Methane Loss from Cationic μ-Methyl Dimers Formed via Trityl Borate Activation of Monocyclopentadienyl Ketimide Complexes Cp[(^{t}Bu)$_2$C=N]Ti(CH$_3$)$_2$ (Cp = C$_5$H$_5$, C$_5$Me$_5$, C$_5$Me$_4$SiMe$_3$)

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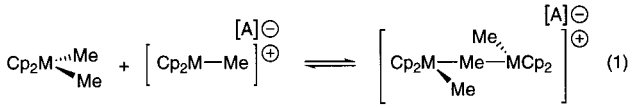
The reactions of the monocyclopentadienyl titanium dimethyl compounds Cp(L)TiMe$_2$ (L = ^{t}Bu$_2$C=N; Cp = C$_5$H$_5$, **1a**; C$_5$Me$_5$, **1b**; C$_5$Me$_4$SiMe$_3$, **1c**) with the trityl borate activator [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ are described. Formation of μ-methyl dimers of formula {[Cp(L)TiMe]$_2$-(μ-Me)}$^+$[B(C$_6$F$_5$)$_4$]$^-$ as a 1:1 mixture of *rac* and *meso* diastereomers is observed when 0.5 equiv of [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ is employed (−25 °C, C$_6$D$_5$Br; Cp = C$_5$H$_5$, *rac*/*meso* **2a**; C$_5$Me$_5$, *rac*/*meso* **2b**; C$_5$Me$_4$SiMe$_3$, *rac*/*meso* **2c**). Dynamic NMR and crossover experiments suggest that the dimers **2** are relatively nonlabile with respect to dissociation, intramolecular methyl group exchange, or diastereomer interconversion. Dimers **2** are observed to undergo methane loss in solution at room temperature, affording the new dimeric compounds **3a**−**c**, {[Cp(L)-Ti]$_2$(μ-CH$_2$)(μ-CH$_3$)}$^+$[B(C$_6$F$_5$)$_4$]$^-$. For the less sterically demanding C$_5$H$_5$ ligand, **3a** is formed as a mixture of *rac*/*meso* diastereomers (7:3), but for the bulkier C$_5$Me$_5$ and C$_5$Me$_4$SiMe$_3$ ligands, the *rac* isomers of **3b** and **3c** are formed exclusively. In contrast to μ-methyl dimers **2**, in which *rac*/*meso* interconversion is not observed, the diastereomers of **3** do undergo interchange, as determined by EXSY spectroscopy, and thus the *rac*/*meso* ratios observed are thermodynamic.

Introduction

Of the several different reagents for activation available for homogeneous olefin polymerization catalysis, those which incorporate the very weakly coordinating tetrakis(pentafluorophenyl)borate counteranion provide catalysts that are among the most active.[2] The corollary to this is that ion pair stability is relatively poor when [B(C$_6$F$_5$)$_4$]$^-$ is the counteranion; as such, metallocenium and related ion pairs are difficult to isolate and fully characterize with this particular anion partner. Because this anion is so weakly coordinating, monomeric ion pairs formed from, for example, [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$[3] and Cp$_2$MMe$_2$ are often prone to μ-methyl dimer formation in the presence of excess neutral dimethylmetallocene (eq 1).[4] In effect, μ-methyl dimer forms because the



(1)

neutral dimethylmetallocene is a better Lewis base toward the cationic center than is the borate counteranion.[5] To the extent that dissociation of the dimer is thought to be necessary to produce an active polymerization catalyst, the presence of excess Cp$_2$MMe$_2$ can dampen catalyst productivity to some degree.

The properties of the μ-methyl dimers in the solid state and in solution have been explored largely by the groups of Bochmann, Marks, and Brintzinger. Solid state structures of a few examples containing the weakly coordinating PBBMe$^-$ anion (PBB = tris(2,2′,2″-perfluorobiphenyl)borane[6]) show that the bridging methyl group is essentially sp^2 hybridized and sandwiched symmetrically between the two metal centers.[7] This is also supported by the $^1J_{CH}$ coupling constants of 131−136 Hz observed for this methyl group.[8] In solution, the rate of exchange between the bridging and terminal methyl groups appears to be related to the size of the metal. For example, exchange is rapid on the NMR time scale in {[Cp*$_2$ThMe]$_2$(μ-Me)}$^+$ but slow under the same conditions for {[(1,2-C$_5$Me$_2$H$_3$)$_2$ZrMe]$_2$(μ-Me)}$^+$.[9] While the mechanism for this exchange process has not been definitively identified, these observations suggest that exchange of the methyl groups may occur without dissociation of the dimer (i.e., the equilibrium in eq 1 is

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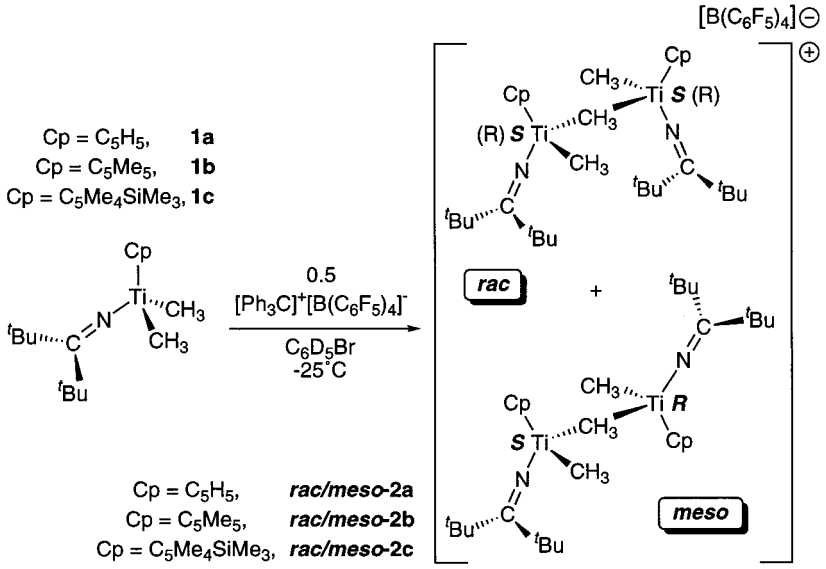
Scheme 1



not involved in methyl exchange). On the other hand, in some systems the equilibrium of eq 1 is detectable by ^{1}H NMR spectroscopy and exchange between both the bridging and terminal methyl groups of the dimer with those of excess Cp_2MMe_2 is observed to be facile.[7,10] Careful NMR studies by Brintzinger et al. have also shown that for μ-methyl dimers generated in the presence of the somewhat more coordinating $H_3CB(C_6F_5)_3^-$ counteranion, an equilibrium between a solvent-separated ion pair and a contact ion pair is detectable.[11] The former is favored at the low concentrations common to typical polymerization processes, while the latter occur at higher concentrations of zirconium and is likely present as an ion quadruple.[12]

The Brintzinger study also concluded (based on polymer molecular weight distributions) that these dimers do not play a direct role in the production of polymer, but perhaps play a stabilizing role for the more active monomeric alkyl cations responsible for olefin enchainment. This is consistent with earlier observations that, in some instances, the availability of these dimers can help to stabilize catalyst systems in which the monomeric cation is quite reactive and result in a macroscopic improvement in catalyst productivity relative to a reaction performed in the absence of excess neutral metallocene.[4a] Thus, while no explicit role for these dimers has been identified, their presence may not be entirely detrimental to the polymerization process.

Most of the μ-methyl dimers in the literature appear to be relatively thermally stable, the only major effect of higher temperatures being to shift the equilibrium toward the monomeric components of the dimer. Other than that, little is known about other thermally induced reaction pathways. Recently we reported the synthesis of the monocyclopentadienyl ketimido catalyst precursors $Cp(L)TiMe_2$ (L = ^{t}Bu$_2$C═N; Cp = C_5H_5, **1a**; C_5Me_5, **1b**; $C_5Me_4SiMe_3$, **1c**) and their reactivity with the common borane activator $B(C_6F_5)_3$.[13] Herein we describe the reactions of these same dimethyl compounds with the activator $[Ph_3C]^+[B(C_6F_5)_4]^-$, incorporating the more weakly coordinating, fully fluorinated borate anion. As for other catalyst systems, μ-methyl dimers are important species in these reactions. In addition to the activation chemistry, we report the formation of another class of dimers formed upon elimination of CH_4 from the μ-methyl compounds generated in situ from compounds **1** and tritylborate.[14]

Results and Discussion

The synthesis of dimethyl titanium complexes supported by one Cp donor and one ketimide ligand has been reported previously.[13a] Compounds **1a**−**c**, which differ only in the Cp donor and contain the (^{t}Bu)$_2$C═N− ketimide ligand, may be converted into relatively stable cationic μ-methyl dimers via treatment with 0.5 equiv of the trityl borate activator $[Ph_3C]^+[B(C_6F_5)_4]^-$; the observed chemistry is outlined in Scheme 1. When these reactions are carried out via addition of a solution of $[Ph_3C]^+[B(C_6F_5)_4]^-$ to the dimethyl titanium compound (−20 °C), formation of the dimers **2** is preferred even when excess trityl borate is present.[15] The dimers **2** form as an essentially 1:1 mixture of diastereomers, as evidenced by the doubling of all the signals in the proton and ^{13}C NMR spectra of these solutions.[4a,10,11] The most diagnostic peaks are those of the μ-Me groups which appear at 0.01 and −0.02 ppm for *rac*/*meso* **2a**, −0.35 and −0.38 ppm for *rac*/*meso* **2b**, and −0.56 and −0.59 ppm for **2c**, each with characteristically large

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(15) Warming solutions of **2a**−**c** that contain a further 0.5 equiv of $[Ph_3C]^+[B(C_6F_5)_4]^-$ results in consumption of the trityl reagent via abstraction of a methide group. In the case of **2a**, a complex mixture results, but for **2b** and **2c**, ^{1}H NMR spectroscopy indicates that monomeric alkyl cations are formed in about 80% yield by ^{1}H NMR spectroscopy.

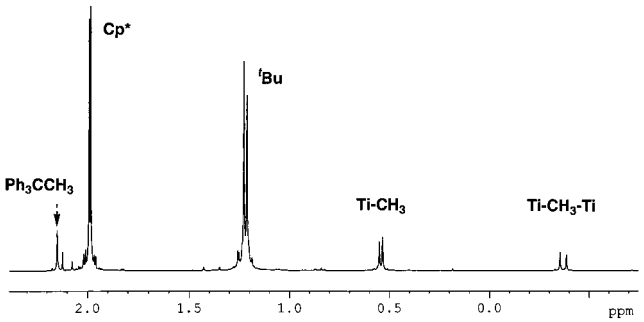
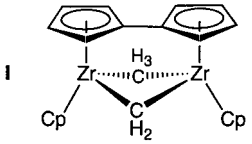


Figure 1. ^{1}H NMR spectrum (300 MHz) of *rac/meso* **2b**, formed in situ via reaction of Cp*(^{t}Bu$_2$C=N)TiMe$_2$ and 0.5 equiv of $[Ph_3C]^+[B(C_6F_5)_4]^-$ in C_6D_5Br.

$^1J_{CH}$ values of 136(1) Hz. A representative ^{1}H NMR spectrum for the dimers *rac/meso* **2b** is shown in Figure 1. Using 2D ROESY experiments, it is possible to determine which signals belong together, but the proton and carbon NMR spectra do not allow for specific assignment of a family of resonances to a given diastereoisomer. For all of the compounds described herein, the ^{19}F and ^{11}B NMR spectra are essentially identical, indicating that, in bromobenzene, these species are solvent-separated ion pairs. The fact that these reactions are not diastereoselective stands in contrast to the remarkable diastereoselectivity observed by Marks et al. in the formation of the μ-methyl dimer from (CGC)-TiMe$_2$ and half an equivalent of $[Ph_3C]^+[B(C_6F_5)_4]^-$ or PBB.[9] All attempts to isolate dimers **2** failed due to their thermal instability (vide infra) and their tendency to form liquid clathrates instead of free flowing powders; thus, all characterizational data were obtained on in situ generated samples. Although dimers **2** are stable for long periods of time in solution at −25 °C, at higher temperatures a process leading to elimination of methane forms a new family of dimeric cations.

Methane elimination from the μ-methyl dimers *rac/meso* **2a**−**c** occurs cleanly in bromobenzene solution at room temperature over the course of a few hours. The loss of methane (identified by ^{1}H NMR spectroscopy) leads to formation of new dimeric cations, **3a**−**c**, in which the titanium centers are bridged by a μ-methyl and a μ-methylene ligand (Scheme 2). While *rac/meso* **3a** and **3c** were generated in situ, *rac* **3b** was isolated as an analytically pure red crystalline solid in 80% yield when preparative quantities of *rac/meso* **2b** were allowed to stand in solution for several hours. In addition to the resonances for the ancillary ligands in **2b**, peaks at 7.44 and −0.98 ppm (integrating in a 2:3 ratio) are characteristic of the μ-CH_2 and μ-CH_3 groups, respectively. $^1J_{CH}$ values of 121 and 112 Hz for these groups are more typical of sp^3 carbon centers and indicate the loss of the linearly bridging μ-methyl group of the starting material. The downfield chemical shift of the μ-CH_2 group is similar to that observed for the diastereotopic methylene protons in the related compound **I**,



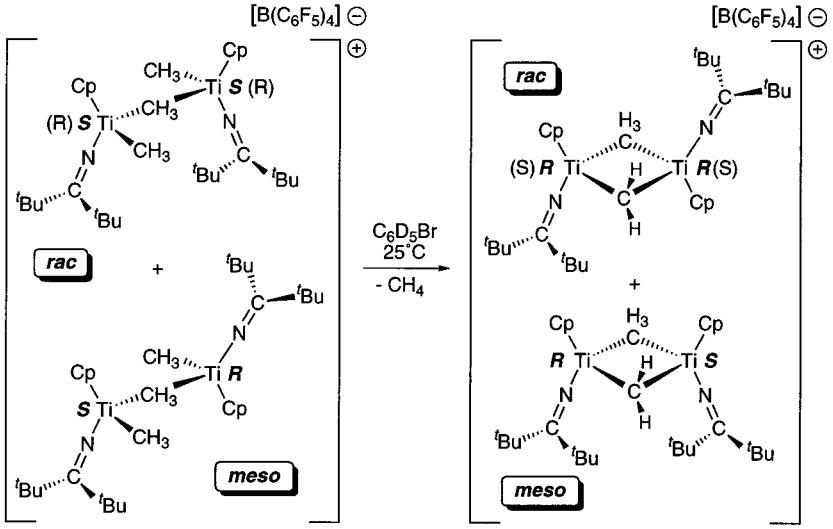
which appear at 4.35 and 9.91 ppm (CD_2Cl_2).[14] In addition to the observed equivalency of the μ-CH_2 protons in the ^{1}H NMR spectra of *rac* **3b** and **3c**, the assignment of these compounds as the *rac* diastereomers was supported by an X-ray structural analysis of **3b**. Unfortunately, refinement to a suitable level was precluded by severe disorder associated with the bridging hydrocarbyl groups; nevertheless, the connectivity of the molecule was confirmed, in particular the placement of the Cp* ligands *trans* to one another across the Ti_2C_2 molecular core. While loss of methane from *rac/meso* **2b** or **2c** proceeds with >95% diastereoselectivity to *rac* **3b** or **3c**, in the C_5H_5 compounds the dimers are formed as a mixture of diastereomers, presumably with *rac* **3a** dominating (*rac* **3a**:*meso* **3a** = 7:3). For reasons outlined below, this is likely a thermodynamic mixture. Evidently, the bulkier Cp ligands in **3b** and **3c** disfavor the more sterically challenged *meso* isomer in which the Cp donors are *cis* disposed about the central Ti_2C_2 core.

Aside from the linked system leading to **I**, this is to our knowledge the first report of methane elimination from a cationic μ-methyl dimer,[16] and to the extent that such species are relevant under typical olefin polymerization conditions, this process has implications for catalyst speciation within a reactor. Several observations indicate that the room-temperature methane loss occurs from the dimers *rac/meso* **2** and does not involve prior dissociation into monomers as in eq 1. Consistent with the observations of Marks concerning μ-methyl dimers involving smaller metals (see Introduction), exchange between the bridging and terminal methyl groups in compounds **2** does not occur on the NMR time scale. Exchange between the *rac* and *meso* isomers of **2a**−**c** is slow on this time scale as well; upon warming, the spectral changes observed are consistent only with the formation of dimers **3**. Furthermore, exchange spectroscopy (EXSY) experiments indicate no interconversion of *rac* and *meso* **2b** on longer time scales either. Since one possible pathway for either of these exchange processes may involve dimer dissociation and re-formation, the lack of exchange suggests that the rate of dissociation is slow for these compounds, at least in bromobenzene.

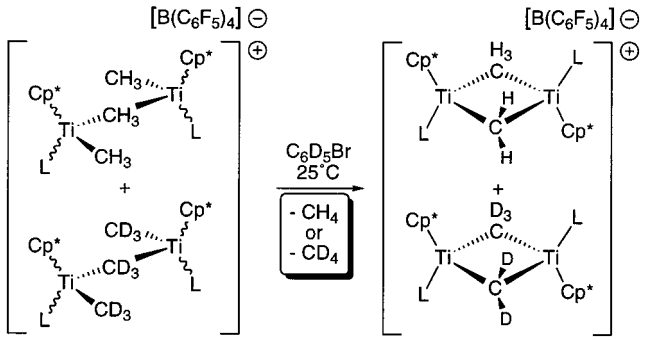
Dimer dissociation appears to be slow on the *chemical* time scale as well. d_9-*rac/meso* **2b**, selectively deuterated in the Ti-Me positions, can be formed via reaction of Cp*(L)Ti(CD_3)$_2$ (d_6-**1b**) and half an equivalent of $[Ph_3C]^+[B(C_6F_5)_4]^-$. When a solution of d_9-*rac/meso* **2b** and a similar solution of the undeuterated material are mixed and allowed to undergo methane loss under normal conditions, the only products observed are CH_4 and CD_4 and *rac* **3b**/d_5-*rac* **3b** (Scheme 3). This indicates that no dimer dissociation (and intermolecular methyl group scrambling) occurs prior to loss of methane, which takes place over the course of several hours at room temperature. Thus, in contrast to metallocene systems such as $\{[(1,2\text{-}C_5Me_2H_3)_2ZrMe]_2(\mu\text{-}Me)\}^+[MePBB]^-$, where exchange with free neutral metallocene is facile,[7] the dimers formed using the Cp/ketimido ligand set are less prone to dissociation under ambient conditions, and it is likely that compounds **2** react as dimers rather than

(16) A zirconium compound related to dimers **3** was recently reported, but arose from deprotonation of a dimeric dimethyl *dication*: Keaton, R. J.; Jayaratne, K. C.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 12909.

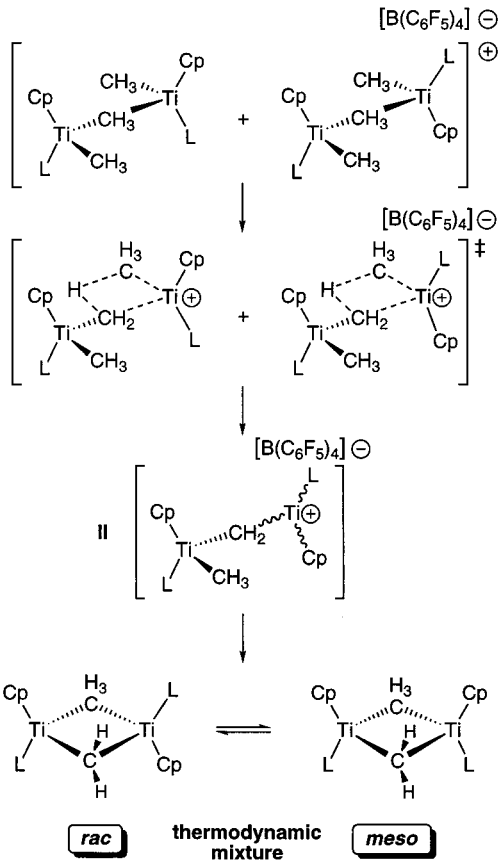
Scheme 2



Scheme 3



Scheme 4



via initial dissociation.[17] Consequently, methane loss likely proceeds via a σ-bond metathesis reaction (Scheme 4) involving a C−H bond of the bridging methyl group, in a reaction similar to that observed in the methane loss from ion pairs of the form $\{Cp(L)TiMe]^+[MeB(C_6F_5)_3]^-$.[13a] If this is an accurate picture of the methane loss reaction, then equilibration of the resulting diastereomers should be possible since the intermediate **II** should be able to undergo epimerization at titanium and/or rotation about the Ti^+-CH_2 bond. Indeed, EXSY spectroscopy on the C_5H_5-substituted mixture *rac/meso* **3a** shows that, unlike the μ-methyl dimers *rac/meso* **2a**, these isomers undergo exchange on this time scale. The fact that only the *rac* isomers of **3b** and **3c** are observed in the methane elimination from *rac/meso* **2b** and **2c** is also supportive of a facile pathway for isomerization. Presumably, this exchange process occurs via an opening of the μ-methyl bridge through the intermediate species **II**. The accessibility of **II** also accounts for the fact that compounds **3** are competent ethylene polymerization catalysts.[18] Thus, these μ-methylene, μ-methyl dimers may be important species in olefin polymerizations using these types of single-site catalysts.

(17) This observation raises the possibility that reaction of **2b** with further $[Ph_3C]^+[B(C_6F_5)_4]^-$ occurs without prior dissociation. See ref 15.

(18) Wang, Q.; Zhang, S.; Piers, W. E. Unpublished results.

Experimental Section

General Comments. General procedures have been described in detail elsewhere.[13a] $[Ph_3C]^+[B(C_6F_5)_4]^-$ was prepared according to the literature procedure or purchased from Boulder Scientific. C_6D_5Br was dried by exposing to activated molecular sieves and distilling in vacuo. Compounds **1a**−**c** and d_6-**1b** were prepared as described previously.[13a]

In Situ Generation of *rac/meso* 2a. Compound **1a** (7.0 mg, 0.025 mmol) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (11.4 mg, 0.012 mmol) were loaded into a sealable J. Young NMR tube in a glovebox.

C_6D_5Br (0.5−0.8 mL) was then vaccum transferred onto the solids at −78 °C. The sample was transferred to the NMR probe, precooled to −25 °C, at which temperature the NMR spectroscopy was carried out. The *rac/meso* isomers were present in a 1:1 ratio and could not be specifically assigned. ^{1}H NMR: 6.11, 6.09 (s, 10H, C_5H_5); 0.98, 0.97 (s, 18H, C(CH_3)$_3$); 0.77, 0.75 (s, 6H, TiCH_3); 0.01, −0.02 (s, 3H, μ-Ti−CH_3). ^{13}C-{^{1}H} NMR: 212.7, 212.7 (*C*═N); 115.6, 115.5 (C_5H_5); 66.9, 66.6 (TiCH_3 $^1J_{C-H}$ = 121 Hz); 45.8, 45.0 (*C*CH_3); 45.8, 45.0 (μ-Ti−CH_3, $^1J_{C-H}$ = 136 Hz); 30.2, 30.2 (C*C*H_3). ^{19}F NMR: −131.9 (*ortho*-F); −161.4 (*para*-F), −165.2 (*meta*-F). ^{11}B NMR: −13.6.

In Situ Generation of *rac/meso* 2b. A solution of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (10.4 mg, 0.012 mmol) in C_6D_5Br (0.3 mL) was added dropwise to a solution of **1b** (8.0 mg, 0.023 mmol) cooled to −20 °C in C_6D_5Br (0.4 mL) in a sealable NMR tube. The tube was sealed and agitated and NMR spectroscopy performed on this sample. Again, the *rac/meso* isomers were present in a 1:1 ratio and could not be specifically assigned. ^{1}H NMR: 1.99, 1.98 (s, 15H, C_5(CH_3)$_5$); 1.23, 1.18 (s, 18H, CCH_3); 0.55, 0.53 (s, 6H, TiCH_3); −0.35, −0.38 (s, 3H, μ-Ti−CH_3). ^{13}C{^{1}H} NMR: 208.9, 208.9 (*C*═N); 60.8, 60.4 (TiCH_3 $^1J_{C-H}$ = 120.6 Hz); 46.4, 46.4 (*C*CH_3); 45.5, 45.4 (μ-Ti−CH_3 $^1J_{C-H}$ = 136 Hz); 29.9, 29.8 (C*C*H_3); 12.7, 12.6 (C_5(*C*H_3)$_5$). ^{19}F NMR: −131.9 (*ortho*-F); −161.4 (*para*-F); −165.2 (*meta*-F). ^{11}B NMR: −13.6.

In Situ Generation of *rac/meso* 2c. A procedure identical to that described above for generation of *rac/meso* **2b** was carried out using compound **1c** (10 mg, 0.025 mmol) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (11.5 mg, 0.0125 mmol). Again, the *rac/meso* isomers were present in a 1:1 ratio and could not be specifically assigned. ^{1}H NMR: 2.02, 2.00, 1.83, 1.82, 1.64, 1.57, 1.53, 1.52 (s, 12H, C_5(CH_3)$_4$); 0.99, 0.95 (s, 18H, CCH_3); 0.69, 0.68 (s, 6H, TiCH_3); 0.22, 0.23 (s, 9H, SiCH_3); −0.56, −0.60 (s, 3H, μ-Ti−CH_3). ^{13}C{^{1}H} NMR: 209.2, 209.0 (*C*═N); 135.3, 135.2, 132.9, 132.1, 131.3, 126.7 (C_5Me_4, others obscured by solvent); 63.4, 61.8 (TiCH_3); 52.0 (*C*CH_3); 46.9, 43.2 (μ-Ti−CH_3); 30.4, 30.1 (*C*CH_3); 15.7, 15.6, 15.5, 15.4, 12.4,,12,4, 12.2, 12.1 (C_5(*C*H_3)$_4$); 1.5, 1.4 (SiCH_3).

In Situ Generation of *rac/meso* 3a. Dimethyl compound **1a** (7.0 mg, 0.025 mmol) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (11.4 mg, 0.012 mmol) were loaded into a sealable J. Young NMR tube. C_6D_5Br (0.5−0.8 mL) was vacuum transferred onto the solids. The sample was warmed to room temperature and monitored by ^{1}H NMR spectroscopy; the reaction was complete in about 6 h. *Rac/meso* **3a** was formed in a 1.9:1 ratio. *Rac* **3a:** ^{1}H NMR (C_6D_5Br): δ 7.86 (s, 2H, TiCH_2Ti), 6.22 (s, 10H, C_5H_5), 1.05 (s, 18H, CCH_3), 0.53 (s, 3H, μ-Ti−CH_3). ^{13}C NMR (C_6D_5Br): 210.5 (*C*═N); 115.5 (C_5H_5); 66.6 (Ti-*C*H_3, $^1J_{CH}$ = 113.1 Hz); 47.1 (*C*CH_3); 30.2 (C*C*H_3); 27.7 (Ti*C*H_2, $^1J_{CH}$ = 125.7 Hz. *Meso* **3a:** ^{1}H NMR (C_6D_5Br): δ 7.28 (s, 1H, TiCH_2Ti, other resonance obscured under phenyl resonances), 6.21 (s, 10H, C_5H_5), 1.16 (s, 18H, CCH_3), 0.61 (s, 3H, μ-Ti−CH_3).

Synthesis of *rac* 3b. A solution of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.26 g, 0.29 mmol) in bromobenzene (10 mL) was added dropwise to a solution of dimethyl derivative **1b** (0.2 g, 0.57 mmol) cooled to −20 °C. The reaction was warmed to room temperature and stirred for 12 h. The solution was layered with hexanes (10 mL), and the product was collected as a red crystalline solid by filtration. Yield: 0.3 g (80%). Anal. Calcd for $C_{64}H_{71}BF_{20}N_2Ti_2$: C, 56.94; H, 4.93; N, 2.07. Found: C, 56.58; H, 5.01; N, 2.07. ^{1}H NMR (C_6D_5Br): 7.44 (s, 2H, TiCH_2); 1.83 (s, 30H, C_5(CH_3)$_5$); 1.25, 1.17 (s, 36H, CCH_3); −0.98 (s, 3H, μ-Ti−CH_3). ^{13}C{^{1}H} NMR (C_6D_5Br): 206.9 (*C*═N); 61.53 (μ-Ti*C*H_3, $^1J_{C-H}$ = 111.8 Hz); 47.5, 46.6 (*C*CH_3); 31.9 (C*C*H_3); 25.3 (μ-Ti−CH_2, $^1J_{C-H}$ = 121 Hz); 13.6 (C_5(*C*H_3)$_5$). ^{19}F NMR (C_6D_5Br): −131.9 (*ortho*-F); −161.4 (*para*-F), −165.2 (*meta*-F). ^{11}B NMR (C_6D_5Br): −13.6.

In Situ Generation of *rac* 3c. A solution of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (11 mg, 0.012 mmol) in C_6D_5Br (0.3 mL) was added dropwise to a solution of dimethyl derivative **1c** (10 mg, 0.025 mmol) in C_6D_5Br (0.3 mL, −10 °C) contained in a sealable NMR tube. After agitation, the tube was sealed and the sample warmed to room temperature and allowed to stand for 12 h. Upon completion of the reaction (>95% clean by ^{1}H NMR), the following data were collected. ^{1}H NMR (C_6D_5Br): 7.66 (s, 2H, TiCH_2); 2.35, 2.22, 1.86, 1.58 (s, 24H, C_5(CH_3)$_4$); 1.18, 1.12 (s, 36H, CCH_3); −0.02 (s, 18H, SiCH_3); −0.77 (s, 3H, μ-Ti−CH_3). ^{13}C{^{1}H} NMR (C_6D_5Br): 207.2 (*C*═N); 134.5, 133.6, 131.2 (C_5-CH_3, others obscured by solvent); 64.9 (μ-Ti*C*H_3); 47.0, 46.1 (*C*CH_3); 30.8, 30.7 (C*C*H_3); 52.1 (μ-Ti−CH_2); 17.1, 16.8, 13.4, 13.0 (C_5(*C*H_3)$_4$); 1.4 (Si*C*H_3). ^{19}F NMR (C_6D_5Br): −131.9 (*ortho*-F); −161.4 (*para*-F), −165.2 (*meta*-F). ^{11}B NMR (C_6D_5Br): −13.6.

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