ (145.3 Hz) for the $C(1)H_2$ group seem rather incompatible with sp^3 hybridization. However, comparisons with the observed and calculated NMR data for **V**, $[Cp_2Ti(Et)]^+$, and $Ti(Et)Cl_3(dmpe)$ (Table 3) suggest that these data are not, in fact, unusual. For both **V** and $[Cp_2TiEt]^+$, the calculated coupling constants $^1J_{CH}$ are about 150 Hz for C(1)−H(1), about 145 Hz for the "normal" C(2)−H(2) bonds, and about 80 Hz for the β-agostic C−H bond. The low values for the β-agostic C−H bonds suggest significant weakening, while the large value of $^1J_{CH}$ in $Ti(Et)Cl_3(dmpe)$ has been attributed to ring strain.[14b,g]

The nature and implications of β-agostic bonding have evolved from the time of the recognition, some 20 years ago, of the phenomenon as having general significance. Initially a model in which electron density in the CH bonding molecular orbital is donated to a vacant orbital on the metal was proposed,[2a,b] and recent, more sophisticated calculations essentially differ only in having the donor orbital more delocalized over the H−C−C σ-bond framework of the alkyl ligand.[2d,g−i] However, the importance of a vacant acceptor orbital on the metal is universally accepted, as is the necessity of the metal center being highly Lewis acidic.

Non-agostic zirconocene complexes of the type $[Cp_2ZrR(L)]^+$ (R = alkyl; L = neutral ligand) are 16-electron species with a single vacant orbital that behaves as the receptor orbital in the β-agostic interaction observed in the cationic species $[(\eta^5\text{-}C_5H_4Me)_2Zr(Et)(PMe_3)]^+$.[15] In contrast, a non-agostic complex of the type $[Cp_2TiR]^+$ is a 14-electron species that not only contains two potential receptor orbitals on the titanium but also is sterically less hindered and presumably more Lewis acidic than it would be were a neutral ligand also coordinated. Therefore, for steric and electronic reasons, the β-agostic interaction in **V** is expected to be stronger than that in $[(\eta^5\text{-}C_5H_4Me)_2Zr(Et)(PMe_3)]^+$.

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(14) (a) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 802. (b) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williamns, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629. (c) McGrady, G. S.; Downs, A. J.; Haaland, A.; Scherer, W.; McKean, D. C. *Chem. Commun.* **1997**, 1547. (d) Cotton, F. A.; Petrukhina, M. A. *Inorg. Chem. Commun.* **1998**, *1*, 195. (e) Scherer, W.; Priermeier, T.; Haaland, A.; Volden, H. V.; McGrady, G. S.; Downs, A. J.; Boese, R.; Bläser, D. *Organometallics* **1998**, *17*, 4406. (f) Scherer, W.; Hieringer, W.; Spiegler, M.; Sirsch, P.; McGrady, G. S.; Downs, A. J.; Haaland, A.; Pedersen, B. *Chem. Commun.* **1998**, 2471. (g) Haaland, A.; Scherer, W.; Ruud, K.; McGrady, G. S.; Downs, A. J.; Swang, O. *J. Am. Chem. Soc.* **1998**, *120*, 3762. (h) Scherer, W.; Sirsch, P.; Shorokhov, D.; Tafipolsky, M.; McGrady, G. S.; Gullo, E. *Chem.*−*Eur. J.* **2003**, *9*, 6057.

(15) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289.

(16) See, for instance: (a) Erker, G.; Schlund, R.; Krüger, C *J. Organomet. Chem.* **1988**, *338*, C4. (b) Gomez, R.; Cuenca, T.; Royo, P.; Hovestreydt, E. *Organometallics* **1991**, *10*, 2516. (c) Eisch, J. J.; Caldwell, K. R.; Werner, S.; Krüger, C. *Organometallics* **1991**, *10*, 3417. (d) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, G.-Y.; Winter, H. H. *J. Am. Chem. Soc.* **1991**, *113*, 8569. (e) Scholz, J.; Rehbaum, F.; Thiele, K.-H.; Goddard, R.; Betz, P.; Krüger, C. *J. Organomet. Chem.* **1993**, *443*, 93. (f) Thewalt, U.; Wöhrle, T. *J. Organomet. Chem.* **1994**, *464*, C17. (g) Petrella, A. J.; Roberts, N. K.; Craig, D. C.; Raston, C. L.; Lamb, R. N. *Chem. Commun.* **2004**, 64.

Table 2. Structural Data for **V**, $[Cp_2Ti(Et)]^+$, $Ti(Et)Cl_3(dmpe)$, and $[(\eta^5\text{-}C_5H_4Me)_2Zr(Et)(PMe_3)]^+$

			$Ti(Et)Cl_3(dmpe)$		$[(\eta^5\text{-}C_5H_4Me)_2Zr(Et)(PMe_3)]^+$	
bond length (Å)/angle (°)	**V**, calcd[a]	$[Cp_2Ti(Et)]^+$, calcd[a]	ref 14e	calcd[a]	ref 15	calcd[a]
M−C(1)	2.169	2.155	2.147(1)	2.162	2.290(9)	2.317
M−C(2)	2.561	2.473	2.501(2)	2.539	2.629(9)	2.621
M−β-hydrogen	2.011	1.999	2.062	2.125	2.16	2.134
C(1)−C(2)	1.510	1.500	1.501(2)	1.516	1.47(2)	1.505
M−C(1)−C(2)	85.7	82.5	84.57(9)	85.4	84.7(5)	83.7
C(1)−agostic H	1.183	1.164	1.03(2)	1.132		1.173

[a] Calculated b-p/TZVP values; this work.

Table 3. NMR Data for β-Agostic Titanium Complexes

	V		$[Cp_2TiEt]^+$, calcd[a]	$Ti(Et)Cl_3(dmpe)$	
	obsd	calcd[a]		ref 14a	calcd[a]
δ C(1)	110.8	112.69	102.50	81.04	83.75
δ C(2)	54.3	66.45	35.64	3.81	2.41
δ H(1)	3.89, 3.99	4.46, 5.26	5.05	2.53	2.69
δ H(2) (agost)	−3.43	−5.10	−6.45		4.60
δ H(2) (non-agost)			2.58		1.34
$^1J_{C(1)H(1)}$, Hz	145.3	146.3, 145.5	150.4	150.2	142.9
$^1J_{C(2)H(2)}$, Hz (agost)	87.2	82.4	81.3		102.7
$^1J_{C(2)H(2)}$, Hz (nonagost)			143.7		132.6
$^2J_{H(1)H(1)}$, Hz		−5.6	−4.6		−6.9
$^3J_{H(1)H(2)}$, Hz (agost)	4.5, <3	4.1, 2.7	4.8		6.4

[a] B3LYP/IGLO-III results; for details see Experimental Section.

Mechanism of Formation of TMP and V: Reaction of DMP with the $Cp_2Ti(CD_3)_2$/$[Ph_3C][B(C_6F_5)_4]$ System. The formation of TMP and **IV** seemed likely to involve combining of the Ti−Me group of **I** with DMP, and we wished to both confirm this and ascertain the position(s) to which the Ti−Me group transferred. To this end we utilized $Cp_2Ti(CD_3)_2$, synthesized as was the undeuterated compound but using CD_3Li. The ^1H NMR spectrum of $Cp_2Ti(CD_3)_2$ exhibited only the expected Cp resonance at δ 6.02, while the ^2D NMR spectrum exhibited only the expected methyl resonance at δ −0.33. On reaction of $Cp_2Ti(CD_3)_2$ with $[Ph_3C][B(C_6F_5)_4]$, a ^1H NMR spectrum exhibited a strong Cp resonance for **I**, a weaker resonance for **II**, and no resonance for **III**, while a ^2D NMR spectrum exhibited methyl resonances of $C(CD_3)Ph_3$ and **I** at δ 2.13 and 1.6, respectively. Thus, synthesis of $[Cp_2Ti(CD_3)(CD_2Cl_2)][B(C_6F_5)_4]$ had been achieved as intended.

On reaction of this solution with DMP at 205 K, it was found that the CD_3 label appeared *only* in the *tert*-butyl groups of TMP and **IV**, as in Scheme 5. No scrambling was observed, nor was any deuterium enrichment observed in **V**.

We suggest in Schemes 6−8 a reasonable mechanism for the formation of TMP, one that incorporates the results of the labeling experiment and is supported computationally. The first two steps would involve formation of DMP complex **VII**, followed by conventional migratory insertion to give the alkyl complex **VIII**; unlike **V**, this contains no β-hydrogen atom. The ultimate product distribution suggests that **VIII** undergoes facile intramolecular σ-bond metathesis, via isomeric ε-agostic species **IX** and **X**, to give alkyltitanium species **XI**. The latter does contain a β-hydrogen atom, is stabilized by a β-agostic interaction (see below), and can undergo β-hydrogen elimination to give, via the alkene hydride complex **XII**, the hydride **XIII** and TMP partially deuterated in the *tert*-butyl group. The hydride would then coordinate a molecule of DMP, which is present in excess, to form **XIV** and then **V** (Scheme 9). Alternatively, free DMP could displace TMP directly from **XII**, a reasonable hypothesis as a NOESY experiment showed that **V** undergoes exchange with free DMP at 220 K. In either case, hydride **XIII** is expected to coordinate DMP to form the alkene complex **XIV** and then undergo migratory insertion as in Scheme 9. The product would be the agostic species **V**, containing no deuterium.

Thus, the formation of TMP and **V** can be rationalized, albeit involving steps with little precedent. For instance, the insertion reaction of Scheme 6 seems somewhat suspect, as migratory insertion reactions of, e.g., isobutene are rare although not unknown,[17] and the zirconium analogue does not undergo insertion.[3a,b]

On the other hand, processes involving σ-bond metathesis are reasonably common for d^0 and f^0 metal systems and have been extensively reviewed.[18] In perhaps the simplest manifestation of such a reaction, methane exchanges intermolecularly with methyl metal compounds of the type L_nMMe via four-centered transition states as in Scheme 10.[18] A recent computational investigation of the mechanism(s) of such a reaction for compounds of the types Cp_2MMe (M = Sc, Y, Ln) suggests that the reactions are best viewed as involving proton transfer between two methyl anions in the field of the electropositive metal.[19a] This finding has been supported recently by observation that a δ-agostic interaction of an isopropyl ligand substituent in a cationic ruthenium complex results in the two geminal hydrogens becoming sufficiently acidic that they are deprotonated more readily than is the agostic hydrogen.[19b] ε-Agostic species and intramolecular processes seem to be relatively unstudied, although an ε-agostic intermediate is believed to be involved during norbornene polymerization catalyzed by a zirconocene complex and is of lower energy than an analogous γ-agostic conformer.[20]

To further assess the feasibility of the mechanism of Schemes 6−9 and to facilitate comparisons with other possible mechanisms, we have carried out a computational investigation of several variations of the sequence of steps proposed.[21] The calculations were carried out as described in the Experimental Section and as elaborated on in Table S1 of the Supporting Information. A free energy diagram of the lowest free energy pathway for the steps of Schemes 6−9 is shown in Figure 5, and this is complemented by Scheme S1 of the Supporting Information, which also shows some of the less important species.[21] (Note that the energies shown for each species in

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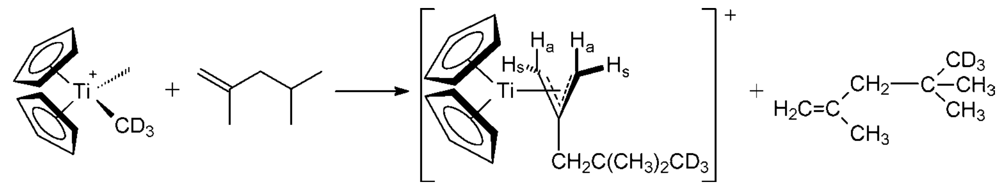
(17) (a) Shaffer, T. D.; Canich, J. A. M.; Squire, K. R. *Macromol* **1998**, *31*, 5145. (b) Shaffer, T. D. *Book of Abstracts, 218th ACS National Meeting*, New Orleans, Aug 22−26 1999; American Chemical Society: Washington, DC, 1999; INOR-264. (c) Shaffer, T. D.; Jasper, S. *Book of Abstracts, 219th ACS National Meeting*, San Francisco, March 26−30, 2000; American Chemical Society: Washington, DC, 2000; INOR-316.

(18) (a) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353. (b) Lin, Z. *Coord. Chem. Rev.* **2007**, *251*, 2280. (c) Hunt, P. A. *Dalton Trans.* **2007**, 1743.

(19) (a) Barros, N.; Eisenstein, O.; Maron, L. *Dalton Trans* **2006**, 3052. (b) Häller, L. J. L.; Page, M. J.; Macgregor, S. A.; Mahon, M. F.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2009**, *131*, 4604, and references therein.

Scheme 5



Scheme 6

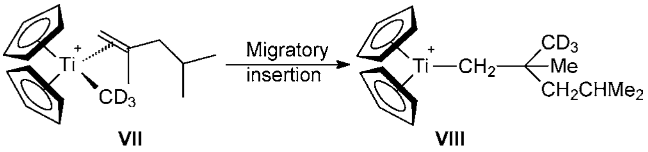


Figure 5 include the energies of molecules consumed and released along the way. Thus, species **VI** occurs twice but at different energies because it is formed via different paths, one releasing CH_4 and the other H_2.)

As is shown, formation of $[Cp_2Ti(Me)(DMP)]^+$ from its constituents, $[Cp_2Ti(Me)(CH_2Cl_2)]^+$ and DMP, is exergonic by 0.5 kcal/mol, with a barrier to insertion of 13.5 kcal/mol; thus, insertion should occur readily. On the other hand, formation of **VIII** is endergonic relative to $[Cp_2Ti(Me)(DMP)]^+$ by 3.7 kcal/mol, even though **VIII** is stabilized by an ε-agostic interaction, as shown in **IX**. Thus, **VIII** would normally not be observed since its equilibrium concentration is small relative to those of **I** or **VII**. In addition, further reaction of **VIII** is predicted to be fast relative to its formation. The intramolecular σ-bond metathesis step, involving conversion of **IX** to ε-agostic isomer **X**, is calculated to have a free energy barrier of 8.1 kcal/mol, and, once formed, **X** should quickly rearrange to the more stable β-agostic structure **XI**. Figure 6 shows the structures of **VIII** and the nearly symmetric transition state for its conversion to **XI**.

The low barrier to 1,5-shift explains why neither **VIII** nor **IX** is observed in reaction mixtures. Once **XI** or **X** has formed, β-elimination, loss of TMP, coordination of a new molecule of DMP, and insertion leading to **V** are all facile steps. In line with experiment, **V** is the lowest point on the energy profile.

To gain further insight into the σ-bond metathesis process, analogous α,ω-shifts of a series of *n*-alkyl titanocene compounds with 3−6 carbon atoms and, for purposes of comparison, the degenerate σ-bond metathesis of $[Cp_2TiMe]^+$ with methane (as in Scheme 10) were also investigated (see Table S6 and Figure S12, Supporting Information). The calculated free energy barrier for the intermolecular $[Cp_2TiMe]^+/CH_4$ exchange process was found to be 15.4 kcal/mol relative to the separated reactants. For α,ω-shifts of *n*-alkyl complexes, the cyclic transition states impose severe geometric constraints, and barriers are noticeably higher: 50.2, 28.6, 22.4, and 28.1 kcal/mol for chain lengths of 3−6 carbon atoms, respectively. Thus, a five-carbon chain is most compatible with the preferred transition-state geometry, and a sequence of consecutive 1,3-shifts can be ruled out. The latter finding has experimental support, since σ-bond metathesis of **VIII** involving a 1,3-shift would generate the intermediate $[Cp_2TiCH(CMe_2CD_3)(CHMe_2)]^+$, which would almost certainly undergo β-hydrogen elimination and release 2,4,4-trimethyl-2-pentene ($Me_2C{=}CHCMe_2CD_3$). Careful comparisons of the ^1H NMR spectra of reaction mixtures with the spectrum of an authentic sample of 2,4,4-trimethyl-2-pentene showed that none was present.

A barrier of 22.4 kcal/mol would still be insurmountable under the reaction conditions employed. However, the barrier calculated for 1,5-shift of **VIII** is only 8.1 kcal/mol, much lower than the 22.4 kcal/mol calculated for an *n*-pentyl rearrangement This difference is largely caused by the fact that **VIII** does not contain any β-hydrogens that can stabilize the molecule via a β-agostic interaction. With $[Cp_2Ti(n\text{-pentyl})]^+$, on the other hand, the reactant is stabilized by a strong β-agostic interaction that needs be broken to get to the much more weakly bound ε-agostic structure that immediately precedes the transition state; this adds ∼10 kcal/mol to the free energy of activation.

A second factor resulting in a lower free energy of activation of 1,5-shift of **VIII** is likely the fact that there are two methyl groups on C(2). It has long been known that the presence of *gem*-dimethyls on a carbon atom in an open carbon chain accelerates the rates and yields of cyclization processes involving the chain ends.[22] The origins of this *gem*-dimethyl effect, or Thorpe−Ingold effect as it is also known, are subject to debate,[22] but there is little reason to doubt that it would enhance the rate of the σ-bond metathesis reaction of **VIII**, shown in Scheme 7, relative to the rate of the analogous process for $[Cp_2Ti(n\text{-pentyl})]^+$. Interestingly, the calculated barrier for the degenerate 1,5-shift in $[Cp_2Ti(CH_2CMe_2CH_2CMe_3)]^+$ is slightly *higher* than for **VIII** (by 1.5 kcal/mol), because there are now two axial Me groups that hinder each other at the transition state.

To put these results for **VIII** further into perspective, we also calculated the energy profile for the analogous zirconium system reported in our earlier work, where the alkene complex $[Cp_2Zr(Me)(DMP)]^+$ could be detected by NMR at low temperature but did not undergo migratory insertion,[3a,b] forming instead an allyl complex via CH_4 elimination. The computational results fully support this difference in behavior: whereas for Ti insertion is easier than CH_4 elimination by 3.3 kcal/mol (13.0 vs 16.2 kcal/mol, see also Figure 5), for Zr we find the reverse ordering (14.8 vs 11.3 kcal/mol, difference of 3.5 kcal/mol, see also Figure S11). The reason for the difference is steric: the CH_4 elimination transition state requires much more space around the metal atom than insertion, and CH_4 elimination is thus more difficult for the smaller Ti atom.

Reaction of TMP with the $Cp_2TiMe_2/[Ph_3C][B(C_6F_5)_4]$ System. As with DMP, calculations indicated that coordination of TMP in a manner analogous to **VII** would be slightly exergonic but that insertion would be endergonic. Furthermore, although the product of insertion, $[Cp_2TiCH_2CMe_2CH_2CMe_3]^+$, might well take part in intramolecular σ-bond metathesis via

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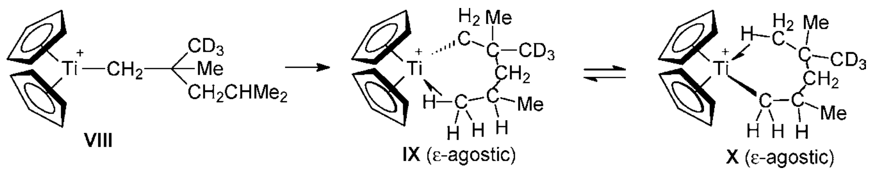
(20) Karafilidis, C.; Hermann, H.; Rufiñska, A.; Gabor, B.; Mynott, R. J.; Breitenbruch, G.; Weidenthaler, C.; Rust, J.; Joppek, W.; Brookhart, M. S.; Thiel, W.; Fink, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2444.

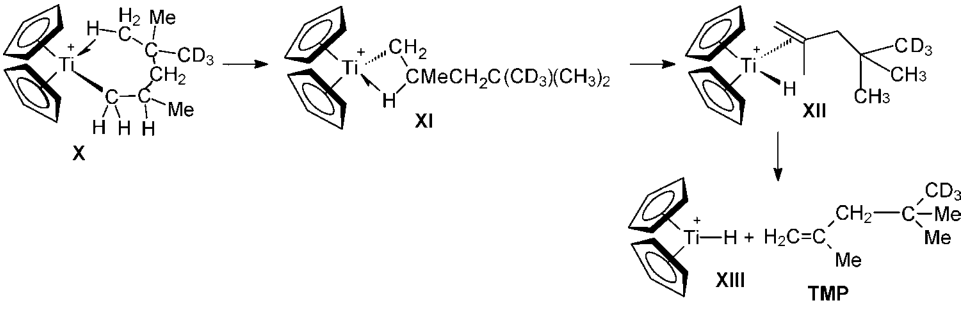
(21) Scheme S1 in the Supporting Information shows the various species and pathways investigated. Species other than those shown in Schemes 6−8 take part in the reactions, but Schemes 6−8 include all important intermediates in the net chemistry involved, and we consider further only these.

(22) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735.

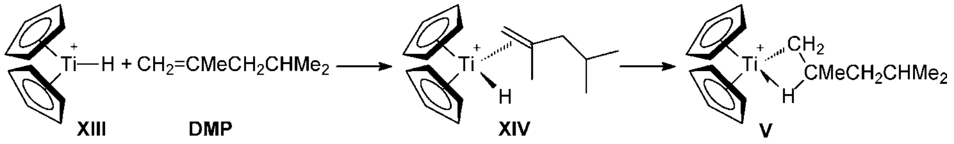
Scheme 7



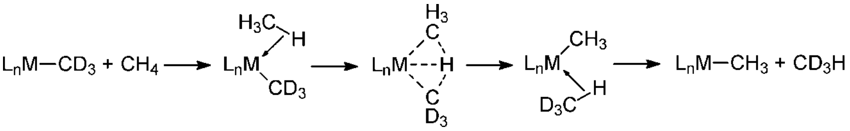
Scheme 8



Scheme 9



Scheme 10



ε-agostic interactions as in Scheme 6, no intermediate species would contain a β-hydrogen atom that might provide a low free energy product. Instead, intramolecular σ-bond metathesis could result in a degenerate exchange of the two ends of the TMP. On the other hand, if σ-bond metathesis cannot lead to a stable product, perhaps formation of $[Cp_2Ti(Me)(CH_2{=}CMeCH_2CMe_3)]^+$ would lead to formation of methane plus **IV**, as in Scheme 4.

Reaction of a solution of **I** with TMP in CD_2Cl_2 at 205 K was monitored by ^1H NMR spectroscopy, but very little reaction appeared to have occurred within an hour, i.e., on the time scale of reactions of DMP. The temperature was then raised in 10-deg stages to 250 K, but the resonances of **I** still had changed little in intensity, and certainly the resonances of **IV** had not appeared. Thus, the C_8 allylic ligand of **IV** was not formed from reaction of **I** with TMP.

Chemical Exchange in V: Formation of Allyl Complexes. The NOESY experiment discussed above for **V** (Figure S7) indicated mutual exchange between the agostic hydrogen atom (δ −3.33), the hydrogen atoms on C(1) (δ 3.89, 3.96), and those of Me(2) (δ 1.42) of **V**, as well as exchange between the hydrogens of the methyl groups Me(5) (δ 0.60, 0.88) of **V**. Two reasonable paths may be proposed for the exchange processes involving the agostic hydrogen, the hydrogens on C(1), and those of Me(2), the first involving β-elimination, rotation of the alkene, and re-insertion to form the tertiary alkyl complex $[Cp_2Ti(CMe_2$-

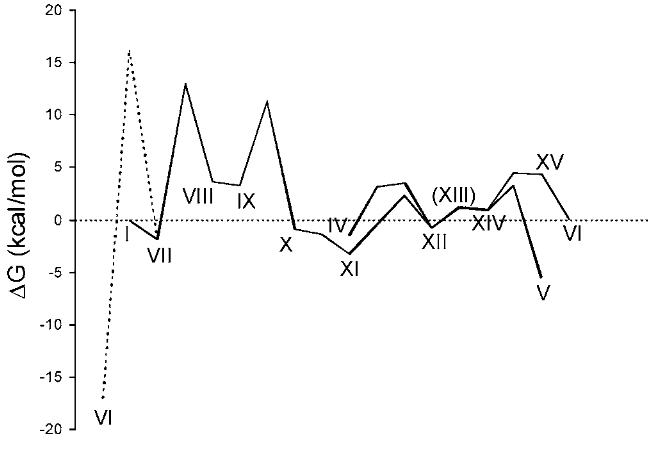


Figure 5. Free energy profile for formation of complex **V**, and paths leading to **IV** and **VI**. All energies are relative to $[Cp_2Ti(Me)(CH_2Cl_2)]^+$ (**I**). See Figure S11 in the Supporting Information for an analogous profile for the zirconocene system.

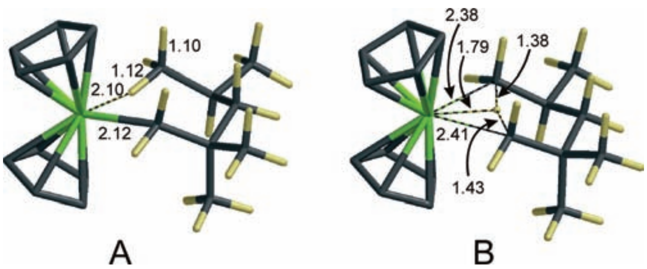
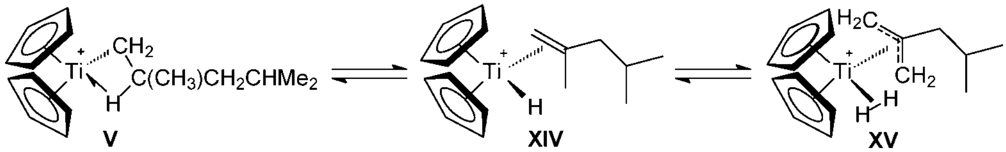
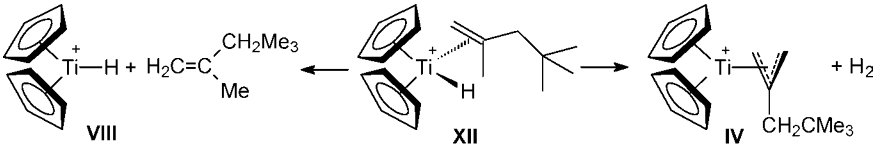


Figure 6. Calculated structures of (A) ε-agostic stabilized **IX** and (B) the 1,5-shift transition state for isomerization to **X** (bond lengths in angstroms). Cyclopentadienyl hydrogens have been omitted for clarity.

Scheme 11. Mechanism of Hydrogen Exchange in **V**



Scheme 12. Mechanism of Formation of **IV**



$CH_2CHMe_2)]^+$, presumably stabilized by a β-agostic interaction (see Scheme S2, Supporting Information). Subsequent β-elimination of a different methyl β-hydrogen and rotation and insertion back to the original alkene could ensue, a process analogous to the site epimerization mechanism often invoked for isotactic propene polymerization at low monomer concentrations.[23] This process has a low calculated free energy barrier, ~9 kcal/mol, and would rationalize the observed exchange. However, the calculations also predict facile and hence competitive elimination of a secondary β-hydrogen to give the alkene hydride complex $[Cp_2TiH(Me_2{=}CHCHMe_2)]^+$, followed by loss of $Me_2C{=}CHCHMe_2$. The NMR spectra of reaction mixtures were searched carefully but revealed no resonances of $Me_2C{=}CHCHMe_2$, and thus a sequence of reversible β-elimination steps is probably not the primary reason for the observed exchange.

An alternative scrambling mechanism also begins with β-elimination but then proceeds with allylic activation of the coordinated DMP and reversible formation of the (dihydrogen)(allylic) species **XV**, as shown in Scheme 11 (see also Scheme S3, Supporting Information).

There would follow rapid rotation of the H_2 and transfer of the other hydrogen atom back to either terminal carbon atom of the allyl group. The calculated barrier for this process, ~11 kcal/mol, is only marginally higher than that of the reversible β-elimination path discussed above, and this process also rationalizes the observed formation of allyl species **VI** (see below). This type of transformation has been hypothesized to occur during metallocene-catalyzed alkene polymerizations in order to account for the formation of H_2 as a byproduct of polymerization and the apparently concomitant formation of dormant allylic complexes during propylene polymerization.[1b,2h,24] Note that barriers for β-hydrogen elimination are systematically underestimated by DFT methods,[25] although it is not clear whether this also applies to allyl-forming H_2 elimination.

Unfortunately, while loss of H_2 from **XV** and the formation of **IV** are anticipated, the concentration of H_2 would not be expected to be very high, and its resonance was found to have a chemical shift (δ 4.55 at 205 K) very close to that of one of the terminal methylene resonances of DMP (δ 4.59). The relative intensities of the DMP resonances at δ 4.59 and 4.66 gave no indication of a hidden resonance under the former, nor did an inversion recovery pulse sequence give any indication that a resonance with a large value of T_1 was hidden in the region. Thus, the presence of H_2 could not be confirmed, although a very low concentration would not have been detected.

However, as shown in Scheme 12, a similar mechanism rationalizes the formation of **IV** from **XII** in competition with the above-mentioned formation of free TMP.

Note that both types of exchange processes could involve intermediates in which the two terminal methyl groups of **V** (δ 0.60 and 0.88) become equivalent. Thus, the observed exchange involving these two resonances, apparent in Figure S7 and noted above, can be readily rationalized by either mechanism.

Implications of This Work for Metallocene-Catalyzed Alkene Polymerization Processes. Cationic, electron-deficient metal−alkyl complexes are highly reactive species that undergo a variety of interesting transformations.[1] While one might perhaps expect that increasing the degree of congestion around the central metal atom by going from zirconium to the smaller titanium would simply alter reaction rates more or less uniformly, the present work demonstrates that such a change can, in fact, drastically alter the nature of the chemistry involved. Thus, we have observed a switch from methane elimination and allyl formation with $[Cp_2Zr(Me)(CH_2{=}CMeCH_2CHMe_2)]^+$ to a cascade of reactions, including an unprecedented 1,5-shift via two isomeric ε-agostic intermediates and a low-energy, β-agostic complex, with $[Cp_2Ti(Me)(CH_2{=}CMeCH_2CHMe_2)]^+$. Although 1,5-shifts via intramolecular σ-bond metathesis, of the type found here for the conversion of **VIII** to **XI**, are likely to be competitive during polymerizations only if intermediate metal polymeryl species do not contain β-hydrogen atoms, they may well be factors worthy of consideration during polymerization of propylene and 1-alkenes. On the other hand, 1,n-shifts where n = 3, 4, or 6 are less likely to happen in competition with alkene polymerization.

In addition to providing further evidence that vinylidene end groups of polypropylene (and poly-1-alkenes) can coordinate to a cationic metal center and convert smoothly to oft-observed allylic species and molecular hydrogen, our research with DMP also provides useful information concerning chain end epimerization processes that are known to occur during isotactic polypropylene formation. This can occur via reversible β-elimination steps,[23] as mentioned above, but reversible allylic activation as in Scheme 12 has also been proposed,[1b,24d] and our evidence for facile hydrogen atom exchange and hence fluxionality in **V**, via the dihydrogen allylic complex shown in

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(25) Talarico, G.; Blok, A. N. J.; Woo, T. K.; Cavallo, L. *Organometallics* **2002**, *21*, 4939.

Scheme 11, lends credence to this proposal. Also, of course, rotation about the C(1)−C(2) bond of vinylidene complex intermediates, as described previously[3b] and indicated in Scheme 2, provides another probably general mechanism for chain-end epimerization during polymerization of propylene and 1-alkenes. It must be noted, of course, that all experiments reported here are carried out at temperatures far lower than those at which polymerizations normally proceed, and thus that relative rates of the various processes may well vary significantly in real systems.

However, our finding that the apparent solvent-separated ion pair **I** reacts with DMP much more readily than does the corresponding contact ion pair **II**[3c] has possibly broader implications for a general understanding of metallocene catalysis of alkene polymerization. While the nature[1e,f,26] and potentially low kinetic relevance[1g,27] of metallocenium contact ion pairs has been a subject of much speculation and discussion over the past decade or more, there has in contrast been reported much less information concerning the existence, properties, and reactions of solvent-separated ion pairs such as **I**.[3a,b,28]

As shown above, NOESY experiments of Cp_2TiMe_2/$[Ph_3C][B(C_6F_5)_4]$ reaction mixtures in the temperature range 205−225 K revealed no indication of intermolecular exchange of either methyl or Cp ligands of **I** and **II**; thus, under the conditions of the experiments described here, there is no exchange between the coordinated solvent molecule and the free $[B(C_6F_5)_4]^-$ counteranion of **I**,[29] and we are able to distinguish between the reactions of the two separate species. To our knowledge, there is little evidence for cationic, solvent-coordinated metallocenium species being more substitutionally labile than the corresponding neutral contact ion pairs, in large part presumably because it has not been possible to directly observe and compare reactions of solvent-separated and contact pair metallocenium complexes with ethylene, propylene, and 1-alkenes, the polymerizable alkenes that are most frequently investigated. Our finding that one can apparently observe such reactions by utilizing a combination of low temperatures and alkenes that do not readily undergo coordination polymerization has changed this situation, and it now seems clear that the solvent-separated ion pair $[Cp_2TiMe(CD_2Cl_2)][B(C_6F_5)_4]$ reacts more quickly with 2,4-dimethyl-1-pentene (DMP) to give the alkene complex $[Cp_2ZrMe(DMP)][B(C_6F_5)_4]$ than does the contact ion pair $[Cp_2TiMeB(C_6F_5)_4]$.

Although, as indicated above, the apparently greater lability of the cationic metallocenium species is reasonable on both steric and electronic grounds, the prevailing lack of experimental evidence for this phenomenon has resulted in the recent mechanistic literature paying little attention to the formation of 14-electron species of the type $[Cp_2MMe]^+$ (M = Ti, Zr, Hf) from the various possible solvent-separated and tight ion pair precursors.[31] Evidence for the importance of ion pair dissociation may possibly be found in recent research, which showed that degrees of incorporation of 1-hexene into propylene/1-hexene copolymers induced by the well-known *rac*-$C_2H_4(Ind)_2ZrCl_2$/MAO catalyst system are actually enhanced by the addition of *n*-decyl methyl ether to the reaction mixture.[32a] It was hypothesized that the sterically rather unencumbered ether group is able to maneuver itself into the space between a cationic catalytic site on zirconium and a bulky MAO-based counteranion, displacing the MAO anion and binding weakly to the metal. When anion−cation separation has been achieved, alkenes can coordinate and polymerization processes can ensue. Once polymerization has begun, of course, the steric requirements of the growing chain presumably keep the MAO anion at a distance.[32b]

This conclusion provides an interesting rationale for some catalyst systems that apparently contain unidentified active and dormant species. For instance a recent, very thorough kinetic characterization of 1-hexene polymerization catalyzed by the *rac*-$C_2H_4(Ind)_2ZrMe_2/B(C_6F_5)_3$ catalyst system in toluene revealed that approximately 50% of the catalyst was inactive throughout the reaction.[33] Since NMR studies revealed that the only detectable species in solution was the contact ion pair, [*rac*-$C_2H_4(Ind)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$], which was presumed to be

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(27) (a) Zurek, E.; Ziegler, T. *Organometallics* **2002**, *21*, 83. (b) Zurek, E.; Ziegler, T. *Faraday Discuss.* **2003**, *124*, 93. (c) Song, F.; Cannon, R. D.; Bochmann, M. *J. Am. Chem. Soc.* **2003**, *125*, 7641. (d) Alonso-Morena, C.; Lancaster, S. J.; Wright, J. A.; Hughes, D. L.; Zuccaccia, C.; Correa, A.; Macchioni, A.; Cavallo, L.; Bochmann, M. *Organometallics* **2008**, *27*, 5474. (e) Babushkin, D. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **2010**, *132*, 452.

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(29) While one might also anticipate observation of separate sets of ^{19}F resonances for free and coordinated $[B(C_6F_5)_4]^-$, such is not the case, as ^{19}F NMR spectra of $Cp_2TiMe_2/[Ph_3C][B(C_6F_5)_4]$ reaction mixtures exhibited only single sets of *o*-, *m*-, and *p*-fluorine resonances in the temperature range 185−205 K. Of relevance, related zirconocene catalyst systems in benzene and toluene undergo facile anionic and neutral ligand substitution reactions via associative processes involving aggregates of nuclearity higher than simple ion pairs.[26a,f,g,27c] In addition, anion exchange reactions in toluene are accelerated by the addition of the more polar 1,2-difluorobenzene.[26f] While we could not, as anticipated,[30] demonstrate aggregation in the relatively polar CD_2Cl_2 using conventional NMR-based diffusion experiments,[26d,f] it is certainly reasonable to postulate that associative exchange of free $[B(C_6F_5)_4]^-$ with the coordinated $[B(C_6F_5)_4]^-$ of **II** would be rapid on the NMR time scale while at the same time not resulting in exchange of the CpTiMe moieties of **I** and **II**. Exchange of *o*-, *m*-, and *p*-fluorine resonances could also arise from intramolecular rotational exchange in **II**, of course.

(30) Macchioni, A., opinion offered at the International Symposium on Homogeneous Catalysis XVI, Florence, Italy, 2008.

(31) See, for instance, a very detailed comparison of zirconocene and hafnocene catalytic systems: Laine, A.; Linnolahti, M.; Pakkanen, T. A.; Severn, J. R.; Kokko, E.; Pakkanen, A. *Organometallics* **2010**, *29*, 1541. Here, because significantly different reactivities of solvent separated and contact ion pairs had not been established, the various possibly relevant modes of formation of $[Cp_2MMe]^+$ (M = Zr, Hf) are not taken into consideration. .

(32) (a) Stojcevic, G.; Baird, M. C. *Dalton Trans.* **2009**, 8864. (b) A similar hypothesis concerning activation of metallocene catalyst systems by ethers was also suggested elsewhere. [26a,j]

(33) Novstrup, K. A.; Travia, N. E.; Medvedev, G. A.; Stanciu, C.; Switzer, J. M.; Thomson, K. T.; Delgass, W. N.; Abu-Omar, M. M.; Caruthers, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 558.

the active species, the identity of the inactive component was not deduced. Not considered was the possibility that [*rac*-$C_2H_4(Ind)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$] was, in fact, the inactive species and that the active species were polymeryl separated ion pairs of the type [*rac*-$C_2H_4(Ind)_2Zr$(polymeryl)][$BMe(C_6F_5)_3$]. Although solvent-separated ion pairs of the type [*rac*-$C_2H_4(Ind)_2ZrR$(solvent)][$BMe(C_6F_5)_3$] are probably not a factor when the solvent is toluene,[26] we note that initiation of polymerization processes is generally slower than propagation,[27c,34] an observation that is consistent with the suggestion above that a growing polymeryl chain would serve to inhibit contact ion pair formation.[34a]

Summary

The compound Cp_2TiMe_2 reacts with $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 at 205 K to give mixtures of the solvent-separated ion pair $[Cp_2TiMe(CD_2Cl_2)][B(C_6F_5)_4]$ (**I**), the contact ion pair $[Cp_2TiMeB(C_6F_5)_4]$ (**II**), and the dinuclear species $[\{Cp_2TiMe\}_2(\mu\text{-}Me)][B(C_6F_5)_4]$ (**III**). In contrast to the analogous zirconium system, which we have previously shown to react with 2,4-dimethyl-1-pentene (DMP) to give $[Cp_2ZrMe(DMP)][B(C_6F_5)_4]$, which is of interest (a) because it is an alkyl alkene complex of a type intermediate in coordination polymerizations but never previously observed, (b) because of a novel near-η^1 mode of alkene coordination, and (c) because the C(1)−C(2) bond is sufficiently weak that the $=C(Me)R$ group rotates relative to the terminal $=CH_2$ group, the titanium DMP complex $[Cp_2TiMe(DMP)]^+$ undergoes migratory insertion to give the σ-alkyl complex $[Cp_2Ti(CH_2CMe_2CH_2CHMe_2)]^+$. The latter rearranges rapidly via an unprecedented 1,5-σ bond metathesis reaction and unusual ε-agostic species to give, ultimately, the C_8 alkene 2,4,4-trimethyl-1-pentene, the allylic complex $[Cp_2TiMe\{\eta^3\text{-}(CH_2)_2CCH_2CMe_3\}]^+$ (**IV**, containing a C_8 allylic ligand), and the hydride complex $[Cp_2TiH]^+$. The latter reacts reversibly with free DMP to give the insertion product $[Cp_2Ti(CH_2C\mathit{H}MeCH_2CHMe_2)]^+$ (**V**), in which the italicized hydrogen atom engages in an essentially static β-agostic interaction with the metal atom. This is the only known example of a β-agostic titanocene complex and, in addition, is a rare example of a transition metal complex in which the ^1H resonance of a β-agostic hydrogen can be identified in the NMR spectrum. Support for the proposed mechanism comes from labeling studies involving $[Cp_2Ti(CD_3)(CD_2Cl_2)]^+$ and from DFT calculations. This work also provides evidence for the role of allylic species during chain end epimerization processes that occur during isotactic polypropylene formation and suggests that solvent-separated and polymer-separated metallocenium ion pairs should be considered in kinetic treatments of polymerization catalyst systems.

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Supporting Information Available: Figures and tables describing and elaborating on the NMR experiments and the theoretical calculations, and complete refs 7a and 8e. This material is available free of charge via the Internet at http://pubs.acs.org.

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