The Mechanism of Methane Elimination in $B(C_6F_5)_3$-Initiated Monocyclopentadienyl-Ketimide Titanium and Related Olefin Polymerization Catalysts

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Abstract: A new class of monocyclopentadienyl titanium olefin polymerization catalysts and their activation with $B(C_6F_5)_3$ is reported herein. Dichlorides Cp[^{t}Bu(R)C═N]TiCl$_2$ {Cp = C_5H_5, R = ^{t}Bu (**1a**); Cp = C_5Me_5, R = ^{t}Bu (**2a**); Cp = $C_5Me_4SiMe_3$, R = ^{t}Bu (**3a**); Cp = C_5Me_5, R = CH_2SiMe_3 (**4a**); Cp = C_5Me_5, R = Me (**5a**)} were prepared in 50−92% yield from $CpTiCl_3$ and ^{t}Bu(R)C═NLi. Analogous dimethyl compounds **1b**−**5b** were prepare via methylation of dichlorides **a** using MeMgBr in 89−92% yield. Dimethyl compound **6b** (L = C_5Me_5, R = $CH(SiMe_3)_2$) was prepared directly from Cp*$TiMe_3$ and ^{t}Bu[$(Me_3Si)_2$CH]C═NH in 40% yield. Dynamic ^{1}H NMR studies showed that the ketimide ligands in compounds **b** rotate rapidly about Ti−N on the NMR time scale, with a $\Delta G^‡$ of 9.6(6) kcal mol^{-1} or less. The mixed alkyl compound Cp*-[^{t}Bu(R)C═N]Ti$(CH_3)CH_2SiMe_3$ {R = ^{t}Bu (**7**)} was prepared via alkylation of the corresponding methyl chloride derivative with $BrMgCH_2SiMe_3$. When treated with $B(C_6F_5)_3$, compounds **1b**−**6b** are rapidly converted into the ion pairs {Cp[^{t}Bu(R)C═N]$TiCH_3$}$^+$[$H_3C(B(C_6F_5)_3]^-$, **1c**−**6c**; mixed alkyl compound **7** yields the ion pair [Cp*(^{t}Bu$_2$C═N)$TiCH_2SiMe_3$]$^+$[$H_3C(B(C_6F_5)_3]^-$, **7c**, exclusively. Multinuclear NMR experiments show that ion pairing is tight in these compounds and that ketimide ligand rotation is occurring with a slightly higher barrier in comparison to the neutral derivatives **b**. Ion pairs **1c**−**5c** undergo a decomposition process involving loss of methane and producing the neutral compounds Cp[^{t}Bu(R)C═N]Ti$(C_6F_5)[CH_2B(C_6F_5)_2]$, **1d**−**5d**. The X-ray crystal structure of **1d** has been determined. Active cationic compounds are not regenerated from neutral compounds **d** in the presence of $B(C_6F_5)_3$ and thus this reaction is a potential deactivation pathway for these particular ion pairs. Detailed kinetic studies on the decomposition of **2c** show the reaction to be first order in [**2c**] with activation parameters of $\Delta H^‡ = 20.6(8)$ kcal mol^{-1} and $\Delta S^‡ = -8.5(10)$ eu, corresponding to $\Delta G^‡_{298}$ of 23.1(8) kcal mol^{-1}. A substantial kinetic isotope effect of $k_H/k_D = 9.1(6)$ was measured using d_6-**2c**. Further mechanistic experiments, including crossover and examination of alkane elimination from mixed alkyl ion pair **7c**, point to a σ-bond metathesis mechanism for the production of compounds **d**. The implications of our results for other, related catalyst systems are discussed.

Introduction

Bis-cyclopentadienyl (bis-Cp) complexes of the early transition metals are highly effective homogeneous olefin polymerization catalysts and the chemistry involved in their operation is relatively well understood.[1] Athough much creativity has been demonstrated in imbueing this family of catalysts with amazing versatility, extensive patent coverage has spurred the development of catalysts that do not contain the bis-Cp ligand framework.[2] One strategy has been to replace one or both of the Cp ligands in metallocenes with other donors. A notable example of this approach is the Cp-amido "constrained geometry" ligand first introduced by Bercaw for scandium-based catalysts[3] and later employed by Dow[4] and Exxon[5] to support more commercially viable titanium derivatives (**I**, Chart 1). Continuing in this vein, McConville replaced both Cp ligands with amido donors, held in a chelating array and substituted with bulky aryl substitutents (**II**);[6] the latter feature is a key element in the observed behavior of compounds **II** as "living" polymerization catalysts.[7,8] More recently, other examples of

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(1) (a) Mohring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1. (b) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (c) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (d) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57. (e) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (f) Jordan, R. F.; Bradley, P. K.; LaPointe, R. E.; Taylor, D. F. *New J. Chem.* **1990**, *14*, 505. (g) *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer: Berlin, 1995. (h) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(2) (a) Britovsek, G. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429. (b) Liang, L.-C.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797. (c) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822.

(3) (a) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, *1*, 74. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623.

(4) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. European Patent Appl. EP 416 815-A2, 1991 (Dow Chemical Co.).

(5) Canich, J. M.; Hlatky, G. G.; Turner, H. W. PCT Appl. WO 92-00333, 1992 (Exxon Chemical Co.).

(6) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241.

(7) (a) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (b) Scollard, J. D.; McConville, D. H.; Vittal, J. J.; Payne, N. C. *J. Mol. Catal. A: Chem.* **1998**, *128*, 201.

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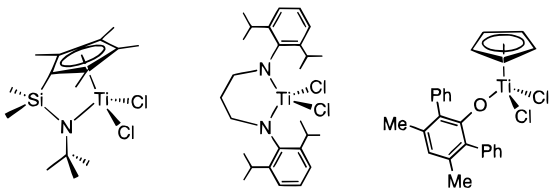
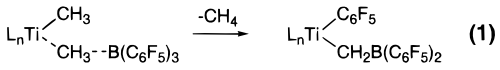
Chart 1



I II III

$Cp(L)TiX_2$ compounds [L = OR^9 (e.g., **III**), alkyl,[10] NR_2,[11] NPR_3,[12] and SR[13]] have been reported along with their behavior in the presence of common olefin polymerization activators. [14]

Generally, in conjunction with cocatalysts such as methylaluminoxane (MAO) or $[Ph_3C]^+[B(C_6F_5)_4]^-$,[15] the aforementioned compounds provide catalysts with high activity, stability, and comonomer incorporation rates, making them viable alternatives to metallocene-based catalyst systems. On the other hand, although relatively stable ion pairs are observable in solution when dimethyl derivatives of these catalysts are treated with $B(C_6F_5)_3$,[16] they are subject to a deactivation pathway involving methane loss and conversion of the cationic titanium complex to inactive neutral compounds (eq 1). Interestingly, a

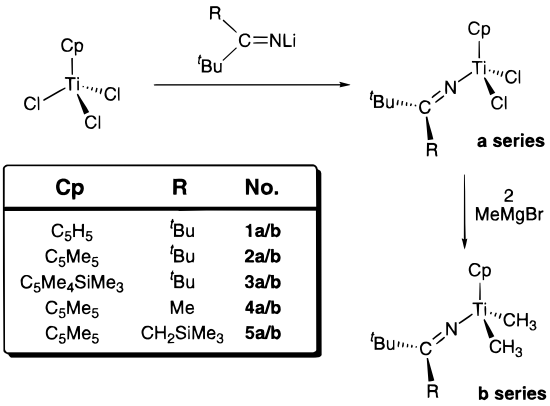


(1)

similar phenomenon is observed in the constrained geometry systems **I**.[17] The stoichiometry of this process is relatively well documented, particularly for **II** and the aryloxide system Cp(OAr)$TiMe_2$ (**III**), where the $L_nTi(C_6F_5)[CH_2B(C_6F_5)_2]$ products have been crystallographically characterized.[9b,18] However, the intimate mechanism of this deactivation process is poorly understood.

Herein we introduce a new family of $Cp(L)TiX_2$ catalysts, where L is N═CRR′, a ketimide ligand. Although titanocene complexes with ketimide ligands are known,[19] only one example of a monocyclopentadienyl ketimide complex of titanium has been reported,[20] and it has not to our knowledge been examined within the context of olefin polymerization. Like the examples **I**−**III** discussed above, bis-alkyl derivatives of this family of compounds constitute an extremely promising group of catalysts for olefin polymerization under industrially relevant conditions.[21] However, when ion pairs are generated with $B(C_6F_5)_3$, methane elimination via the process shown in eq 1 is operative. Given the apparent generality of this ion pair decomposition, we have used the Cp-ketimides described herein to perform a detailed mechanistic study on this deactivation process.

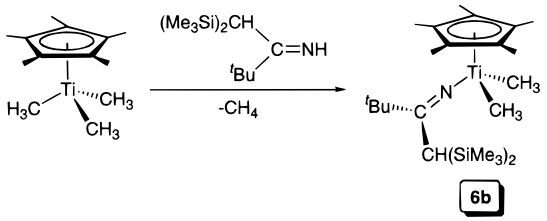
Scheme 1



Cp	R	No.
C_5H_5	^{t}Bu	**1a/b**
C_5Me_5	^{t}Bu	**2a/b**
$C_5Me_4SiMe_3$	^{t}Bu	**3a/b**
C_5Me_5	Me	**4a/b**
C_5Me_5	CH_2SiMe_3	**5a/b**

Results and Discussion

Synthesis. A variety of titanium dichlorides supported by one Cp donor and one ketimide ligand may be prepared from mono-Cp trichlorides and the lithium salt of the ketimide (isolated[22] or generated in situ via reaction of RLi with ^{t}BuCN) using a procedure analogous to that originally reported by Leigh.[20] The range of compounds prepared is shown in Scheme 1 and eq 2.



(2)

Conversion of the dichloride series (compounds **a**) to the analogous dimethyl derivatives (series **b**) is accomplished via treatment with 2 equiv of MeMgBr; organolithium reagents lead to lower yields and less clean reactions due to competitive reduction at titanium. A further member of the dimethyl series of compounds, containing the bulky bis-trimethylsilylmethyl-substituted ketimide (**6b**), is best generated using a methane elimination protocol, from Cp^*TiMe_3 ($Cp^* = C_5Me_5$) and the free ketimine (eq 2).

We required access to mixed alkyl complexes of the Cp-ketimide ligand set for some of the mechanistic experiments described below and found that such compounds, exemplified

(8) Deng, L.; Ziegler, T.; Woo, T. K.; Margl, P.; Fan, L. *Organometallics* **1998**, *17*, 3240.

(9) (a) Vilardo, J. S.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Chem. Commun.* **1998**, 2425. (b) Thorn, M. G.; Vilardo, J. S.; Fanwick, P. E.; Rothwell, I. P. *Chem. Commun.* **1998**, 2427. (c) Sarsfield, M. J.; Ewart, S. W.; Tremblay, T. L.; Roszak, A. W.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3097. (d) Ewart, S. W.; Sarsfield, M. J.; Jeremic, D.; Tremblay, T. L.; Williams, E. F.; Baird, M. C. *Organometallics* **1998**, *17*, 1502. (e) For a related chelating system see: Chen, Y.-X.; Fu, P.-F.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 5958.

(10) (a) Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 476. (b) Ewart, S. W.; Baird, M. C. *Top. Catal.* **1999**, *7*, 1.

(11) (a) Bai, Y.; Roesky, H. W.; Noltmeyer, M. *Z. Anorg. Allg. Chem.* **1991**, *31*, 3887. (b) Schiffino, R. S.; Crowther, D. J. U.S. patent No. 5,625,016, 1997 (Exxon Chemical).

(12) Stephan, D. W.; Stewart, J. C.; Guerin, F.; Spence, R. E. v. H.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *18*, 1116.

(13) Klapötke, T.; Laskowski, R.; Köpf, H. *Z. Naturforsch., Teil B* **1987**, *42*, 777.

(14) Related examples: (a) Richter, J.; Edelmann, F. T.; Noltmeyer, M.; Schmidt, H.-G.; Shmulinson, M.; Eisen, M. S. *J. Mol. Catal. A: Chem.* **1998**, *130*, 149. (b) Yoon, S. C.; Bae, B.-J.; Suh, I.-H.; Park, J. T. *Organometallics* **1999**, *18*, 2049. (c) Amor, F.; Butt, A.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836.

(15) (a) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1. (b) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.

(16) (a) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218. (b) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, 345.

(17) Allusions to the thermal instability of ion pairs generated from (CGC)$TiMe_2$ and $B(C_6F_5)_3$ can be found in the literature, but no details on the process have been mentioned to our knowledge. We found that this ion pair indeed decomposes as indicated in eq 1, producing (CGC)Ti(C_6F_5)-$[CH_2B(C_6F_5)_2]$ (see Experimental Section).

(18) Scollard, J. D.; McConville, D. H.; Rettig, S. J. *Organometallics* **1997**, *16*, 1810.

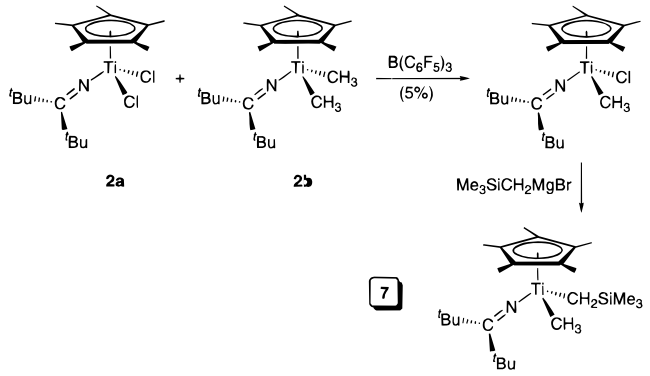
(19) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148.

(20) Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 377.

(21) McMeeking, J.; Gao, X.; Spence, R. E. v. H.; Brown, S. J.; Jeremic, D. PCT WO 99/14250, 1999 (Nova Chemicals Ltd.).

(22) Armstrong, D. R.; Barr, D.; Snaith, R.; Mulvey, R. E.; Wade, K.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1987**, 1071.

Scheme 2

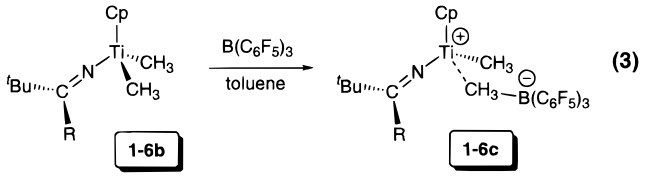


by Cp*(^{t}Bu$_2$C═N)Ti(CH$_2$SiMe$_3$)CH$_3$, **7**, can be prepared cleanly using the method shown in Scheme 2. Typically, mixed alkyl titanocenes are prepared from Cp$_2$Ti(R)Cl type precursors, which themselves are prepared in rather low-yielding monoalkylation reactions starting from Cp$_2$TiCl$_2$;[23] alternatively, oxidative alkylation of Cp$_2$TiCl derivatives with CdR$_2$ has been used to access these precursors.[24] We discovered that B(C$_6$F$_5$)$_3$ catalyzes the disproportionation of a given **a**/**b** pair of compounds (in this case, **2a**/**b**), providing an extremely convenient route to the required methyl chloride derivative, which can be subsequently alkylated with a second hydrocarbyl group. The disproportionation presumably occurs via B(C$_6$F$_5$)$_3$ abstraction of a methyl group from **2b**, followed by chloride transfer from **2a** to the titanium methyl cation; collapse of the putative [Cp*(^{t}Bu$_2$C═N)TiCl]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ ion pair furnishes the other equivalent of Cp*(^{t}Bu$_2$C═N)TiMeCl and releases B(C$_6$F$_5$)$_3$. Alkylation of Cp*(^{t}Bu$_2$C═N)TiMeCl is accomplished in the usual way using a Grignard reagent. This procedure also works for C$_5$H$_5$ compounds **1**. The process in Scheme 2 represents a very clean, high-yielding and possibly general method for preparing L$_n$Ti(R)Cl compounds, although we have not explored its utility in other systems (i.e., differing L$_n$ or R) in detail.

The X-ray crystal structure of the related compound Cp(^{n}Bu^{t}BuC═N)TiCl$_2$ was reported by Leigh et al. in 1986,[20] and showed the complex to be monomeric with a near-linear Ti−N−C linkage of 171.3(4)°. In the solid state, the plane of the ketimide ligand is approximately perpendicular to the Cp$_{centroid}$−Ti vector. The authors noted that the relatively short Ti−N bond length of 1.872(4) Å was consistent with some double bond character in this linkage. For comparison, the Ti−N bond length in constrained geometry complex **I** is 1.909 Å,[25] indicating that the π bond between the ketimide ligand and titanium is somewhat stronger than that in **I**. On the other hand, in the unconstrained analogue Cp[N(SiMe$_3$)$_2$]TiCl$_2$, which is perhaps more closely related to the ketimide compounds, the Ti−N distance is 1.879(3) Å.[11a]

All of the neutral titanium ketimide compounds described above were characterized by NMR spectroscopy and elemental analysis. The ^{1}H NMR spectroscopic data for the ketimide complexes **1a**−**5a** and **1b**−**6b** suggest that similar structural features to those found for Cp(^{n}Bu^{t}BuC═N)TiCl$_2$ obtain in solution but that rotation about the Ti−N bond of the ketimide ligand is rapid on the NMR time scale. For C_s symmetric compounds **1**−**3**, the ^{t}Bu groups of the ketimide ligand remain equivalent at all accessible temperatures, suggesting a perpendicular orientation of the ketimide ligand (with respect to the Cp−Ti vector) in the ground state as observed in the solid state for Cp(^{n}Bu^{t}BuC═N)TiCl$_2$. With this orientation, dimethyl compounds **4b**, and **5b**, containing unsymmetrical ketimide ligands, should have diastereotopic methyl groups. However, the methyl groups appear as a single resonance down to −80 °C in the ^{1}H NMR spectrum. The most reasonable explanation for this behavior is rapid rotation of the ketimide ligand about the Ti−N bond, which exchanges the titanium methyl environments. For the more sterically bulky **6b**, this process is observable spectroscopically. The signal for the Ti−Me groups undergoes coalescence behavior and two signals at 0.71 and 0.49 ppm emerge when the sample is cooled to −90 °C. Analysis of the spectra yields a $\Delta G^{\ddagger}$ of 9.6(6) kcal mol^{-1} for ketimide rotation in this compound.[26] As the size of R decreases, this free energy barrier also is lowered and the low-temperature limits are not accessible for **4b** or **5b**. The low barrier to rotation of the ketimide ligand may be due to participation of the C═N π orbitals in the process, such that the π component to the Ti−N bond is not lost in the parallel orientation of the ligand,[27] the other limiting configuration during rotation.

Reactions with B(C$_6$F$_5$)$_3$. When activated with B(C$_6$F$_5$)$_3$, dimethyl compounds **1b**−**6b** are highly active ethylene polymerization catalysts at room temperature.[28] We thus examined in detail the reactions of these dimethyl compounds with B(C$_6$F$_5$)$_3$ to probe the stability of the resulting ion pairs in solution. Rapid formation of ion pairs **1c**−**6c** is observed upon admixture of the dimethyl precursor with 1 equiv of B(C$_6$F$_5$)$_3$ in toluene (eq 3). Compounds **c** are relatively stable at room



(3)

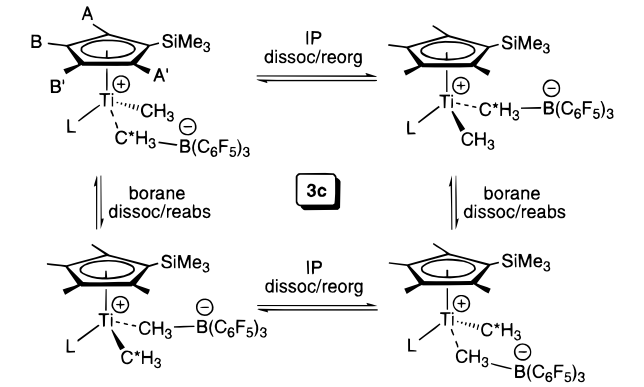
temperature under these conditions, slowly decomposing over the course of ≈24 h as described below. However, they are persistent enough to fully characterize spectroscopically, and **2c** is also isolable as an analytically pure solid.

Spectroscopic data for the ion pairs **1c**−**6c** suggest that ion−ion contact is relatively tight in these systems. The positions of the ^{1}H NMR signals for the B−CH$_3$ in **1c**−**6c** are upfield of the range of ≈1.2−1.4 ppm generally noted for the unassociated [MeB(C$_6$F$_5$)$_3$]$^-$ anion in aromatic solvents.[29] Furthermore, the position of this resonance spans a relatively large range (0.21 to 0.81 ppm) indicating a high degree of sensitivity to the variations in ancillary ligation. These spectroscopic features are typical of contact ion pairing in which a Ti−(μ-CH$_3$)−B contact is present.[12,30]

The lack of certain types of temperature dependence in the ^{1}H NMR spectra of ion pairs **c**, and particularly **3c**, indicates that the associated structure for these ion pairs is rather static in toluene solution in comparison to other systems. Marks and

(23) Waters, J. A.; Mortimer, G. A. *J. Organomet. Chem.* **1970**, *22*, 417.
(24) Luinstra, G. A.; Teuben, J. H. *J. Organomet. Chem.* **1991**, *420*, 337.
(25) Stevens, J. C. In *Catalyst Design for Tailor Made Polyolefins, Studies in Surface Science and Catalysis*; Soga, K., Terano, M., Eds; Elsevier: Amsterdam, 1994; Vol. 89, p 277.
(26) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.
(27) A similar low barrier to rotation in compounds Cp(NH^{t}Bu)TiCl$_2$ has been rationalized in this fashion: Giolando, G. M.; Kirschbaum, K.; Graves, L. J.; Bolle, U. *Inorg. Chem.* **1992**, *31*, 3887.
(28) Gao, X.; Wang, Q. Unpublished results.
(29) (a) Horton, A. D. *Organometallics* **1996**, *15*, 2675. (b) Beck, S.; Prosenc, M. H.; Brintzinger, H. H. *J. Mol. Catal. A: Chem.* **1998**, *128*, 41. (c) Beswick, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2410.
(30) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

Scheme 3



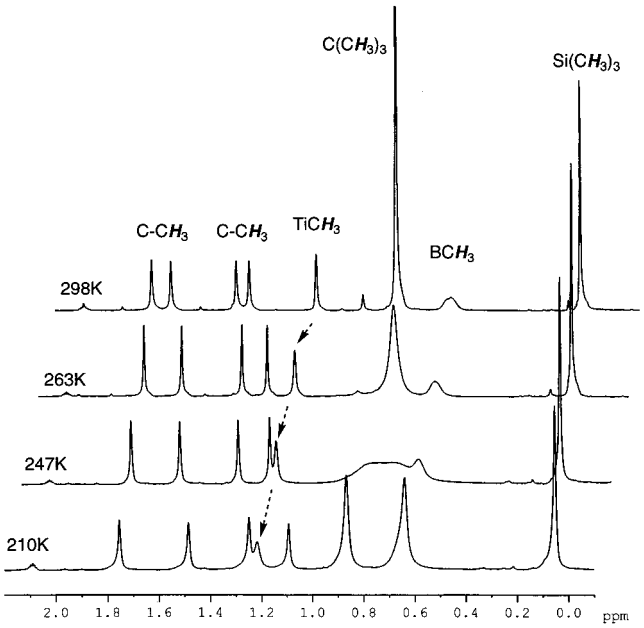
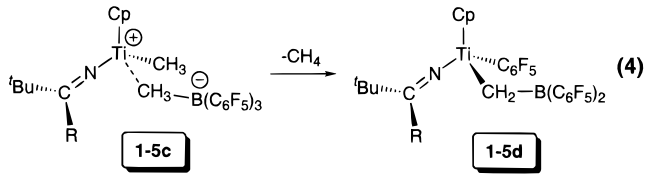


Figure 1. ^{1}H NMR spectra (400 MHz) of **3c** taken at various temperatures (d_8-toluene).

co-workers have shown that ion pairs generated from metallocene or constrained geometry catalyst precursors and perfluoroaryl borane activators exhibit complex behavior associated with two distinct dynamic processes, namely ion pair dissociation/reorganization and borane dissociation/reabstraction. These two processes as they would be occurring in **3c** are illustrated in Scheme 3. The two dynamic processes can be studied independently by dynamic NMR techniques, since the former process exchanges diastereotopic Cp substitutents (A/A′ and B/B′), while the latter also permutes the two methyl groups (CH_3 and C^*H_3).[31]

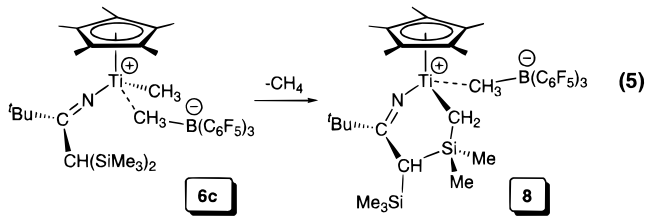
Figure 1 shows a series of ^{1}H NMR spectra for ion pair **3c** at various temperatures. As can be seen, separate resonances for the four Cp methyl groups are observed at all temperatures. There is some temperature dependence on the chemical shifts of these resonances, but no hint of the onset of exchange between the pairs of diastereotopic Cp methyl groups is observed as the temperature of the samples is raised, although it must be noted that the decomposition accelerates significantly at higher temperatures (>60 °C). Furthermore, the signals due to the Ti-Me and B-Me groups also remain distinct at all temperatures examined, indicating that the borane dissociation/reabstraction process is also quite slow in these systems. The data indicate that both exchange processes are slow in the Cp-ketimide ion pairs relative to metallocene-based ion pairs and must occur with a higher $\Delta G^{\ddagger}$ than that of the decomposition process discussed below. The only changes in these spectra are associated with the resonance for the ketimide *tert*-butyl group, which coalesce and reappear as two resonances in the low-temperature limit where ketimide rotation is slow. This process is also observable in the ion pair **2c**, and free energies of activation of 11.6(4) and 11.8(9) kcal mol^{-1} are measured for **2c** and **3c**, respectively. Although ion pair dissociation/reorganization would also exchange the diastereotopic ^{t}Bu groups, since the Cp-methyl groups in **3c** remain diastereotopic during ^{t}Bu coalescence, this latter phenomenon must be a manifestation of arrested ketimide ligand rotation. The $\Delta G^{\ddagger}$ values for this process in the ion pairs are slightly higher than that observed in the neutral dimethyl compound **6b** (vide supra), consistent with a higher degree of π-bonding between N and the more electrophilic titanium centers in the cationic compounds.[32]

As has been mentioned, ion pairs **1c**−**5c** decompose at room temperature in toluene solution over the course of several hours to eliminate methane and produce the neutral complexes Cp-(^{t}BuRC═N)Ti(C_6F_5)[$CH_2B(C_6F_5)_2$], **1d**−**5d** (eq 4).[9b,18] Ion pair



(4)

6c is also susceptible to loss of methane, but the product in this case is formulated as the metalated species **8** (eq 5); this ion



(5)

pair is relatively stable toward further reaction. Compounds **1d** and **2d** were fully characterized, including an X-ray crystallographic analysis of **1d**; **3d**−**5d** were characterized in situ via multinuclear spectroscopy. Because of the unsymmetrical ligation at titanium, groups with the same connectivity in these molecules are diastereotopic, although again ketimide ligand rotation is rapid on the NMR time scale and exchanges ^{t}Bu groups in **1d**−**3d**. The methylene protons of the $CH_2B(C_6F_5)_2$ ligand, however, appear as separate resonances; because of their low intensity and broadness due to coupling with boron, HMQC experiments[33] were required to locate their resonances.

The molecular structure of **1d** is shown in Figure 2, along with selected metrical data; full details are available as Sup-

(31) (a) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 6128. (b) Siedle, A. R.; Newmark, R. A. *J. Organomet. Chem.* **1995**, *497*, 119. (c) Chen, Y. X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287. (d) Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772. (e) Luo, L.; Marks, T. J. *Top. Catal.* **1999**, *7*, 97.

(32) These observations were made in toluene; in the more polar solvents C_6D_5Br and CD_2Cl_2, the Cp-methyl peaks are close to the fast exchange limit at room temperature, indicating that, as expected, ion pair reorganization is faster in these more polar solvents. Quantitative evaluation of the temperature-dependent spectra was precluded by the onset of decomposition at the higher temperatures necessary to reach the fast exchange limit.

(33) Bax, A.; Subramanian, S. *J. Magn. Reson.***1986**, *67*, 565.

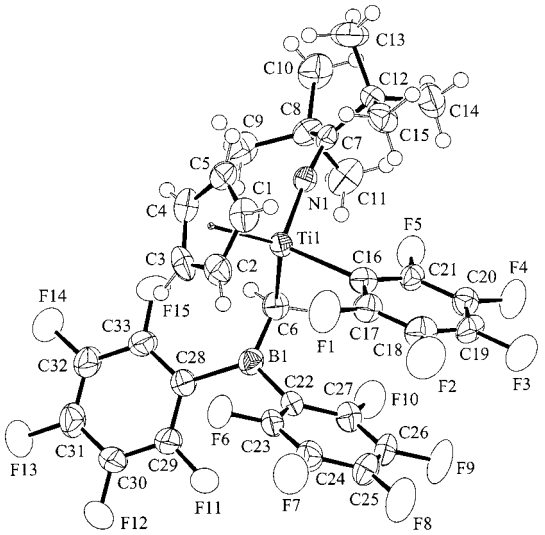


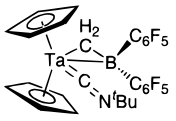
Figure 2. Molecular structure of **1d**. Selected bond distances (Å): Ti(1)−N(1), 1.830(4); N(1)−C(7), 1.264(5); C(7)−C(8), 1.556(6); C(7)−C(12), 1.543(6); Ti(1)−C(16), 2.263(2); Ti(1)−C(6), 2.182(5); C(6)−B(1), 1.479(6); C(22)−B(1), 1.610(4); C(28)−B(1), 1.6625; $Cp_{centrod}$−Ti(1), 2.033(5). Selected bond angles (deg): N(1)−Ti(1)−C(6), 100.02(17); N(1)−Ti(1)−C(16), 105.19(13); C(6)−Ti(1)−C(16), 97.63(14); N(1)−Ti(1)−$Cp_{centroid}$, 110.2(18); C(6)−Ti(1)−$Cp_{centroid}$, 122.7(18); C(16)−Ti(1)−$Cp_{centroid}$, 118.2(17); Ti(1)−N(1)−C(7), 173.5(3); N(1)−C(7)−C(8), 116.2(4); N(1)−C(7)−C(12), 118.7(4); C(8)−C(7)−C(12), 125.0(4); Ti(1)−C(6)−B(1), 110.8(3); C(6)−B(1)−C(22), 118.5(2); C(6)−B(1)−C(28), 121.7(2); C(22)−B(1)−C(28), 119.82(18).

Table 1. Metrical Parameters for **1d** and Related Compounds[a]

	compound		
parameter	**II**[b]	**III**[c]	**1d**
Ti−C_6F_5	2.191(4)	2.176(2)	2.263(2)
Ti−CH_2	2.111(4)	2.115(2)	2.182(5)
H_2C−B	1.503(6)		1.479(6)
C−Ti−C	121.5(2)	98.73(8)	97.63(14)
B−C−Ti	125.1(3)		110.8(3)
$\sum_{C-B-C}$	360.0		360.0

[a] Bond distances in Å; bond angles in deg. [b] Reference 15. [c] Reference 9b.

porting Information. The ketimide ligand is structurally similar to that found in Cp(^{t}Bu^{n}BuC═N)$TiCl_2$,[20] with a near linear C(7)−N(1)−Ti(1) angle of 173.5(5)° and a Ti(1)−N(1) distance of 1.830(4) Å. For comparison, key data for **1d** and crystallographically characterized examples of this type of ion pair decomposition product for catalyst precursors **II** and **III** (Chart 1) are given in Table 1. The titanium center is tetrahedrally coordinated in this chiral "piano stool" molecule and the metrical parameters associated with the geometry about titanium are similar to those found in Rothwell's related compound (Table 1). The $-CH_2B(C_6F_5)_2$ ligand is essentially a σ-alkyl donor to titanium in all of these complexes as indicated by the normal Ti−CH_2 distances of 2.182(5) (**1d**), 2.111(4) (**II**), and 2.115(2) Å (**III**) (cf. the value of 2.170(2) Å in Cp_2TiMe_2[34]), values of Ti−C−B which are near the tetrahedral ideal, and trigonal planar boron centers. We have noted recently, however, that this ligand may be viewed as being a boron ylide (i.e. $[CH_2{=}B(C_6F_5)_2]^-$), which can also interact with metals in a side-on binding mode reminiscent of alkene bonding. This type of bonding is in fact observed in the tantalum complex **IV**,[35] where the larger metal

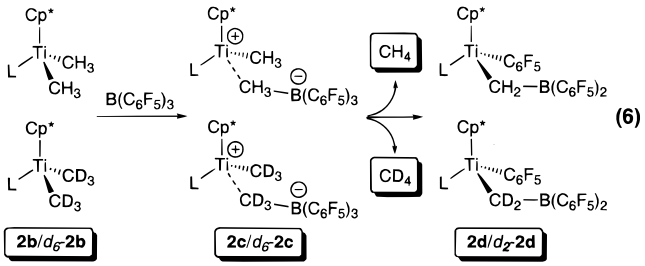


IV

and less crowded ligand environment allows for side-on approach of this ligand. In the present titanium compounds, the boron ylide ligand is sterically prevented from engaging in such π-interaction with the metal.

Mechanistic Studies. Compounds **d** are unreactive toward $B(C_6F_5)_3$ and are thus not reactivated in the presence of excess $B(C_6F_5)_3$, so the reaction of eq 4 represents a fatal deactivation pathway for these catalysts. This seems to be a relatively general fate for catalysts of this type when activated by $B(C_6F_5)_3$. As mentioned, both Rothwell[9b] and McConville[18] type catalysts exhibit this chemistry and the ion pair formed from the constrained geometry catalyst ($C_5Me_4SiMe_2N^tBu$)$TiMe_2$ and $B(C_6F_5)_3$ also decomposes in this manner in the absence of olefin when heated to 60 °C for 1 h.

Of the possible mechanisms for this process which may be envisioned, bimolecular pathways identified for metallocene systems[36] may be excluded on the basis of the deuterium labeling crossover experiment shown in eq 6. When a 1:1



(6)

mixture of **2b** and d_6-**2b** (selectively labeled in the methyl groups) is treated with a stoichiometric quantity of $B(C_6F_5)_3$, only ion pairs **2c** and d_6-**2c** are produced; no scrambling of the methyl groups to produce isotopomers of d_6-**2c** is observed. This indicates that, unlike dichloride **2a**, the dimethyl analogue is not basic enough to displace [$MeB(C_6F_5)_3$] from **2c** (cf. Scheme 2) and is consistent with the observed lack of ion pair reorganization in toluene solution for these systems. When this mixture of **2c**/d_6-**2c** is allowed to decompose, CH_4 and CD_4 are the only methane isotopomers detected by ^{1}H and ^{2}H NMR spectroscopy, strongly implying an intramolecular pathway for methane elimination.

The unimolecularity of methane elimination is also indicated by kinetic studies carried out by monitoring the reaction using ^{1}H NMR spectroscopy in d_8-toluene ($\epsilon = 2.37$). No intermediates are observed in the conversion of **2c** to **2d** and the reaction is cleanly first order in the concentration of the ion pair over several half-lives with a rate constant of $4.5(3) \times 10^{-5}$ s^{-1} at room temperature. A typical first-order plot is given in Figure 3, along with the analogous data collected for the conversion of d_6-**2c** to d_2-**2d**. A substantial kinetic isotope effect of 9.1(6) is observed in this system. The decomposition of **2c** was also followed at several different temperatures, and from the resulting Eyring plot (Figure 4), activation parameters of $\Delta H^{\ddagger} = 20.6(8)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8.5(10)$ eu are obtained. The rate of the reaction is accelerated somewhat when carried out in a more

(34) Thewalt, U.; Worthle, T. *J. Organomet. Chem.* **1994**, *464*, C17.
(35) Cook, K. S.; Piers, W. E.; Rettig, S. J. *Organometallics* **1999**, *18*, 1575.
(36) Bochmann, M.; Cuenca, T.; Hardy, D. T. *J. Organomet. Chem.* **1994**, *484*, C10.

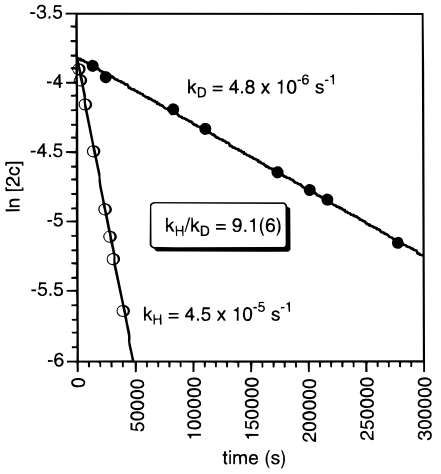


Figure 3. Typical first-order plots for the thermal decomposition of ion pairs **c**, using **2c** and d_6-**2c** as examples.

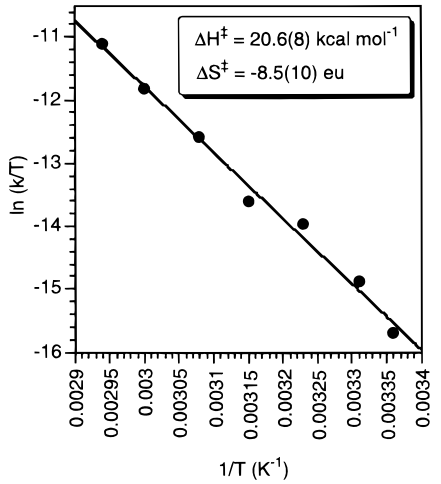


Figure 4. Eyring plot for the thermal decomposition of ion pair **2c** at various temperatures.

Table 2. First-Order Rate Constants for the Decomposition of Ion Pairs **1**−**5c**

ion pair	T (K)	solvent	$10^{-4}k$ (s^{-1})
1c	298	C_7D_8	1.49(5)
2c	298	C_7D_8	0.45(5)
3c	298	C_7D_8	0.89(5)
4c	298	C_7D_8	0.25(5)
5c	298	C_7D_8	0.18(5)
d_6-**2c**	298	C_7D_8	0.04(5)
2c	302	C_7D_8	0.99(5)
2c	310	C_7D_8	2.66(5)
2c	317	C_7D_8	3.91(5)
2c	325	C_7D_8	11.05(5)
2c	333	C_7D_8	23.87(5)
2c	340	C_7D_8	51.06(5)
2c	298	C_6D_5Br	1.16(5)

polar solvent ($k_{obs} = 11.1(5) \times 10^{-5}$ s^{-1} in C_6D_5Br, $\epsilon = 5.40$).[37] For comparison, first-order rate constants for the decomposition of compounds **1c** and **3c**−**5c** were also obtained; all of the rate constants measured are collected in Table 2.

Three reasonable unimolecular pathways for methane elimination are shown in Scheme 4. In principle, these may be distinguished by analysis of the products formed via decomposition of an ion pair derived from a mixed alkyl precursor, since both ion pair reorganization and borane dissociation/reabstraction processes are slow in these systems. It was for this purpose that mixed alkyl derivative **7** was prepared; as shown at the top of Scheme 4, reaction of **7** with $B(C_6F_5)_3$ results exclusively in abstraction of the less sterically hindered methyl group[29c,38] to give ion pair **7c**.[39] The spectroscopic data for **7c** suggest that it also has a static contact ion pair structure.

This selectivity is crucial for distinguishing between the mechanistic possibilities put forward in Scheme 4. The first (**path a**) involves elimination of alkane from the neutral dialkyl compound and necessitates borane dissociation prior to loss of RH. This is a possibility since the diamido complex $[(C_6H_{11})_2N]_2TiMe_2$ has been observed to decompose with loss of methane to form the dimeric μ-methylidene derivative $\{[(C_6H_{11})_2N]_2Ti(\mu\text{-}CH_2)\}_2$.[40] For ion pair **7c**, this path would be expected to yield a mixture of alkanes and alkylidene products; electrophilic attack by $B(C_6F_5)_3$ on the alkylidene ligands would lead to products **7d** and **9**.[41] The second possible pathway (**path b**) is reminiscent of the alkane elimination process thought to be operative in the formation of Tebbe's reagent.[42] This path would require ion pair dissociation to attain the concerted six-membered transition state via which RH loss and $-C_6F_5$ transfer to titanium occurs in a concerted fashion. Methane and titanium complex **9** would be the only products expected from this pathway.

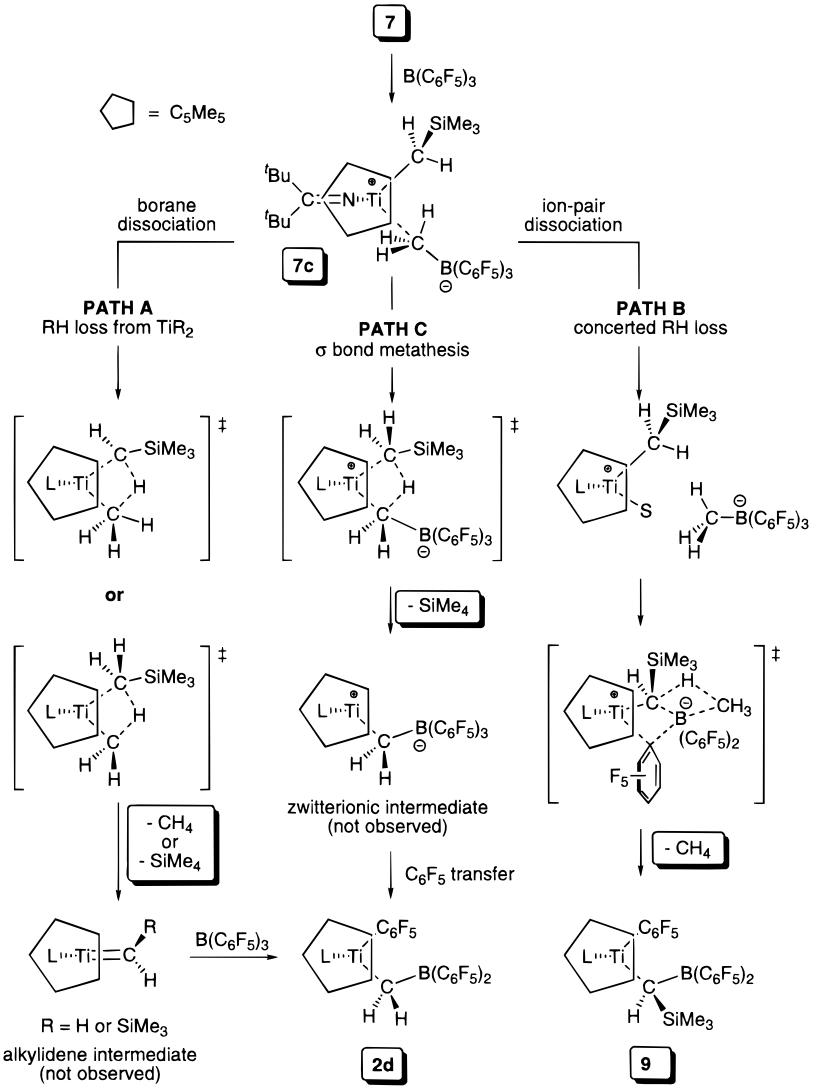
Since we have already established that both borane dissociation and ion pair reorganization are slow in these systems (relative to the decomposition process), a priori neither of these pathways seem likely. A third option, **path c**, involves a σ-bond metathesis reaction[43] between $Ti-CH_3$ and $H-CH_2B(C_6F_5)_3$. From ion pair **7c**, this path would yield only $SiMe_4$ and **2d** as products. As Figure 5 shows, this is the product mixture which results when **7c** is allowed to decompose at room temperature. While the rate of decomposition for this ion pair is qualitatively much slower than that observed for the related ion pair **2c**, the product mixture clearly consists of **2d** and $SiMe_4$; within the detection limits of ^1H NMR spectroscopy, no methane is produced, nor are any signals consistent with the generation of **9** observed. This experiment provides strong support for the σ-bond metathetical mechanistic option of **path c**. While σ-bond metathesis reactions involving the Zr−C bonds of zirconium-based cations are relatively common,[1e,44] to our knowledge, such reactions involving the Ti−C bonds for cationic titanium alkyls and C−H bonds are less well defined.

In this picture of the reaction, σ-bond metathesis occurs from a tight contact ion pair prior to full dissociation of the $[MeB(C_6F_5)_3]^-$ anion from the titanium cation via a typical

(37) Attempts to measure the rate of this reaction in CD_2Cl_2 ($\epsilon = 9.08$) were hampered by side reactions which we believe involved chloride abstraction from the solvent.

(38) Temme, B.; Erker, G. *J. Organomet. Chem.* **1995**, *488*, 177.
(39) Use of the less hindered C_5H_5 analogue of **7**, i.e., $C_5H_5(L)Ti(CH_3)CH_2SiMe_3$, resulted in competitive trimethylsilylmethyl abstraction (≈30%).
(40) Scoles, L.; Minhas, R.; Duchateau, R.; Jubb, J.; Gambarotta, S. *Organometallics* **1994**, *13*, 4978.
(41) While the order in [Ti] is unknown for the loss of methane from $[(C_6H_{11})_2N]_2TiMe_2$, the conclusions here would be the same for a bimolecular elimination of RH.
(42) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149. (c) Ott, K. C.; deBoer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223.
(43) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203 and references therein.
(44) (a) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546. (b) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. C. *Organometallics* **1989**, *8*, 2892. (c) Siedle, A. R.; Lamanna, W. M.; Newmark, R. A.; Schroepfer, J. N. *J. Mol. Catal. A: Chem.* **1998**, *128*, 257. (d) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362.

Scheme 4



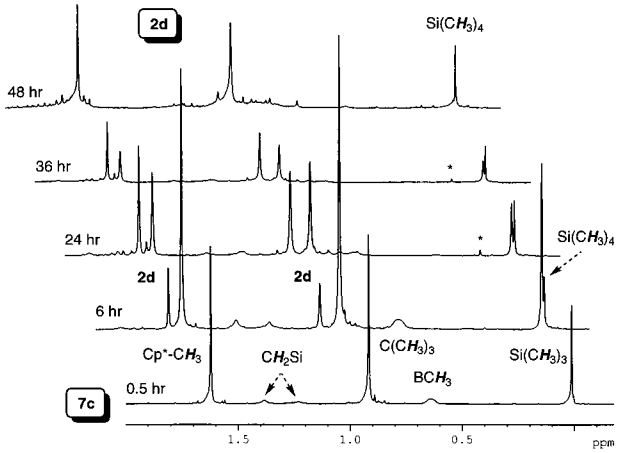


Figure 5. ^{1}H NMR spectra (400 MHz) of the decomposition of ion pair **7c** (d_8-toluene). The peak marked with an asterisk is not due to CH_4.

4-centered transition state. The activation parameters obtained for the decomposition of **2c** are consistent with this notion. The activation entropy of −8.5(10) eu is substantially less negative than those observed for other σ-bond metathesis reactions (≈ −34 eu[43]), but this is consistent with the reaction developing from the contact ion pair, an inherently more organized structure than two neutral reactants coming together to engage in metathesis. The dissociative character of both **path a** and **path b** would be expected to exhibit a positive activation entropy. The large k_H/k_D of 9.1(6) at room temperature is less smoothly rationalized, given that a quite different value of 2.8(2) (80 °C) was found in the σ-bond methathesis reaction of (d_{15}-Cp*)$_2$-ScCH$_3$ with C_6X_6 (X = H, D).[43] It should be noted, however, that in contact ion pairs involving [MeB(C_6F_5)$_3$]$^-$, the anions typically interact with the cation through two or more of the C−H bonds of the abstracted methyl group.[12,30] Furthermore, an inversion of stereochemistry during the abstraction process at the methyl carbon is indicative of substantial hybridization changes at this carbon atom in the abstraction/reattachment process.[45] It is therefore not inconceivable that the observed k_H/k_D is a composite of a moderate normal primary kinetic isotope effect associated with C−H(D) bond breakage in the σ-bond metathesis reaction and some relatively large secondary kinetic isotope effects associated with the two C−H(D) bonds not directly involved in the elimination of $CH(D)_4$. Indeed, secondary effects associated with the C−H(D) bonds of the nonabstracted methyl group may also be contributing to the overall effect.

(45) Spence R. E. v H.; Piers, W. E.; Sun, Y.; Parvez, M.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 2459.

Although we were unable to obtain the activation barrier for ion pair dissociation for any of these compounds, clearly it is higher than 23.1(8) kcal mol^{-1}, the value for $\Delta G^{\ddagger}$ at 298 K for the methane elimination process in **2c**. This is substantially higher than $\Delta G^{\ddagger}$ for ion pair dissociation of 14.2(10) kcal mol^{-1} reported for the constrained geometry system **I** in d_8-toluene[31d] and that of 12.4(5) kcal mol^{-1} (−25 °C) reported for alkoxide derivative **III** in the same solvent. This perhaps indicates that the ketimide ligand is a comparatively poorer donor versus the amide or alkoxide moieties, although the diverse steric properties of these three systems undoubtedly play a role in this effect. Nonetheless, the susceptibility of ion pairs [Cp(L)TiMe]$^+$[MeB(C_6F_5)$_3$]$^-$ toward this σ-bond metathetical deactivation process is likely related to the donor abilities of L. Ligands which are able to delocalize positive charge from titanium should effectively lower the electrophilicity of the cationic titanium center and make it a poorer σ-bond metathesis partner. This also in all likelihood lowers the free energy barrier to anion dissociation relative to σ-bond metathesis by decreasing the electrostatic attraction between the ions. However, to the extent each family of catalysts undergoes methane loss with essentially equal facility, these effects are less relevant under above ambient conditions.

Although the range of rate constants is quite small, comparisons within the various ketimide-supported ion pairs reported here may be rationalized on this basis as well. For example, the rate of methane evolution in **4c** is roughly half that observed for **2c**. The only difference between these compounds is that for **4c**, R = CH_2SiMe_2, while in **2c**, R = ^{t}Bu. Presumably, the trimethylsilylmethyl substituent is able to stabilize positive charge on the ketimide carbon via the β-silicon effect,[46] lowering the titanium center's electrophilicity and raising the barrier to σ-bond metathesis. Indeed, the apparently slower rate of alkane elimination from **7c** may also have its root in the β-silicon effect, since the $-CH_2SiMe_3$ group might be expected to partially stabilize the positive charge on titanium[47] through hyperconjugation.[48] As Table 2 also indicates, the decomposition of C_5H_5-substituted **1c** is approximately 3 times faster than C_5Me_5-ligated **2c**. Although steric effects cannot be discounted here, we believe the difference in the stabilities of these two species is primarily due to the more electron donating Cp* ligand decreasing the electrophilicity of the titanium center.

Conclusions. A detailed understanding of ion−ion interactions in olefin polymerization catalysts is crucial for the design of new and superior catalysts for this important process. In this paper, we have shown that the commonly observed methane elimination process for ion pairs of general formula [Cp(L)TiCH_3]$^+$[H_3CB(C_6F_5)$_3$]$^-$ takes place via a σ-bond metathetical elimination of methane from a contact ion pair. In the absence of monomer, this process should be more facile than dissociation of the contact ion pair, and once it has taken place, the catalyst is resistant to reactivation. This process is probably related to the observed evolution of CH_4 in MAO-activated metallocene systems,[49] which has been proposed to occur via σ-bond metathesis between the active cationic center and the C−H bonds of aluminum (or aluminate)-bound methyl groups.[1b] Unlike the deactivation products **1d**−**5d**, reactivation is possible in the MAO-activated systems, possibly mediated by the "$AlMe_3$" inevitably present in the MAO.[50]

For catalysts based on the Cp(L)Ti molecular fragment and activated by B(C_6F_5)$_3$, the properties of L are likely important for influencing the facility of alkane elimination. A ligand L which will attenuate the electrophilicity of the titanium center by delocalization of some of the cationic charge renders the catalyst less susceptible to this deactivation pathway. The prevalence of this termination step in B(C_6F_5)$_3$-activated catalysts is also related, presumably, to the electron-rich nature of the C−H bonds in the methyl borate anion. It is notable that each of the catalysts discussed perform at a significantly higher level when other types of activators are employed.

Experimental Section

General Details. Unless otherwise noted all manipulations were carried out under argon using an Innovative Technology System One drybox and/or standard Schlenk techniques on double manifold vacuum lines.[51] Toluene, hexanes, and THF were dried and deoxygenated using the Grubbs solvent purification system[52] and were stored in evacuated glass vessels over titanocene[53] or sodium benzophenone. Deuterated NMR solvents d_6-benzene (C_6D_6) and d_8-toluene (C_7D_8) were dried and distilled from sodium/benzophenone ketyl, and d_2-dichloromethane (CD_2Cl_2) and d_5-bromobenzene (C_6D_5Br) were dried and distilled from calcium hydride. NMR spectra were recorded on Bruker AC 200, AM 400, or AMX2 300 MHz spectrometers at room temperature in C_7D_8 unless otherwise specified. Proton and carbon spectra were referenced to solvent signals, boron spectra to external BF_3·Et_2O at 0.0 ppm, and fluorine spectra to $CFCl_3$ at 0.0 ppm. NMR data are given in ppm; ^{13}C resonances for the C_6F_5 groups were not obtained. Elemental analyses were performed in the microanalytical laboratory of the Department of Chemistry at the University of Calgary. Trimethylacetonitrile, 1,2,3,4-tetramethylcyclopentadiene, (C_5Me_5)$TiCl_3$, and (C_5H_5)$TiCl_3$ (Aldrich Chemicals) were used as received. $C_5Me_4SiMe_3$,[54] (C_5Me_5)$TiMe_3$,[55] and ^{t}Bu[CH($SiMe_3$)$_2$]C=N$SiMe_3$[56] were synthesized using literature methods. Ketimide ligands ^{t}Bu(R)C=NLi (R = ^{t}Bu, CH_2SiMe_3, Me) were generated in situ by treating ^{t}BuCN with RLi in THF.

Synthesis of Cp(^{t}Bu$_2$C=N)$TiCl_2$, 1a. A solution of ^{t}Bu$_2$C=NLi (0.67 g, 4.55 mmol) in toluene (10 mL) was added slowly to $CpTiCl_3$ (1.0 g, 4.55 mmol) in toluene (15 mL) at −78 °C. A yellow to orange color change was observed. The reaction mixture was warmed to room temperature and stirred for 12 h. The mixture was filtered, the filtrate was concentrated to ≈5 mL, and hexane (≈25 mL) was added. The product crystallized at −30 °C as purple crystals. Yield: 90% (1.3 g). Anal. Calcd for $C_{14}H_{23}Cl_2NTi$: C, 51.88; H, 7.15; N, 4.32. Found: C, 52.20; H, 7.25; N, 4.28. ^{1}H NMR: δ 6.12 (s, 5H, C_5H_5), 1.04 (s, 18H, C(CH_3)$_3$). ^{13}C NMR: δ 204.06 (*C*=N), 117.08 (C_5H_5), 46.71 (*C*CH_3), 30.16 (C(*C*H_3)$_3$).

Synthesis of Cp*(^{t}Bu$_2$C=N)$TiCl_2$, 2a. A solution of ^{t}Bu$_2$C=NLi (0.5 g, 3.45 mmol) in toluene (10 mL) was added slowly to Cp*$TiCl_3$ (1.0 g, 3.45 mmol) in toluene (15 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. The red solution was filtered and concentrated to 5 mL and hexane (25 mL) was added. The product crystallized at −30 °C as red orange crystals. Yield: 92% (1.2 g). Anal. Calcd for $C_{19}H_{33}Cl_2NTi$: C, 57.88; H, 8.43; N, 3.55. Found: C, 57.77; H, 8.70; N, 3.61. ^{1}H NMR: δ 1.98 (s, 15H, C_5(*C*H_3)$_5$), 1.15 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C NMR: δ 202.35 (*C*=N), 128.61 (C_5Me_5), 46.87 (*C*CH_3), 30.68 (C*C*H_3), 13.28 (C_5(*C*H_3)$_5$).

(46) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.
(47) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.
(48) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 108.
(49) (a) Kaminsky, W.; Steiger, R. *Polyhedron* **1988**, *7*, 2375. (b) Kaminsky, W.; Bark, A.; Steiger, R. *J. Mol Catal.* **1992**, *74*, 109.
(50) Reddy, S. S.; Shasidhar, G.; Sivaram, S. *Macromolecules* **1993**, *26*, 1180.
(51) Burger, B. J.; Bercaw, J. E. *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symp. Ser. 357; American Chemical Society: Washington, DC, 1987.
(52) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(53) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.
(54) Courtot, P.; Pichon, R.; Salaun, J. Y.; Toupet, L. *Can. J. Chem.* **1991**, *69*, 661.
(55) Mena, M.; Royo, P.; Serrano, R.; Pellinghell, M. A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 476.
(56) Hitchcock, P. B.; Lappert, M. F.; Layh, M. *J. Organomet. Chem.* **1997**, *529*, 243.

Synthesis of ($C_5Me_4SiMe_3$)$TiCl_3$. BuLi (10 mL of a 1.6 M solution in hexanes) was slowly added to a stirred solution of $C_5Me_4HSiMe_3$ (3.15 g, 16 mmol) in hexane (60 mL) at −78 °C; the mixture was stirred and warmed to room temperature over 8 h. The hexanes were pumped off under vacuum. The residue was suspended in THF (50 mL) and Me_3SiCl (1.75 g, 16 mmol) was added. The resulting solution was stirred for 6 h. The reaction mixture was poured into 100 mL of cold, distilled water, and the organosilicon product was extracted into hexane. The extract was concentrated to give 1,1-bis-trimethylsilyl-2,3,4,5-tetramethylcyclopentadiene as a yellow oil, (purity, >90% by GC/MS, 3.8 g, 85%). ^{1}H NMR ($CDCl_3$): δ 1.97(s, 6H, C_5CH_3), 1.82 (s, 6H, C_5CH_3), 0.01 (s, 18H, $SiCH_3$). $C_5Me_4(SiMe_3)_2$ (1.75 g, 6.6 mmol) was slowly added to titanium tetrachloride (1.25 g, 6.6 mmol) dissolved in 20 mL of toluene. The reaction mixture was stirred for a further 12 h and the solvent then evaporated under vacuum to leave red precipitate of ($C_5Me_4SiMe_3$)$TiCl_3$. Yield: 96% (2.2 g). Anal. Calcd for $C_{12}H_{25}Cl_3SiTi$: C, 40.99; H, 7.17. Found: C, 40.52; H, 6.86. ^{1}H NMR ($CDCl_3$): δ 2.51, 2.31 (s, 12H, C_5CH_3), 0.41 (s, 9H, $SiCH_3$).

Synthesis of $C_5Me_4SiMe_3$(^{t}Bu_2C=N)$TiCl_2$, 3a. A procedure analogous to that used in the preparation of **2a** was employed using ^{t}Bu_2C=NLi (0.42 g, 2.89 mmol) and $C_5Me_4SiMe_3TiCl_3$ (1.0 g, 2.89 mmol) to give **3a** as orange crystals. Yield: 90% (1.17 g). Anal. Calcd for $C_{14}H_{23}Cl_2NTi$: C, 51.88; H, 7.15; N, 4.32. Found: C, 52.20; H, 7.25; N, 4.28. ^{1}H NMR (C_6D_6): δ 2.29 (s, 6H, $C_5(CH_3)_4$), 1.87 (s, 6H, $C_5(CH_3)_4$), 1.19 (s, 18H, $C(CH_3)_3$), 0.59 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR: δ 202.07 (C=N), 130.62, 129.73, 129.08 ($C_5(CH_3)_4$), 46.93 ($C(CH_3)_3$), 30.62 ($C(CH_3)_3$), 16.55, 12.89 ($C_5(CH_3)_4$)), 1.76 ($SiCH_3$).

Synthesis of Cp*[^{t}Bu(Me$_3$SiCH$_2$)C=N]$TiCl_2$, 4a. A procedure analogous to that used for the synthesis of **2a** was employed from (^{t}Bu)(CH_2SiMe_3)C=NLi (0.51 g, 3.46 mmol) and Cp*$TiCl_3$ (1.0 g, 3.46 mmol). Compound **4a** was isolated as red crystals. Yield: 50% (0.74 g). Anal. Calcd for $C_{18}H_{35}NCl_2SiTi$: C, 52.43; H, 8.56; N, 3.40. Found: C, 51.91; H, 8.42; N, 3.73. ^{1}H NMR: δ 1.99 (s, 15H, $C_5(CH_3)_5$), 1.89 (s, 2H, CH_2SiMe_3), 1.03 (s, 9H, $C(CH_3)_3$), 0.16 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR: δ 198.51 (C=N), 129.09 ($C_5(CH_3)_5$), 45.43 ($C(CH_3)_3$), 31.09 (CH_2), 28.69 ($C(CH_3)_3$), 13.19 ($C_5(CH_3)_5$, 0.86 ($Si(CH_3)_3$).

Synthesis of Cp*[^{t}Bu(Me)C=N]$TiCl_2$, 5a. A procedure analogous to that used for the synthesis of **2a** was employed from ^{t}Bu(Me)C=NLi (0.36 g, 3.46 mmol) and Cp*$TiCl_3$ (1.0 g, 3.46 mmol). Compound **5a** was isolated as orange crystals. Yield: 75% (0.91 g). Anal. Calcd for $C_{15}H_{27}Cl_2NTi$: C, 52.96; H, 8.00; N, 4.12. Found: C, 52.62; H, 7.68; N, 4.56. ^{1}H NMR: δ 1.95 (s, 15H, $C_5(CH_3)_5$), 1.65 (s, 3H, CH_3), 0.91 (s, 9H, $C(CH_3)_3$. ^{13}C NMR: δ 192.52 (C=N), 130.34 ($C_5(CH_3)_5$), 44.21 ($C(CH_3)_3$), 27.88 ($C(CH_3)_3$), 22.42 (CH_3), 13.22 ($C_5(CH_3)_5$).

Synthesis of Cp*(^{t}Bu_2C=N)$TiMe_2$, 2b. MeMgBr (1.7 mL of a 3M in Et_2O) was added to a toluene solution (30 mL) of dichloride **2a** (1.0 g, 2.52 mmol) at −78 °C. After the addition was complete, the solution was warmed to room temperature; after 30 min the solvent was removed in vacuo. The residue was extracted with hexanes (30 mL) and the slurry was filtered. The filtrate was pumped to dryness to give the pure product as an orange solid. Yield: 89% (0.89 g). Anal. Calcd for $C_{21}H_{39}NTi$: C, 71.36; H, 11.35; N, 3.96. Found: C, 71.44; H, 11.35; N, 3.98. ^{1}H NMR (C_6D_6): δ 1.89 (s, 15H, $C_5(CH_3)_5$), 1.28 (s, 18H, $C(CH_3)_3$), 0.53 (s, 6H, $Ti-CH_3$). ^{13}C NMR: δ 197.04 (C=N), 112.90 ($C_5(CH_3)_5$), 51.54 ($Ti-CH_3$, J_{C-H} 118.9 Hz), 46.43 ($C(CH_3)_3$), 31.17 ($C(CH_3)_3$), 12.36 ($C_5(CH_3)_5$). d_6-**2b** was prepared in an analogous fashion with CD_3MgBr.

Synthesis of Cp(^{t}Bu_2C=N)$TiMe_2$, 1b. A procedure analogous to that employed for preparing **2b** was used starting from **1a** (1.0 g, 3.08 mmol). Yield: 90% (0.79 g). Anal. Calcd for $C_{16}H_{29}NTi$: C, 67.83; H, 10.31; N, 4.70. Found: C, 67.63; H, 10.29; N, 4.94. ^{1}H NMR (C_6D_6): δ 6.04 (s, 5H, C_5H_5), 1.16 (s, 18H, $C(CH_3)_3$), 0.73 (s, 6H, $Ti-CH_3$). ^{13}C NMR: δ 197.21 (C=N), 112.66 (C_5H_5), 51.54 ($Ti-CH_3$, J_{C-H} = 120.6 Hz), 46.31 ($C(CH_3)_3$), 31.01 ($C(CH_3)_3$).

Synthesis of $C_5Me_4SiMe_3$(^{t}Bu_2C=N)$TiMe_2$, 3b. A procedure analogous to that employed for preparing **2b** was used starting from **3a** (1.0 g, 2.2 mmol). Yield: 90% (0.82 g). Anal. Calcd for $C_{23}H_{45}NSiTi$: C, 67.12; H, 11.02; N, 3.40. Found: C, 67.27; H, 11.08; N, 3.34. ^{1}H NMR (C_6D_6): δ 2.15 (s, 6H, $C_5(CH_3)_4$), 1.69 (s, 6H, $C_5(CH_3)_4$), 1.22 (s, 18H, $C(CH_3)_3$), 0.66 (s, 6H, $Ti-CH_3$), 0.44 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR: δ 194.51 (C=N), 129.03, 128.92, 125.86 ($C_5(CH_3)_4$), 52.51 ($Ti-CH_3$, J_{C-H} = 118.9 Hz), 47.21 ($C(CH_3)_3$), 31.41($C(CH_3)_3$), 15.41 ($C_5(CH_3)_4$), 12.54 ($C_5(CH_3)_4$), 0.56 ($SiCH_3)_3$).

Synthesis of Cp*[^{t}Bu(Me$_3$SiCH$_2$)C=N]$TiMe_2$, 4b. A procedure analogous to that employed for preparing **2b** was used starting from **4a** (1.0 g, 2.35 mmol). Yield: 90% (0.81 g). Anal. Calcd for $C_{21}H_{41}NSiTi$: C, 65.76; H, 10.77; N, 3.65. Found: C, 65.74; H, 10.29; N, 3.34. ^{1}H NMR (C_6D_6): δ 2.08 (s, 2H, CH_2Si), 1.93 (s, 15H, $C_5(CH_3)_3$), 1.09 (s, 9H, $C(CH_3)_3$), 0.51 (s, 6H, $Ti-CH_3$), 0.15 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR: δ 192.29 (C=N), 121.16 ($C_5(CH_3)_5$), 51.02 ($Ti-CH_3$, J_{C-H} = 118.9 Hz), 45.36 ($C(CH_3)_3$), 31.34 (CH_2Si), 28.79 ($C(CH_3)_3$), 12.37 ($C_5(CH_3)_5$).

Synthesis of Cp*[^{t}Bu(Me)C=N]$TiMe_2$, 5b. A procedure analogous to that employed for preparing **2b** was used starting from **5a** (1.0 g, 2.84 mmol). Yield: 92% (0.81 g). Anal. Calcd for $C_{18}H_{33}NTi$: C, 69.44; H, 10.68; N, 4.49. Found: C, 69.01; H, 10.48; N, 4.36. ^{1}H NMR (C_6D_6): δ 1.90 (s, 15H, $C_5(CH_3)_3$), 1.85 (s, 3H, CH_3), 1.07 (s, 9H, $C(CH_3)_3$), 0.53 (s, 6H, $Ti-CH_3$). ^{13}C NMR: δ 187.63 (C=N), 120.87 ($C_5(CH_3)_3$), 49.13 ($Ti-CH_3$, J_{C-H} = 118.9), 43.99 ($C(CH_3)_3$), 28.33 ($C(CH_3)_3$), 20.97 (CH_3), 12.01 ($C_5(CH_3)_5$).

Synthesis of ^{t}Bu[(SiMe$_3$)$_2$CH]C=NH. HCl (4.4 mL, 4.4 mmol, 1 M in Et_2O) was added via syringe to a solution of $Bu^t[CH(SiMe_3)_2]C=NSiMe_3$ (1.32 g, 4.4 mmol) in Et_2O (20 mL) at −78 °C. The solution was allowed to warm to room temperature over 30 min; the solvent was removed under reduced pressure to give a lime green oil in quantitative yield. ^{1}H NMR: δ 1.66 (s, 1 H, N*H*), 1.10 (s, 1H, C*H*), 0.96 (s, 9H, $C(CH_3)_3$), 0.14 (s, 18H, $Si(CH_3)_3$).

Synthesis of Cp*{^{t}Bu[(SiMe$_3$)$_2$CH]C=N}$TiMe_2$, 6b. ^{t}Bu[$(SiMe_3)_2$-CH]C=NH (0.67 g, 2.71 mmol) in toluene (10 mL) was added to a solution of Cp*$TiMe_3$ (0.62 g, 2.71 mmol) in toluene (10 mL). The mixture was stirred for 48 h at room temperature. The solvent was pumped off and the residue recrystallized from pentane to give yellow crystals of **6b**. Yield: 40% (0.5 g). Anal. Calcd for $C_{24}H_{49}NSi_2Ti$: C, 63.26; H, 10.84; N, 3.07. Found: C, 62.84; H, 10.35; N, 3.47. ^{1}H NMR: δ 2.53 (s, 1H, C*H*), 1.94 (s, 15H, $C_5(CH_3)_3$), 1.05 (s, 9H, $C(CH_3)_3$), 0.54 (s, 6H, $Ti-CH_3$), 0.27 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR: δ 195.46 (C=N), 109.41 ($C_5(CH_3)_5$), 52.36 ($Ti-CH_3$, J_{C-H} = 119.6 Hz), 46.57 ($C(CH_3)_3$), 34.33 (*C*H), 29.72 ($C(CH_3)_3$),12.41 ($C_5(CH_3)_5$), 2.15 ($Si(CH_3)_3$).

Synthesis of Cp*(^{t}Bu_2C=N)TiMeCl. Dimethyl compound **2b** (200 mg, 0.57 mmol), dichloride **2a** (200 mg, 0.51 mmol), and $B(C_6F_5)_3$ (23 mg, 0.045 mmol) were charged into a 50 mL reaction flask in the glovebox. On the vacuum line, toluene (20 mL) was then vacuum transferred into the flask at −78 °C. The mixture was slowly warmed to room temperature and stirred for 1 h and the solvent removed in vacuo. The residue was extracted with hexanes (25 mL) and the slurry was filtered. The filtrate was concentrated to 10 mL. The product crystallized at −30 °C and isolated as red orange crystals. Yield: 90% (0.35 g). Anal. Calcd for $C_{20}H_{36}ClNTi$: C, 64.26; H, 9.71; N, 3.75. Found: C, 64.17; H, 10.38; N, 3.85. ^{1}H NMR (C_6D_6): δ 1.91 (s, 15H, $C_5(CH_3)_5$), 1.18 (s, 18H, $C(CH_3)_3$), 0.90 (s, 3H, $Ti-CH_3$). ^{13}C NMR: δ 199.90 (C=N), 124.16 ($C_5(CH_3)_5$), 55.41 ($Ti-CH_3$, J_{C-H} = 122.9 Hz), 46.68 ($C(CH_3)_3$), 31.17 ($C(CH_3)_3$), 12.83 ($C_5(CH_3)_5$).

Synthesis of Cp*(^{t}Bu_2C=N)Ti(CH$_2$SiMe$_3$)Me, 7. Me_3SiCH_2MgBr (0.6 mL of a 1 M solution in Et_2O) was added to a toluene solution (15 mL) of Cp*(^{t}Bu_2C=N)TiMeCl (0.2 g, 0.53 mmol) at −78 °C. After the addition was complete, the solution was allowed to warm to room temperature at which time the solvent was removed in vacuo. The residue was extracted with hexanes (30 mL) and the slurry filtered. The filtrate was pumped to dryness to give the pure product as an orange oil. Yield: 98% (0.22 g) Anal. Calcd for $C_{24}H_{47}NSiTi$: C, 67.73; H, 11.13; N, 3.29. Found: C, 67.01; H, 10.84; N, 3.47. ^{1}H NMR (C_6D_6): δ 1.89 (s, 15H, $C_5(CH_3)_5$), 1.23 (s, 18H, $C(CH_3)_3$), 0.54 (s, 3H, $Ti-CH_3$), 0.28 (s, 9H, $Si(CH_3)_3$), 0.76 (d, 1H, CH_2, $^2J_{HH}$ = 11.6 Hz), 0.09 (d, 1H, CH_2). ^{13}C NMR (C_6D_6): δ 196.36 (C=N), 120.98 ($C_5(CH_3)_5$), 65.87 ($TiCH_2$, J_{C-H} = 109.7 Hz), 54.59 ($Ti-CH_3$, J_{C-H} = 120.1 Hz), 46.32 ($C(CH_3)_3$), 30.84 ($C(CH_3)_3$), 12.47 ($C_5(CH_3)_5$), 2.84 ($Si(CH_3)_3$).

In Situ Generation of [Cp(^{t}Bu_2C=N)TiMe]$^+$[MeB(C_6F_5)$_3$]$^-$, 1c. **1b** (7.7 mg, 0.027 mmol) and $B(C_6F_5)_3$ (14 mg, 0.027 mmol) were dissolved in C_7D_8 in a J-Young NMR tube. Reaction was immediate and the sample was assayed by NMR spectroscopy. ^{1}H NMR: δ 5.67

(s, 5H, C_5H_5), 0.97 (s, 3H, Ti−CH_3), 0.72 (s, 18H, (C(CH_3)$_3$), 0.55 (br. 3H, BCH_3). ^{13}C NMR: δ 214.04 (*C*═N), 116.5 (C_5H_5), 64.1 (Ti*C*H$_3$, J_{C-H} = 122.3 Hz), 47.00 (*C*(CH$_3$)$_3$), 40.08 (*C*H$_3$B), 29.47 (C(*C*H$_3$)$_3$). ^{19}F NMR: δ −133.3 (d, $^3J_{F-F}$ = 28.3 Hz, 6F, *o-F*), −159.1 (t, $^3J_{F-F}$ = 30.0 Hz, 3F, *p-F*), −164.1 (t, $^3J_{F-F}$ = 30.0 Hz, 6F, *m-F*). ^{11}B NMR: δ −13.4.

Synthesis of Cp*[(^{t}Bu$_2$C═N)TiMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$, 2c. **2b** (0.11 g, 3.1 mmol) and B(C$_6$F$_5$)$_3$ (0.16 g, 3.1 mmol) were charged into a 50 mL reaction flask in the glovebox. On the vacuum line, toluene (15 mL) was condensed into the flask at −78 °C. The mixture was stirred for 30 min and the solvent removed in vacuo. The residue was triturated with hexanes to give an orange solid. Yield: 92% (0.25 g). Anal. Calcd for $C_{38}H_{39}BF_{15}NTi$: C, 54.12; H, 4.54; N, 1.61. Found: C, 53.69; H, 4.37; N, 1.66. ^{1}H NMR: δ 1.52 (s, 15H, $C_5(CH_3)_5$), 0.82 (s, 18H, C(*CH*$_3$)$_3$), 1.00 (s, 3H, Ti*CH*$_3$), 0.57 (br. 3H, B*CH*$_3$). ^{13}C NMR: δ 210.79 (*C*═N), 128.82 (C_5(CH$_3$)$_5$), 64.83 (Ti*C*H$_3$, J_{C-H} = 110.4 Hz), 46.71 (*C*(*C*H$_3$)$_3$), 34.29 (*C*H$_3$B), 29.93 (C(*CH*$_3$)$_3$), 12.13 (C_5(*CH*$_3$)$_5$. ^{19}F NMR: δ −132.8 (d, $^3J_{F-F}$ = 20.18 Hz, 6F, *o-F*), −159.5 (t, $^3J_{F-F}$ = 19.14 Hz, 3F, *p-F*), −164.3 (t, $^3J_{F-F}$ = 21.21 Hz, 6F, *m-F*). ^{11}B NMR: δ −13.5.

In Situ Generation of [C$_5$Me$_4$SiMe$_3$(^{t}Bu$_2$C═N)TiMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$, 3c. **3b** (7.7 mg, 0.019 mmol) and B(C$_6$F$_5$)$_3$ (9.5 mg, 0.019 mmol) were dissolved in C_7D_8 in a J-Young NMR tube. Reaction was immediate and the sample was assayed by NMR spectroscopy. ^{1}H NMR: δ 1.80, 1.68, 1.45, 1.36 (s, 12H, $C_5(CH_3)_4$), 0.84 (s, 18H, C(C*H*$_3$)$_3$), 1.19 (s, 3H, Ti*CH*$_3$), 0.65 (br. 3H, B*CH*$_3$), 0.14 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR: δ 211.04 (*C*═N), 136.81, 131.58, 130.45 (C_5(CH$_3$)$_4$), 66.13 (Ti*C*H$_3$, J_{C-H} = 123.1 Hz), 47.05 (*C*(CH$_3$)$_3$), 34.08 (B*C*H$_3$), 30.06 (C(*C*H$_3$)$_3$), 12.17, 12.47, 14.68, 15.74 (C_5(*C*H$_3$)$_4$), 0.84 (Si(*C*H$_3$)$_3$). ^{19}F NMR: δ −132.5 (d, $^3J_{F-F}$ = 30.0 Hz, 6F, *o-F*), −159.8 (t, $^3J_{F-F}$ = 30.0 Hz, 3F, *p-F*), −164.4 (t, $^3J_{F-F}$ = 28.3 Hz, 6*F*, *m*-F). ^{11}B NMR: δ −14.3.

In Situ Generation of Cp*{[^{t}Bu(Me$_3$SiCH$_2$)C═N]TiMe}$^+$[MeB(C$_6$F$_5$)$_3$]$^-$, 4c. **4b** (7.8 mg, 0.02 mmol) and B(C$_6$F$_5$)$_3$ (10.3 mg,0.02 mmol) were dissolved in C_7D_8 in a J-Young NMR tube. Reaction was immediate and the sample was assayed by NMR spectroscopy. ^{1}H NMR: δ 2.02 (d, 1H, C*H*$_2$Si), 1.49 (d, 1H, C*H*$_2$Si), 1.56 (s, 15H, C_5(C*H*$_3$)$_5$), 0.89 (s, 3H, Ti*CH*$_3$), 0.78 (br, 3H, B*CH*$_3$), −0.03 (s, 9H, Si(CH$_3$)$_3$). ^{13}C NMR: δ 207.08 (*C*═N), 65.09 (Ti*C*H$_3$, J_{C-H} = 123.1 Hz), 44.78 (*C*(CH$_3$)$_3$), 34.03 (B*C*H$_3$), 27.82 (C(*C*H$_3$)$_3$, 0.14 (Si(CH$_3$)$_3$), 11.95 (C_5(*C*H$_3$)$_5$). ^{19}F NMR: δ −132.7 (d, $^3J_{F-F}$ = 24.31 Hz, 6F, *o-F*), −159.6 (t, $^3J_{F-F}$ = 19.66 Hz, 3F, *p-F*), −164.2 (t, $^3J_{F-F}$ = 19.66 Hz, 6F, *m-F*). ^{11}B NMR: δ −14.4.

In Situ Generation of Cp*{[^{t}Bu(Me)C═N]TiMe}$^+$[MeB(C$_6$F$_5$)$_3$]$^-$, 5c. **5b** (8.2 mg, 0.026 mmol) and B(C$_6$F$_5$)$_3$ (13.5 mg, 0.026 mmol) were dissolved in C_7D_8 in a J-Young NMR tube. Reaction was immediate and the sample was assayed by NMR spectroscopy. ^{1}H NMR: δ 1.57 (s, 3H, Ti*CH*$_3$), 1.51 (s, 15H, C_5(*CH*$_3$)$_5$), 1.45 (s, 3H, C*H*$_3$), 0.81 (br, 3H, B*CH*$_3$), 0.70 (s, 9H, C(*CH*$_3$)$_3$). ^{13}C NMR: δ 208.54 (*C*═N), 61.86 (Ti*C*H$_3$, J_{C-H} = 121.7 Hz), 44.28 (*C*(CH$_3$)$_3$), 33.17 (B*C*H$_3$), 26.75 (C(*C*H$_3$)$_3$), 11.42 (C_5(*C*H$_3$)$_5$). ^{19}F NMR: δ −132.4 (d, $^3J_{F-F}$ = 21.73 Hz, 6F, *o-F*), −159.4 (t, $^3J_{F-F}$ = 19.11 Hz, 3F, *p-F*), −164.2 (t, $^3J_{F-F}$ = 19.11 Hz, 6F, *m-F*). ^{11}B NMR: δ −13.3.

In Situ Generation of [Cp*{^{t}Bu[(Me$_3$Si)$_2$CH]C═N}TiMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$, 6c. **6b** (7.2 mg, 0.016 mmol) and B(C$_6$F$_5$)$_3$ (8.1 mg, 0.016 mmol) were dissolved in C_7D_8 in a J-Young NMR tube. Reaction was immediate and the sample was assayed by NMR spectroscopy. ^{1}H NMR: δ 2.32 (s, 1H, C*H*Si), 1.23 (s, 3H, TiCH$_3$), 0.64 (s, 9H, C(C*H*$_3$)$_3$), 0.21 (br, 3H, BC*H*$_3$), 0.00 (br, 18H, Si(C*H*$_3$)$_3$). ^{13}C NMR: δ 211.05 (*C*═N), 128.61 (C_5(CH$_3$)$_5$), 59.50 (Ti*C*H$_3$, J_{C-H} = 124.44 Hz), 44.43 (*C*(CH$_3$)$_3$), 37.78 (*C*H), 29.25 (B*C*H$_3$), 28.67 (C(*C*H$_3$)$_3$), 12.57 (C_5(*C*H$_3$)$_5$), 1.72 (Si(*C*H$_3$)$_3$). ^{19}F NMR: δ −132.4 (d, $^3J_{F-F}$ = 21.73 Hz, 6F, *o-F*), −159.6 (br, 3F, *p-F*), −164.2 (br, 6F, *m*-F). ^{11}B NMR: δ −13.3.

In Situ Generation of [Cp*(^{t}Bu$_2$C═N)Ti(CH$_2$SiMe$_3$)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$, 7c. Mixed dialkyl derivative **7** (7 mg, 0.016 mmol) and B(C$_6$F$_5$)$_3$ (8.4 mg, 0.016 mmol) were dissolved in C_7D_8 in a J-Young NMR tube. Reaction was immediate and the sample was assayed by NMR spectroscopy. ^{1}H NMR: δ 1.62 (s, 15H, C_5(C*H*$_3$)$_5$), 1.38 (br, 1H, TiC*H*$_2$Si), 1.22 (br, 1H, TiC*H*$_2$Si), 0.91 (s, 18H, C(C*H*$_3$)$_3$), 0.63 (br, 3H, BC*H*$_3$), 0.01 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR: δ 210.86 (*C*═N), 129.27 (C_5(CH$_3$)$_5$), 94.83 (TiCH$_2$, J_{C-H} = 123.1 Hz), 47.00 (*C*(CH$_3$)$_3$), 32.08 (BCH$_3$), 30.54 (C(*C*H$_3$)$_3$), 11.95 (C_5(*C*H$_3$)$_5$), 2.67 (Si(*C*H$_3$)$_3$). ^{19}F NMR: δ −131.4 (d, $^3J_{F-F}$ = 22.62 Hz, 6F, *o-F*), −159.8 (t, $^3J_{F-F}$ = 18.87 Hz, 3F, *p-F*), −164.5 (t, $^3J_{F-F}$ = 18.87 Hz). ^{11}B NMR: −14.0. Over the course of 48 h, **7c** decomposed to neutral complex **2d** (see below for spectroscopic data) and SiMe$_4$.

Synthesis of Cp(^{t}Bu$_2$C═N)Ti(C$_6$F$_5$)[CH$_2$B(C$_6$F$_5$)$_2$], 1d. Dimethyl derivative **1b** (0.1 g, 0.35 mmol) and B(C$_6$F$_5$)$_3$ (0.18 g, 0.35 mmol) were loaded into a 50 mL reaction flask in the glovebox. Toluene (15 mL) was condensed into the vessel at −78 °C, and the solution was stirred at room temperature for 24 h. The solvent was removed under vacuum and the residue extracted with hexane and filtered. The solvent was removed under vacuum and the red solid collected. Yield: 92% (0.25 g). Anal. Calcd for $C_{33}H_{25}BF_{15}NTi$: C, 50.08; H, 3.28; N, 1.82. Found: C, 49.58; H, 3.26; N, 1.33. ^{1}H NMR (C_6D_6): δ 5.18 (s, 10H, C_5H_5), 3.89 (br, 1H, C*H*$_2$B), 3.55 (br, 1H, C*H*$_2$B), 1.16 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (C_6D_6): δ 208.49 (*C*═N), 116.46 (C_5H_5), 106.06 (*C*H$_2$B), 46.38 (*C*(CH$_3$)$_3$), 30.21 (C(*C*H$_3$)$_3$). ^{19}F NMR (C_6D_6): −112.1 (d, 2F, J_{F-F} = 21.0 Hz, *o-F*), −127.6, −129.7 (br, 4F, *o-F*), −152.7 (br, 2F, *p-F*), −154.6 (m, 4F, *p-F*), −160.9 (m, 2F, *m-F*), −161.5 (br, 4F, *m-F*). ^{11}B NMR (CD_2Cl_2): δ 51.8.

Synthesis of Cp*(^{t}Bu$_2$C═N)Ti(C$_6$F$_5$)[CH$_2$B(C$_6$F$_5$)$_2$], 2d. Dimethyl derivative **2b** (0.1 g, 0.28 mmol) and B(C$_6$F$_5$)$_3$ (0.15 g, 0.28 mmol) were loaded into a 50 mL reaction flask in the glovebox. Toluene (15 mL) was condensed in at −78 °C, and the solution was stirred at room temperature for 24 h. The solvent was removed under vacuum to yield a red solid. Yield: 90% (0.22 g). Anal. Calcd for $C_{38}H_{35}BF_{15}NTi$: C, 53.73; H, 4.15; N, 1.65. Found: C, 53.03; H, 4.15; N, 1.32. ^{1}H NMR (C_6D_6): δ 3.52 (br, 1H, C*H*$_2$Ti), 2.68 (br, 1H, C*H*$_2$Ti), 1.64 (s, 15H, C_5(C*H*$_3$)$_5$), 0.99 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ 212.30 (*C*═N), 130.27 (C_5(CH$_3$)$_5$), 102.88 (*C*H$_2$B), 47.81 (*C*(CH$_3$)$_3$), 31.08 (C(*C*H$_3$)$_3$), 13.85 ((C_5(*C*H$_3$)$_5$). ^{19}F NMR (C_6D_6): −109.4 (d, 2F, *o-F*, $^3J_{F-F}$ = 21.0 Hz), −130.1 (br, 4F, *o-F*), −154.3 (br, 2F, *p-F*), −154.6 (m, 4F, *p-F*), −162.2 (m, 2F, *m-F*), −164.2 (br, 4F, *m-F*). ^{11}B NMR (CD_2Cl_2): δ 50.2.

In Situ Generation of C$_5$Me$_4$SiMe$_3$(^{t}Bu$_2$C═N)Ti(C$_6$F$_5$)[CH$_2$B(C$_6$F$_5$)$_2$], 3d. Dimethyl derivative **3b** (8.2 mg, 0.026 mmol) and B(C$_6$F$_5$)$_3$ (13.5 mg, 0.026 mmol) were loaded into a J-Young NMR tube and dissolved in C_7D_8. Ion pair **3c** was produced immediately and decomposed at room temperature to **3d** with elimination of CH_4 over the course of 15 h. ^{1}H NMR: δ 2.12, 1.96, 1.68, 1.53 (s, 12H, C_5(C*H*$_3$)$_4$), 1.08 (s, 18H, C(CH$_3$)$_3$), 0.22 (s, 9H, Si(CH$_3$)$_3$). ^{13}C NMR: δ 211.91 (*C*═N), 106.76 (*C*H$_2$B), 47.11 (*C*(CH$_3$)$_3$), 30.16 (C(CH$_3$)$_3$), 16.77, 16.17, 12.97 (C_5(*C*H$_3$)$_4$), 1.48 (Si(CH$_3$)$_3$). ^{19}F NMR: −107.2 (d, 2F, *o-F*, $^3J_{F-F}$ = 22.1 Hz), −130.1 (br, 4F, *o-F*), −153.9 (br, 2F, *p-F*), −154.4 (t, 4F, *p-F*, $^3J_{F-F}$ = 19.2 Hz), −162.1 (m, 2F, *m-F*), −163.3 (br, 4F, *m-F*). ^{11}B NMR: δ 63.6.

In Situ Generation of Cp*[^{t}Bu(Me$_3$SiCH$_2$)C═N]Ti(C$_6$F$_5$)[CH$_2$B(C$_6$F$_5$)$_2$], 4d. Dimethyl derivative **4b** (8.2 mg, 0.026 mmol) and B(C$_6$F$_5$)$_3$ (13.5 mg, 0.026 mmol) were loaded into a J-Young NMR tube and dissolved in C_7D_8. Ion pair **4c** was produced immediately and decomposed at room temperature to **4d** with elimination of CH_4 over the course of 15 h. ^{1}H NMR: δ 2.95 (br, 2H, C*H*$_2$B), 2.26 (d, 1H, C*H*$_2$Si), 2.19 (d, 1H, C*H*$_2$Si), 1.72 (s, 15H, C_5(C*H*$_3$)$_5$), 0.76 (s, 9H, C(C*H*$_3$)$_3$), 0.13 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR: 205.57 (*C*═N), 133.39 (C_5(CH$_3$)$_5$), 101.61 (*C*H$_2$B), 44.26 (*C*(CH$_3$)$_3$), 35.86 (*C*H$_2$Si), 28.69 (C(*C*H$_3$)$_3$), 12.78 (C_5(*C*H$_3$)$_5$), 0.53 (Si(*C*H$_3$)$_3$). ^{19}F NMR: δ −108.7 (br, 2F, *o*-F), −129.7 (br, 4F, *o*-F), −152.8 (br, 2F, *p-F*), −154.2 (t, 1F, *p-F*, $^3J_{F-F}$ = 19.14 Hz), −161.6 (t, 2F, *m-F*, $^3J_{F-F}$ = 19.66 Hz), −163.11 (br, 4F, *m-F*). ^{11}B NMR: δ 62.2.

In Situ Generation of Cp*[^{t}Bu(Me)C═N]Ti(C$_6$F$_5$)[CH$_2$B(C$_6$F$_5$)$_2$], 5d. Dimethyl derivative **5b** (8 mg, 0.026 mmol) and B(C$_6$F$_5$)$_3$ (13.1 mg, 0.026 mmol) were loaded into a J-Young NMR tube and dissolved in C_7D_8. Ion pair **5c** was produced immediately and decomposed at room temperature to **5d** with elimination of CH_4 over the course of 15 h. ^{1}H NMR: δ 3.15 (br, 1H, C*H*$_2$B), 2.95 (br, 1H, C*H*$_2$B), 1.81 (s, 15H, C_5(C*H*$_3$)$_5$), 1.54 (s, 3H, CC*H*$_3$), 0.81 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR: 208.1 (*C*═N), 133.3 (C_5(CH$_3$)$_5$), 105.2 (*C*H$_2$B), 46.8 (*C*(CH$_3$)$_3$), 29.2 (C(*C*H$_3$)$_3$), 28.7 (C*C*H$_3$), 12.8 (C_5(*C*H$_3$)$_5$). ^{19}F NMR: δ −113.1 (br, 2F, *o*-F), −130.5 (br, 4F, *o*-F), −153.8 (br, 2F, *p-F*), −154.5 (t, 1F,

p-F), −159.1 (t, 2F, *m-F*, $^3J_{F-F}$ = 19.6 Hz), −164.1 (br, 4F, *m-F*). ^{11}B NMR: δ 56.8.

In Situ Generation of Ion Pair 8. Dimethyl derivative **6b** (8.2 mg, 0.018 mmol) and $B(C_6F_5)_3$ (9.2 mg, 0.018 mmol) were loaded into a J-Young NMR tube and dissolved in C_7D_8. Ion pair **6c** was produced immediately and decomposed at room temperature to **8** with elimination of CH_4 over the course of 15 h. ^{1}H NMR: δ 2.22 (s, 1H, C*H*), 1.83 (s, 15H, $C_5(CH_3)_5$), 0.74 (s, 9H, $C(CH_3)_3$), 0.53 (d, 1H, $TiCH_2$), 0.48 (d, 1H, $TiCH_2$), 0.27 (br, 3H, BCH_3), 0.04 (s, 3H, $SiCH_3$), −0.11(s, 3H, $SiCH_3$), −0.03 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR: δ 206.37 (*C*═N), 69.98 (CH_2Si), 42.84 ($C(CH_3)_3$), 38.42 (C*H*), 29.80 (BCH_3), 28.36 ($C(CH_3)_3$), 12.49 ($C_5(CH_3)_5$), 3.23 ($Si(CH_3)_2$), 2.29 ($Si(CH_3)_3$). ^{19}F NMR: δ −132.3 (d, 2F, *o-F*, $^3J_{F-F}$ = 19.6 Hz), −159.7 (t, 1F, *p-F*, $^3J_{F-F}$ = 18.62 Hz), −164.40 (m, 2F, *m-F*, $^3J_{F-F}$ = 18.62 Hz). ^{11}B NMR: δ −13.6.

In Situ Decomposition of [($C_5Me_4SiMe_2N^tBu$)$TiCH_3$][$CH_3B(C_6F_5)_2$]. The constrained geometry ion pair was generated according to the literature procedure in d_8-toleune. The sample was heated at 60 °C until decomposition was complete. The product of this decomposition, [$C_5Me_4SiMe_2N^tBu$]$Ti(C_6F_5)[CH_2B(C_6F_5)_2]$, was characterized by ^{1}H and ^{19}F NMR spectroscopy. ^{1}H NMR: δ 2.63 (br, 2H, CH_2B), 2.06 (s, 3H, $C_5(CH_3)_4$), 1.85 (s, 3H, $C_5(CH_3)_4$), 1.48 (s, 3H, $C_5(CH_3)_4$), 1.44 (s, 3H, $C_5(CH_3)_4$), 1.14 (s, 9H, $C(CH_3)_3$), 0.43 (s, 3H, $SiCH_3$), 0.41 (s, 3H, $SiCH_3$). ^{19}F NMR: δ −106.5 (br, 1F, *o*-F), −117.6 (br, 1F, *o*-F), −130.3 (br, 4F, *o*-F), −152.6 (t, 1F, *p*-F, $^3J_{F-F}$ = 19.7 Hz), −153.4 (br, 2F, *p*-F), −160.2 (br, 1F, *m*-F), −162.0 (br, 1F, *m*-F), −162.1 (br, 4F, *m*-F).

Kinetic Studies. A 1 mL volumetric flask was charged with dimethyl compound **1b**−**5b** (0.05 mmol) and $B(C_6F_5)_3$ (0.05 mmol). The solution was brought to volume with d_8-toluene. A J-Young NMR tube was charged with 0.5 mL of this solution. The disappearance of the ion pair complexes $Cp(L)TiMe^+MeB(C_6F_5)_3^-$ was followed by ^{1}H NMR spectroscopy for a period of at least 3 half-lives by integration of suitable baseline separated resonances. Alternatively, the concentrations of ion pair complexes were determined by integration against a Cp_2Fe standard. A relaxation delay of 5 s (based on T_1 measurements on Cp_2Fe and **2c**) was used to ensure that measured integrals accurately reflected solution concentrations. Measurements used to determine the isotope effect were perfromed in triplicate.

X-ray Crystallographic Analysis of 1d. Suitable crystals were coated with Paratone-8277 oil (Exxon) and mounted onto a glass fiber. Crystal data and refinement details are collected in Table 3. Measurements were made on a Rigaku AFC6S diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å) at −103 °C. The structure was solved by direct methods and expanded using Fourier techniques. Phenyl rings were constrained as regular hexagons. The non-hydrogen atoms were refined anisotropically. Disordered molecules of solvents C_7H_8 and C_6H_{14} were located over inversion centers with electron density scrambled over a large region; 10 sites were allowed with partial occupancy factors which led to the equivalent of 6 C-atoms, giving a 0.46 contribution of the C_7H_8 and C_6H_{14} solvates. Hydrogen atoms of the complex were included at geometrically idealized positions and were not refined; H atoms of the solvates were ignored. All calculations were performed using the TEXSAN[57] crystallographic software package of Molecular Structure Corporation.

Table 3. Data Collection and Structure Refinement Details for **1d**

formula	$C_{33}H_{25}NBF_{15}Ti\cdot0.46(C_7H_8/C_6H_{14})$
fw	861.40
cryst syst	triclinic
a, Å	13.469(6)
b, Å	14.866(5)
c, Å	10.893(4)
α, deg	109.16(3)
β, deg	112.08(3)
γ, deg	74.06(3)
V, Å^3	1880(1)
space group	$P\bar{1}$
Z	2
F(000)	876.00
d_{calc}, mg m^{-3}	1.521
μ, mm^{-1}	0.333
R	0.0588
R_w	0.1622
gof	1.014

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Supporting Information Available: Experimental details and full listings of crystallographic data, atomic parameters, hydrogen parameters, atomic coordinates, and complete bond distances, angles, and torsion angles for **1d** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA994378C

(57) Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.