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Neutral and Cationic Aluminum and Titanium Complexes Incorporating Sterically Demanding Organosilicon Ligands

Virginia Amo,[†] Román Andrés,[*,†] Ernesto de Jesús,[†] F. Javier de la Mata,[†]
Juan C. Flores,[†] Rafael Gómez,[*,†] M. Pilar Gómez-Sal,[†] and John F. C. Turner[‡]

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario,
E-28871 Alcalá de Henares, Spain, and Department of Chemistry, University of Tennessee,
409 Buehler Hall, Knoxville, Tennessee 37996-1600

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New complexes of aluminum and titanium containing sterically demanding ligands and their reaction with $B(C_6F_5)_3$ are reported. Treatment of $[(Ph_2MeSiCH_2CH_2)_3Si]NCN[Si(CH_2CH_2SiMePh_2)_3]$ (**1**) or $Si(CH_2CH_2SiMePh_2)_3OH$ (**2**) with 1 equiv of $AlMe_3$ results in the formation of the neutral dimethylaluminum complexes $\{MeC[NSi(CH_2CH_2SiMePh_2)_3]_2\}AlMe_2$ (**3**) and $[(Ph_2MeSiCH_2CH_2)_3SiOAlMe_2]_2$ (**4**). Reaction of **3** with 1 equiv of $B(C_6F_5)_3$ forms the neutral complex $\{MeC[NSi(CH_2CH_2SiMePh_2)_3]_2\}AlMe(C_6F_5)$ (**5**) and $BMe(C_6F_5)_2$. In the case of **4**, the analogous reaction produced the dimer $[(Ph_2MeSiCH_2CH_2)_3SiOAl]_2Me_3(C_6F_5)$ (**6**). Treatment of **1** with $Ti(C_5Me_5)Me_3$ fails to afford the corresponding amidinate complex. However, reaction of **2** with the same titanium half-sandwich complex cleanly gives $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me_2$ (**7**). Reaction of **7** with 1 equiv of $B(C_6F_5)_3$ leads to the formation of the ion pair $\{Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me\}[BMe(C_6F_5)_3]$ (**8**), which is relatively stable at room temperature, slowly decomposing ($t_{1/2} \approx 48$ h) to give a mixture of two neutral titanium complexes, $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3][CH_2B(C_6F_5)_2](C_6F_5)$ (**9**) and $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me(C_6F_5)$ (**10**). However, when this reaction is carried out in a 1:0.5 stoichiometry, the decomposition process occurs over the course of 22 h, giving complex **10** selectively. The implications of these results with related Ziegler−Natta catalyst systems are discussed.

Introduction

There has been considerable interest in the use of alternative ligands either with or in place of the Cp moieties for homogeneous olefin polymerization catalysis. Replacement of one of the cyclopentadienyl rings in dicyclopentadienyl derivatives by other alternative donor groups of the same charge has been the most common way for developing such complexes, and a wide range of $MCpLX_2$ precatalysts have been prepared.[1] Such systems may provide more reactive species and hence unforeseen reactivity, because of their lower electron-donating properties and in some cases their lower steric encumberance. In addition, when they are activated by a cocatalyst such as methylaluminoxane (MAO), $B(C_6F_5)_3$, $[CPh_3][B(C_6F_5)_4]$, or $[NHR_3][B(C_6F_5)_4]$, they generate catalysts with moderate or high activities, making them viable alternatives to their metallocene counterparts.[2] However, they have a greater tendency to suffer from deactivation processes, leading to irreversible systems and loss of activity.

Extensive work with $B(C_6F_5)_3$ has been conducted to synthesize ionic or zwitterionic species via methyl abstraction from neutral dialkyl derivatives and to explore olefin polymerization mechanisms. The ion pairs generated are thermally unstable, and two main deactivation pathways have been observed experimentally: (i) σ-bond metathesis,[3] which involves hydrogen transfer from the counteranion $[MeB(C_6F_5)_3]^-$ to the alkyl group bonded to the metal with subsequent C_6F_5 transfer, affording a neutral complex of type $L_2M[CH_2B(C_6F_5)_2](C_6F_5)$, and (ii) aryl transfer from the counteranion to the metal[4,5] leading to another neutral complex of type $L_2M(CH_3)(C_6F_5)$ (see Scheme 1). The latter pathway has been observed in the organometallic chemistry of both

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* To whom correspondence should be addressed. Tel: (34) 918854677. Fax: (34) 918854683. E-mail: roman.andres@uah.es.

[†] Universidad de Alcalá.

[‡] University of Tennessee.

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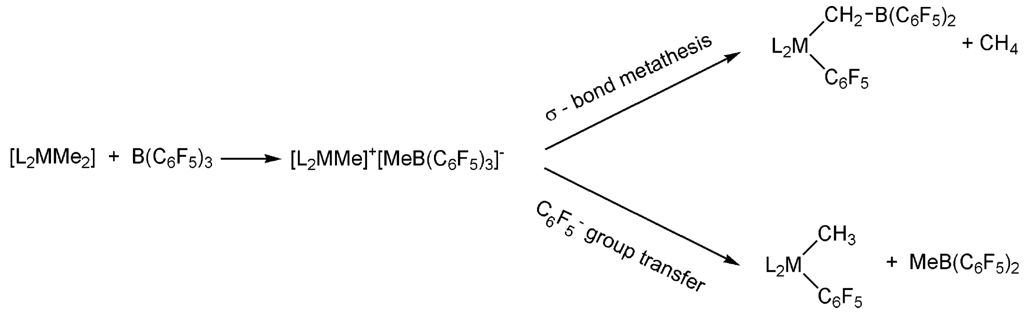
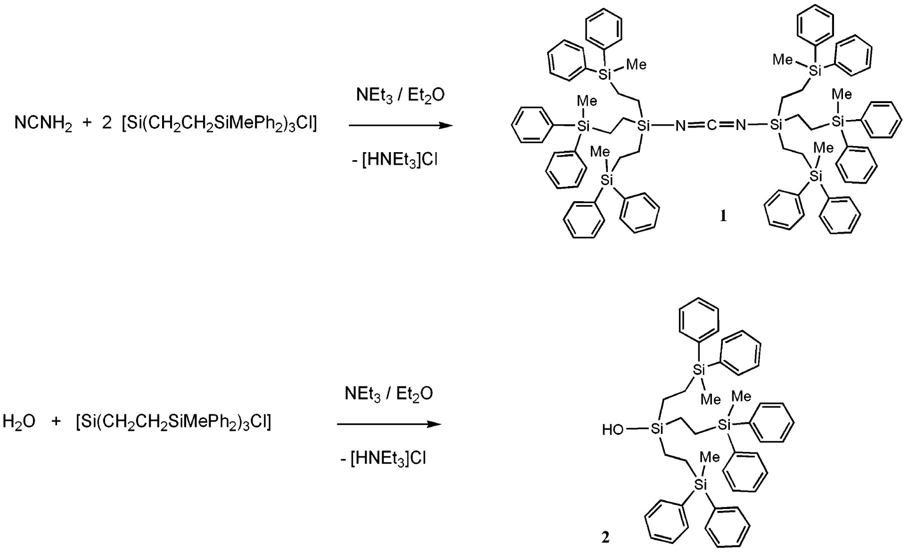
10.1021/om049010p CCC: $30.25

Scheme 1



Scheme 2



groups 4 and 13, though the former mechanism has been detected only for Ti. In addition, the σ-bond metathesis deactivation pathway has not been identified in dicyclopentadienyl systems in which the most common deactivating side reaction involves $C_6F_5^-$ group transfer. However, prior to this report, deactivation reactions by pathways (i) and (ii) have been mutually exclusive for a single complex, although their activation barriers are of the same magnitude.[6] The electronic and steric effects of the ancillary ligands around the metal center may play an important role in modulating the activation barrier of these process. We report here the synthesis of neutral sterically encumbered aluminum and titanium complexes and their reactivity with $B(C_6F_5)_3$. The deactivation processes of the corresponding ionic species are studied, showing, to our knowledge, the first time in which both deactivation mechanisms are present simultaneously in the same complex.

Results and Discussion

Synthesis of Sterically Demanding Organosilicon Ligands. Treatment of cyanamide $NCNH_2$ with 2 equiv of the known chlorosilane $Si(CH_2CH_2SiMePh_2)_3$-Cl[7] in diethyl ether in the presence of triethylamine led to the corresponding carbodiimide, $[(Ph_2MeSiCH_2CH_2)_3$-$Si]NCN[Si(CH_2CH_2SiMePh_2)_3]$ (**1**), as a white solid. Similar treatment of the chlorosilane with 1 equiv of water and NEt_3 afforded the silanol, $Si(CH_2CH_2$-$SiMePh_2)_3OH$ (**2**), as a colorless oil (Scheme 2). This smooth procedure contrasts with those found in sterically crowded arylchlorosilanes.[8] Both products are soluble in common solvents, but only slightly soluble in aliphatic solvents. Compound **1** is water stable, in contrast to the analogous less sterically demanding system $Me_3SiNCNSiMe_3$.[9] Bulky substituted N-based compounds are known to be stable toward hydrolysis.[10]

The ^1H and ^{13}C NMR data of the silyl groups in **1** and **2** are identical, showing no variation on changing N(sp hybridization) to an O donor atom (see Experimental Section). The central C atom of the N=C=N fragment appears at 123.1 ppm, similar to that found for the ligand $Me_3SiNCNSiMe_3$,[9] indicating comparable electronic properties for both silyl substituents.

In addition, single crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation of saturated pentane. An ORTEP drawing of the molecular structure is shown in Figure 1, and crystal data are collected in Table 1 (for selected bond distances and

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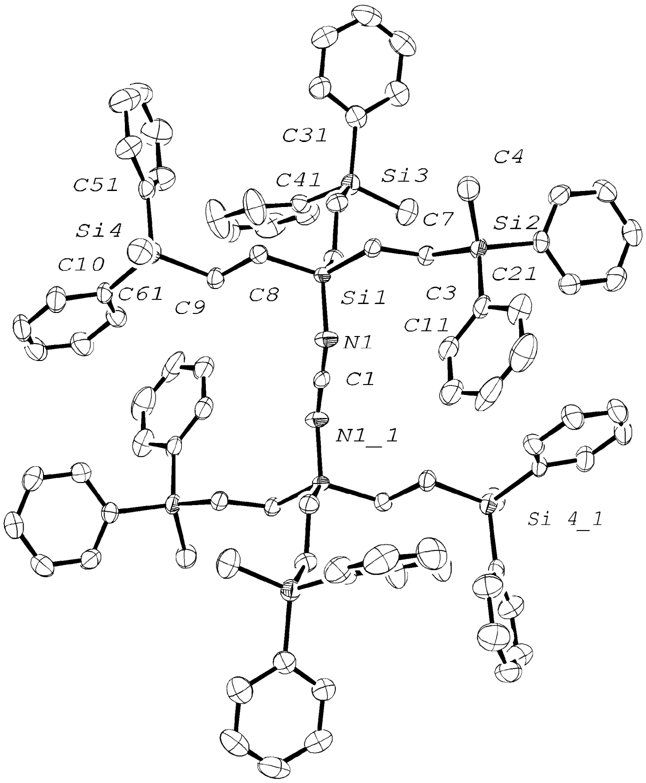

Figure 1. ORTEP (50% termal ellipsoids) view of [(MePh$_2$SiCH$_2$CH$_2$)$_3$Si]NCN[Si(CH$_2$CH$_2$SiMePh$_2$)$_3$] (**1**). Selected bond lengths (Å) and angles (deg): C(1)−N(1) 1.213(3), Si(1)−N(1) 1.725(3), N(1)−C(1)−N(1)# 180.0(2), C(1)−N(1)−Si(1) 148.42(19).

Table 1. Crystal Data and Structure Refinement for Compound 1

empirical formula	$C_{91}H_{102}N_2Si_8$
fw	1448.47
temperature	170(2) K
wavelength	0.71073 Å
cryst syst, space group	monoclinic, $P2_1/c$
unit cell dimens	$a = 13.394(3)$ Å $b = 32.088(3)$ Å, $\beta = 101.74(10)°$ $c = 10.1033(19)$ Å
volume	4251.3(13) Å^3
Z, calcd density	2, 1.132 Mg/m^3
absorp coeff μ	0.171 mm^{-1}
F(000)	1548
cryst size	0.30 × 0.23 × 0.10 mm
θ range for data collection	5.01 to 27.51°
limiting indices	$-17 \leq h \leq 17$, $-41 \leq k \leq 41$, $-13 \leq l \leq 13$
reflns collected/unique	44338/9611 [R(int) = 0.1659]
reflns observed [$I > 2\sigma(I)$]	6001
completeness to $\theta = 27.51$	98.3%
absorption correction	none
method	full-matrix least-squares on F^2
data/restraints/params	9611/0/661
goodness-of-fit on F^2	0.997
final R indices [$I>2\sigma(I)$]^a	R1 = 0.0664, wR2 = 0.1389
R indices (all data)^a	R1 = 0.1203, wR2 = 0.1624
largest diff peak and hole	0.638 and −0.552 e Å^3

[a] $R1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$; $wR2 = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$.

angles see caption of Figure 1 and Supporting Information). The molecular structure consists of two moieties related by a crystallographic 2-fold axis passing through the central C of the N=C=N fragment, which is linear. The silicon atoms have a standard tetrahedral coordination, and in the crystal the molecule seems well ordered.

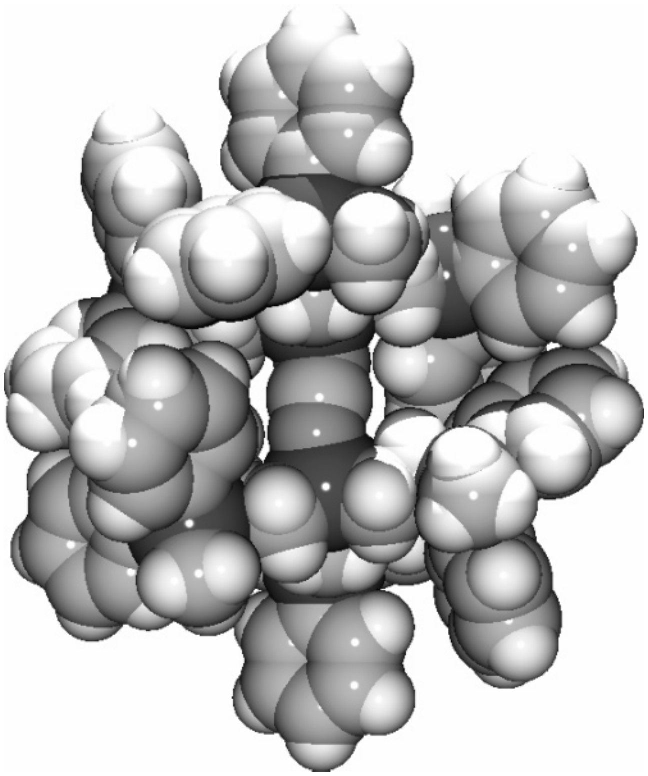

Figure 2. Space-filling model for complex [(MePh$_2$SiCH$_2$CH$_2$)$_3$Si]NCN[Si(CH$_2$CH$_2$SiMePh$_2$)$_3$] (**1**).

The branches of the system have lost the C_3 symmetry, as seen in Figure 1. This situation could be described by the torsion angle N−Si−C−C (N1−Si1−C8−C9 is 58.8°, N1−Si1−C5−C6 is 173.1°, and N1−Si1−C2−C3 is 71.8°), which shows different values. Besides the apparent steric congestion around the central N=C=N fragment, the C_2 symmetry provides a vacancy in the direction of the C_2 axis (see Figure 2) that may allow the attack of different reagents, although in solution the NMR data show that the three arms and phenyl rings are equivalent, indicating a very flexible system.

Synthesis of Aluminum Complexes. Addition of $AlMe_3$ to a solution of the carbodiimide **1** in toluene at 70 °C resulted in the formation of the amidinate complex {MeC[NSi(CH$_2$CH$_2$SiMePh$_2$)$_3$]$_2$}AlMe$_2$ (**3**) as a colorless oil after removal the volatiles. The reaction proceeded perceptibly only above 50 °C. The reaction of the silanol **2** with $AlMe_3$ in toluene did take place at room temperature to give the siloxy compound [(Ph$_2$MeSiCH$_2$CH$_2$)$_3$SiOAlMe$_2$]$_2$ (**4**) as a colorless oil (see Scheme 3). The dimeric nature of **4** was determined by osmometry[11] (calcd: 1554.6 amu; found: 1534.7 amu) and reactivity (see below formation of compound **6**) and is assumed on the basis of the literature[8,12] and the existence of complex **3**. Complex **3** shows the Al-Me and *Me*-C resonances at −0.29 and 1.48 ppm in the ^{1}H NMR and at −8.5 and 23.8 ppm in the ^{13}C NMR spectra, respectively, in C_6D_6, while the C$_{ipso}$ signal of the amidinate appears at 181.3 ppm. All these signals are almost

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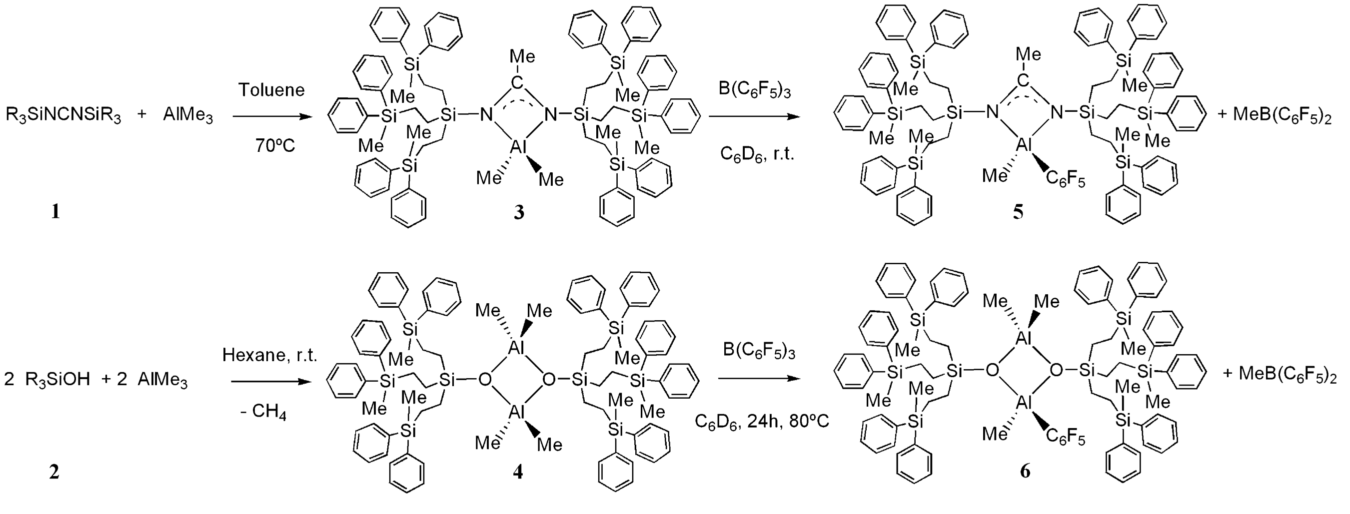
Scheme 3



identical to those shown by the analogous complex $[MeC(NSiMe_3)_2]AlMe_2$.[9a] For complex **4** the Al-Me resonances appear at −0.51 and −6.4 ppm in the ^1H and ^{13}C NMR spectra, respectively.

We have examined the methyl abstraction of complexes **3** and **4** with $B(C_6F_5)_3$ by monitoring the reactions by NMR. The reaction between equimolar amounts of **3** and $B(C_6F_5)_3$ in C_6D_6 at room temperature led to the formation of a 1:1 mixture of the neutral complex $\{MeC[NSi(CH_2CH_2SiMePh_2)_3]_2\}AlMe(C_6F_5)$ (**5**) and $BMe(C_6F_5)_2$[13] (see Scheme 3). However, the formation of the expected cationic aluminum species by methyl abstraction was not observed under these conditions. The formation of a mixture of **5** and $BMe(C_6F_5)_2$ can be envisaged as a degradation pathway of the expected zwitterionic complex $[\{MeC[NSi(CH_2CH_2SiMePh_2)_3]_2\}AlMe]^+[MeB(C_6F_5)_3]^-$, which decomposes by transfer of a $C_6F_5^-$ group from the borate anion to the aluminum center. The activation of **3** with $B(C_6F_5)_3$ under an ethylene atmosphere in a Teflon-valved NMR tube led to the formation of polyethylene. However, if the olefin monomer is added when **5** is formed, negligible amounts of polymer were detected. This feature supports the formation of the ion pair mentioned above. This metathetical decomposition process has been reported previously for amidinate,[4a,b] diketiminato,[4c] or aminophenolate[4d] aluminum complexes. In addition, if the reaction is carried out with aluminum−boron ratios of 2:1 or 3:1, the same complex **5** is observed, although further $C_6F_5^-$ transfer occurred, leading to the formation of $BMe_2(C_6F_5)$[14] or BMe_3, respectively; interestingly, in no case were species of type $LAl(C_6F_5)_2$ detected. Taking this behavior into account, complex **5** was isolated in a synthetic experiment. These ligand redistribution processes have been observed in the reaction of $AlMe_3$ with the borane $B(C_6F_5)_3$ to give $Al(C_6F_5)_3$ and BMe_3. However, the more electrophilic properties of the $AlMe_3$ are responsible for the transfer of more than one aryl group per aluminum.[15] Compound **5** shows a high-field broad singlet at −0.04 ppm in the ^1H NMR spectrum and a resonance at −8.7 ppm in the ^{13}C NMR spectrum corresponding to the Me-Al. The presence of a $C_6F_5^-$ is confirmed by the ^{19}F NMR spectrum (see Experimental Section) and the broadness of the proton Me-Al signal, which is due to a $^5J_{H-F}$ coupling.

No reaction of dimer **4** was observed when it was treated with 2 equiv of $B(C_6F_5)_3$ below 70 °C for several days. This behavior might be attributed to steric hindrance and strongly contrasts with that observed in the case of **3** or in other bulky siloxyaluminum complexes when reacted with $[NHR_3]^+[B(C_6F_5)_4]^-$.[8,12] However, at 80 °C the neutral complex $[(Ph_2MeSiCH_2CH_2)_3SiOAl]_2Me_3(C_6F_5)$ (**6**) and $BMe(C_6F_5)_2$ were cleanly produced, while unreacted $B(C_6F_5)_3$ remained unchanged in the reaction mixture. Compound **6** shows three resonances at −0.20 ppm ($^5J_{H-F} = 1.7$ Hz), −0.46 ppm ($^7J_{H-F} = 1.2$ Hz), and −0.54 ppm at high field in the ^1H NMR spectrum, attributed to each one of the three inequivalent Me-Al groups. 1D NOESY experiment shows that the two signals with long-range H−F couplings correspond to the $AlMe(C_6F_5)$ grouping and to the Me group *cis* to the C_6F_5 fragment, respectively.

Synthesis of Titanium Complexes. We have also explored the reactivity of **1** and **2** toward $Ti(C_5Me_5)Me_3$. Treatment of **1** with 1 equiv of $Ti(C_5Me_5)Me_3$ at 60 °C in toluene failed to give the desired complex via insertion of the carbodiimide into a Ti−Me bond, as the process was extremely slow, probably because of the presence of the bulky ligands.[16] Nevertheless, the reaction of **2** with 1 equiv of $Ti(C_5Me_5)Me_3$ cleanly produced the dimethyl complex $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me_2$ (**7**) as a yellow oil in good yield via methane elimination (see Scheme 4). The ^1H and ^{13}C NMR spectra of **7** show resonances at 0.53 and 52.1 ppm, respectively, attributed to the Ti−Me bond, as the most diagnostic peaks. When activated with 1 equiv of $B(C_6F_5)_3$ in C_6D_6 at room temperature, complex **7** rapidly formed the ion pair $\{Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me\}[BMe(C_6F_5)_3]$ (**8**) as the sole product. Compound **8** is relatively stable at room temperature

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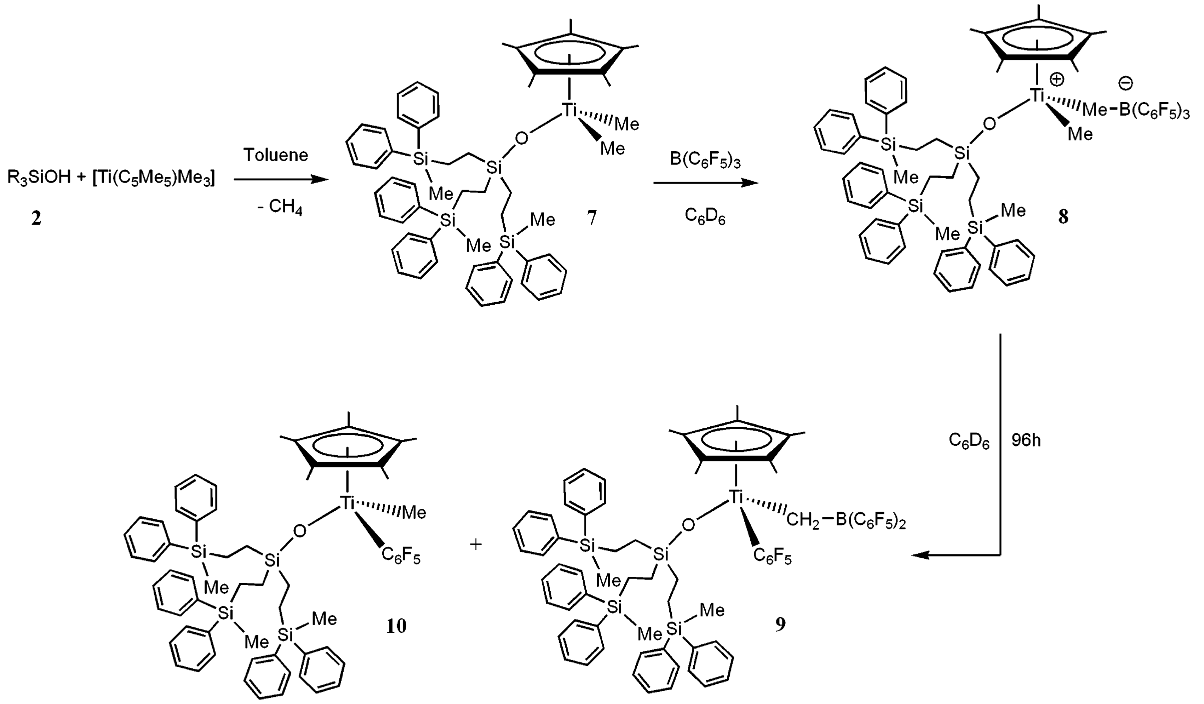
(13) Data for $BMe(C_6F_5)_2$: ^1H NMR (300 MHz, C_6D_6): δ 1.32 ($^5J_{HF}$ = 1.8 Hz, 3H, Me). ^{19}F NMR (282.3 MHz, C_6D_6): δ −130.3 (*o*-C_6F_5), −147.3 (*p*-C_6F_5), −161.7 (*m*-C_6F_5). See also ref 5a.

(14) For NMR data of $BMe_2(C_6F_5)$: ^1H NMR (300 MHz, C_6D_6): δ 0.96 (m, 6H, Me). ^{19}F NMR (282.3 MHz, C_6D_6): δ −129.6 (*o*-C_6F_5), −150.1 (*p*-C_6F_5), −161.2 (*m*-C_6F_5). See also: Köhler, K.; Piers, W. E.; Jarvis, A. P.; Xin, S.; Feng, Y.; Bravakis, A. M.; Collins, S.; Clegg, W.; Yap, G. P. A.; Marder, T. B. *Organometallics* **1998**, *17*, 3557−3566.

(15) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908−5912.

(16) Sita, L. R.; Babcok, J. R. *Organometallics* **1998**, *17*, 5228−5230.

Scheme 4



under these conditions, slowly decomposing as described below (see Scheme 4). However, it can be fully characterized spectroscopically. The ^{1}H NMR spectrum of **8** shows a resonance at 1.11 ppm attributed to the Ti-Me fragment and a broad singlet for the B-Me group at 0.56 ppm, upfield of the range 1.2−1.4 ppm generally observed for an unassociated $[MeB(C_6F_5)_3]^-$ anion in an aromatic solvent[3d,17] (see Figure 3). The Ti-Me carbon atom resonates at 70.8 ppm, significantly downfield of the parent neutral dimethyl complex **7**, and the B-Me carbon atom appears at 31.9 ppm as a broad signal, both in the expected region observed for other ion-paired systems.[5] The ^{19}F NMR spectrum of **8** revealed a large difference of 5.2 ppm in the $\Delta(F_m-F_p)$ value, establishing that the $[MeB(C_6F_5)_3]^-$ anion is strongly associated with the titanium center in C_6D_6.[18]

As mentioned before, compound **8** decomposes at room temperature (296 K) over the course of several hours ($t_{1/2} \approx 48$ h) to produce a 1:1 mixture of two neutral titanium complexes, $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3][CH_2B(C_6F_5)_2](C_6F_5)$ (**9**) and $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me(C_6F_5)$ (**10**)[19] (Scheme 4). Compound **9** is the result of the σ-bond metathesis mechanism that consists of a hydrogen transfer from the methyl group of the $[MeB(C_6F_5)_3]^-$ anion and subsequent methane elimination. Analogous deactivation pathways have been observed for the decomposition of related complexes such as aryloxide,[3b,e] chelate diamide,[3a] ketimide,[3d] and constrained geometry systems.[3c,d] Compound **10** is the consequence of a $C_6F_5^-$ group transfer from the anion to the cationic titanium center and the formation of $BMe(C_6F_5)_2$. This is the most common deactivation process, which has been observed in group 4 metallocenes,[5a,e] diaryloxides,[5b] and phosphinimides.[5c] To our knowledge, this is the first time in which both deactivation pathways have been detected simultaneously in the same complex.

The most indicative peaks in the ^{1}H and ^{3}C NMR spectra of **9** are the two expected broad resonances attributed to the diastereotopic protons of the $CH_2B(C_6F_5)_2$ fragment and the resonance of the methylene carbon atom at 102.2 ppm. The ^{19}F NMR spectrum reveals the existence of two broad peaks at −113.8 and −114.5 ppm for the unequivalent *ortho* fluorine atoms of the Ti-C_6F_5 group, showing restriction in the aryl rotation.[20] In the case of compound **10**, the Ti-Me group appears at 1.10 ppm in the ^{1}H NMR and at 70.3 ppm in the ^{13}C NMR spectrum. {^{1}H−^{13}C} HMQC experiments were used to locate methylene (**9**) and methyl (**10**) resonances. The ^{19}F NMR data confirm unambiguously the presence of a perfluoroaryl group in **10** (see Experimental Section). The presence of a single multiplet for the *ortho* $C_6F_5^-$ group at −115.1 ppm for **10** shows that rapid rotation occurs on the NMR time scale. It is clear that the barrier to aryl C_6F_5 rotation in complex **9** is higher than that of **10** or even of the aluminum complex **5**, probably due to a higher steric hindrance around the metal center in **9**.

Complex **7** has also been reacted with 0.5 equiv of $B(C_6F_5)_3$ in C_6D_6 at room temperature and assayed by NMR spectroscopy. Only the ion pair **8** and the excess of the dimethyl complex **7** were detected initially. Signals attributed to the expected binuclear complex of type $[(L_2MMe)_2(\mu\text{-}Me)]^+[MeB(C_6F_5)_3]^-$ [21,22] in which the anion is solvent separated were not detected under these

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(17) (a) Horton, A. D.; *Organometallics* **1996**, *15*, 2675−2677. (b) Becks, S.; Prosenc, M. H.; Brintzinger, H. H. *J. Mol. Catal. A.: Chem.* **1998**, *128*, 41−52. (c) Beswick, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2410−2412.

(18) Horton, A. D.; de With, J.; van der Linden, A.; van de Weg, H. *Organometallics* **1996**, *15*, 2672−2674.

(19) Less than 2% of the decomposition of complex **8** corresponds to unidentified products.

(20) The ^{19}F NMR spectrum recorded at 313 K for **9** shows only one broad peak at 113.6 ppm attributed to the two *ortho* fluorines of the Ti-C_6F_5 group, indicating a fluxional behavior due to no restriction in the aryl rotation.

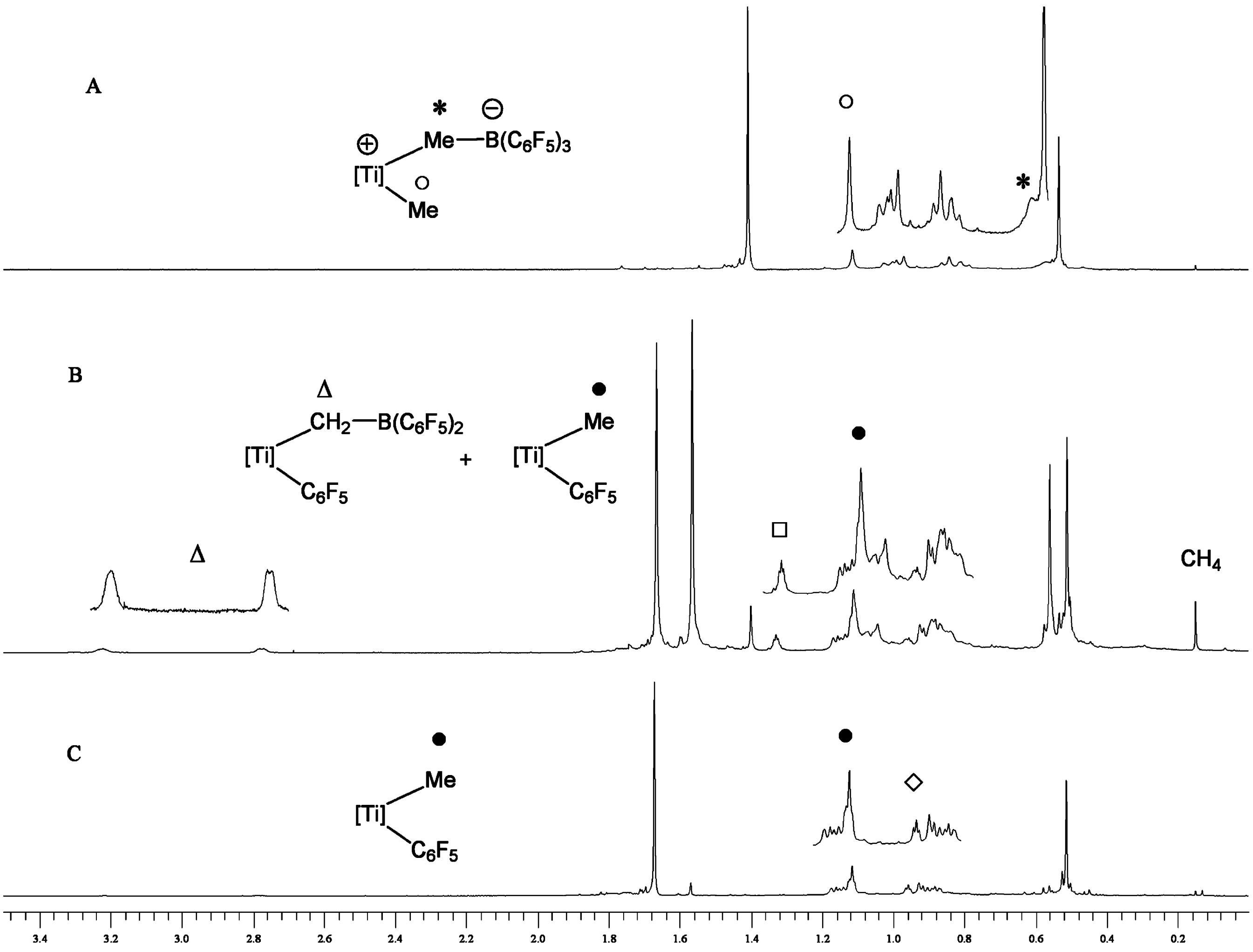

Figure 3. ^{1}H NMR spectra of (A) complex **8**, (B) a mixture of complexes **9** and **10** from a 1:1 molar ratio of **7** and $B(C_6F_5)_3$, and (C) a mixture of complexes **9** and **10** from a 1:0.5 molar ratio of **7** and $B(C_6F_5)_3$. □ denotes $BMe(C_6F_5)_2$; ◇ denotes $BMe_2(C_6F_5)$.

conditions. It has been reported that complexes with sterically demanding ligands do not form dinuclear cationic species.[21] In this case, the small size of the titanium center with respect to the steric demands of the siloxy and the permethylated cyclopentadienyl ligands may prevent the formation of the Me-bridged dinuclear cation. In this situation, deactivation took place over the course of 22 h, leading selectively to **10** in 97% and **9** in less than 3% yield. In addition, the neutral dimethyl complex is always consumed in the process, due to subsequent reaction with $BMe(C_6F_5)_2$ to lead again to **10** and $BMe_2(C_6F_5)$.[14] On the basis of this feature, complex **10** was prepared in a synthetic experiment. Hence, it is noteworthy that the selectivity and the rate of the degradation of **8** depends on the Ti:B ratio. Figure 3 shows the ^{1}H NMR spectra for the mixture **9** and **10** in two different reaction conditions, as well as the spectrum of the parent complex **8**. In an attempt to shed light on this behavior, complex **7** was reacted with $B(C_6F_5)_3$ in excess using C_6D_6 as solvent or 1:1 ratio in C_6D_5Cl, affording in both cases ~1:1 mixtures of **9** and **10** with similar rates ($t_{1/2} \approx 48$ h).

The σ-bond metathesis occurs from a tight contact ion pair prior to full dissociation of the anion $[MeB(C_6F_5)_3]^-$ from the titanium cation via a typical four-center transition state.[3d] All the factors that contribute to the dissociation of the anion may reduce the formation of complex **9**. However, the enhancement of electron deficiency around the metal center as the anion dissociation occurs may increase the tendency to accept the $C_6F_5^-$ group.[6b] Although the origins of the decomposition selectivity are presently unknown, from these results a tentative explanation may be rationalized on the basis of dissociation or elongation of the coordinated borate anion. The presence of an excess of the dimethyl compound **7** in the 1:0.5 stoichiometry may modify the complex behavior associated with the distinct dynamic processes shown by the ion pair species,[23] giving preference to the dissociation/reorganization exchange.

In conclusion, new dimethyl complexes of aluminum **3** and **4** and titanium **7** have been described. Reaction

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(21) For examples of μ-methyl dimers containing the anion $[MeB(C_6F_5)_3]^-$ see: (a) Beck, S.; Prosenc, M.-H.; Brintzinger, H. H.; Goretzki, R.; Herfert, N.; Fink, G. *J. Mol. Catal. A* **1996**, *111* 67–79. (b) Bochmann, M.; Green M. L. H.; Powell, A. K.; Sassmannshausen, J.; Triller, M. U.; Wocadlo, S. *J. Chem. Soc., Dalton Trans.* **1999**, 43–49.

(22) For examples of μ-methyl dimer complexes containing the anion $[B(C_6F_5)_4]^-$ see: Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840–842 (b) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33* 1634–1637. (c) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842–857 (d) Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. C. *Organometallics* **2001**, *20*, 1808–1819. (e) Zhang, S.; Piers, W. E. *Organometallics* **2001**, *20*, 2088–2092.

of **3** or **4** with the methyl-abstracting agent $B(C_6F_5)_3$ produced the standard decomposition pathway observed for aluminum complexes. However in the case of the siloxy titanium compound **7**, the reaction with the borane gave the ion-paired complex **8**, which slowly decomposed to a mixture of two neutral complexes, **9** and **10**. The ratio of these two latter complexes depends on the reaction conditions such as stoichiometry of the reactants. The reason for this feature is not yet understood. Further studies concerning the use of different cyclopentadienyl or siloxy ligands will be the focus of future work in order to explain these results.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a drybox. Solvents used were previously dried and freshly distilled under argon: tetrahydrofuran from sodium benzophenone ketyl, toluene from sodium, and hexane from sodium−potassium. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $[Ti(C_5Me_5)Me_3]$[24] and $[Si(CH_2CH_2SiMePh_2)_3Cl]$[7] were prepared according to reported methods. ^1H, ^{13}C, and ^{19}F spectra were recorded on a Varian Unity VXR-300 or Varian 500 plus instruments. Chemical shifts (δ ppm) were measured relative to residual ^1H and ^{13}C resonances for chloroform-d_1 and benzene-d_6 used as solvents, while ^{19}F was referenced to $CFCl_3$. C, H analyses were carried out with a Perkin-Elmer 240 C microanalyzer.

Synthesis of $[(Ph_2MeSiCH_2CH_2)_3Si]NCN[Si(CH_2CH_2SiMePh_2)_3]$ (1). A solution of $NCNH_2$ (28 mg, 0.67 mmol) in diethyl ether (10 mL) was added to a solution of $Si(CH_2CH_2SiMePh_2)_3Cl$ (1 g, 1.35 mmol), in diethyl ether (30 mL). Immediately, NEt_3 (0.20 mL, 1.43 mmol) was syringed into the mixture and the reaction mixture was stirred for 12 h at room temperature. The solution was filtered and the solvent removed at reduced pressure. The product was extracted with pentane (30 mL), and the extracts were filtered, concentrated to half volume, and stored overnight at −40 °C, causing the precipitation of a colorless crystalline solid (0.70 g, 72%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.44 (m, 24H, C_6H_5), 7.29 (m, 36H, C_6H_5), 0.89 and 0.58 [A and B part of an A_2B_2 spin system, 24H, $Si(CH_2)_2Si$], 0.46 (s, 18H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.9 (*i*-C_6H_5), 134.4 (*m*- or *o*-C_6H_5), 129.1 (*p*-C_6H_5), 127.8 (*o*- or *m*-C_6H_5), 123.1 (N*C*N), 5.6 and 5.5 [$Si(CH_2)_2Si$], −5.1 (CH_3). Anal. Calcd for $C_{91}H_{102}N_2Si_8$: C, 75.46; H, 7.10; N, 1.93. Found: C, 75.40; H, 7.05; N, 1.90.

Synthesis of $(Ph_2MeSiCH_2CH_2)_3SiOH$ (2). To a mixture of $Si(CH_2CH_2SiMePh_2)_3Cl$ (1.00 g, 1.35 mmol) and NEt_3 (0.20 mL, 1.43 mmol) in diethyl ether (40 mL) was added H_2O (24 μL, 1.35 mmol), and the reaction mixture was stirred for 12 h at room temperature. The solution was filtered and the solvent removed at reduced pressure. The product was extracted with pentane (30 mL), the extract filtered, and the solvent removed at reduced pressure to give a white solid, which at room temperature turned to a colorless oil (0.80 g, 82%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.44 (m, 12H, C_6H_5), 7.31 (m, 18H, C_6H_5), 1.22 (s, 1H, OH), 0.88 and 0.54 [A and B part of an A_2B_2 spin system, 12H, $Si(CH_2)_2Si$], 0.50 (s, 9H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.0 (*i*-C_6H_5), 134.5 (*m*- or *o*-C_6H_5), 129.1 (*p*-C_6H_5), 127.8 (*o*- or *m*-C_6H_5), 5.6 and 5.5 [$Si(CH_2)_2Si$], −5.1 (CH_3). Anal. Calcd for $C_{45}H_{52}OSi_4$: C, 74.94; H, 7.27. Found: C, 75.01; H, 7.34.

Synthesis of $\{MeC[NSi(CH_2CH_2SiMePh_2)_3]_2\}AlMe_2$ (3). To a solution of the carbodiimide $[(Ph_2MeSiCH_2CH_2)_3Si]NCN[Si(CH_2CH_2SiMePh_2)_3]$ (**1**) (0.47 g, 0.32 mmol) in toluene (40 mL) was added $AlMe_3$ (0.32 mmol, 0.16 mL of a 2 M heptane solution), and the mixture was stirred at 70 °C for 12 h. The solvent was removed at reduced pressure and the product extracted with pentane (30 mL). After filtration of the extacts, the solvent was removed at reduced pressure to give **3** as a colorless oil (0.36 g, 74%). ^1H NMR (300 MHz, C_6D_6): δ 7.51 (m, 24H, C_6H_5), 7.15 (m, 36H, C_6H_5), 1.48 (s, 3H, *Me*-C), 1.01 and 0.75 [A and B part of an A_2B_2 spin system, 24H, $Si(CH_2)_2Si$], 0.46 (s, 18H, Me), −0.29 (s, 6H, *Me*-Al). (CD_2Cl_2): δ 7.44 (m, 24H, C_6H_5), 7.29 (m, 36H, C_6H_5), 1.56 (s, 3H, *Me*-C), 0.82 and 0.56 [A and B part of an A_2B_2 spin system, 24 H, $Si(CH_2)_2Si$], 0.49 (s, 18H, Me), −0.85 (s, 6H, Me-Al). ^{13}C NMR (75 MHz, C_6D_6): δ 181.3 (Me-*C*), 137.1 (*i*-C_6H_5), 134.9 (*m*- or *o*-C_6H_5), 129.5 (*p*-C_6H_5), 128.2 (*o*- or *m*-C_6H_5), 23.8 (Me-C), 6.5 and 6.2 [$Si(CH_2)_2Si$], −4.5 (CH_3), −8.5 (Me-Al). (CD_2Cl_2): δ 181.1 (Me-*C*), 137.2 (*i*-C_6H_5), 134.6 (*m*- or *o*-C_6H_5), 129.3 (*p*-C_6H_5), 128.0 (*o*- or *m*-C_6H_5), 23.9 (Me-C), 6.2 and 5.4 [$Si(CH_2)_2Si$], −5.0 (CH_3), −9.1 (Me-Al). Anal. Calcd for $C_{94}H_{111}N_2Si_8Al$: C, 74.25; H, 7.36; N, 1.84. Found: C, 73.93; H, 7.18; N, 1.77.

Synthesis of $[(Ph_2MeSiCH_2CH_2)_3SiOAlMe_2]_2$ (4). To a solution of the silanol $(Ph_2MeSiCH_2CH_2)_3SiOH$ (**2**) (0.62 g, 0.86 mmol) in hexane (40 mL) was added $AlMe_3$ (0.86 mmol, 0.43 mL of a 2 M heptane solution), and the mixture was stirred at room temperature for 12 h. The solvent was removed at reduced pressure and the product extracted with pentane (30 mL). After filtration of the extracts, the solvent was removed at reduced pressure to give **4** as a colorless oil (0.49 g, 73%). ^1H NMR (300 MHz, C_6D_6): δ 7.53 (m, 24H, C_6H_5), 7.16 (m, 36H, C_6H_5), 1.03 and 0.81 [A and B part of an A_2B_2 spin system, 24H, $Si(CH_2)_2Si$], 0.51 (s, 18H, Me), −0.51 (s, 12H, Me-Al). ^{13}C NMR (75 MHz, C_6D_6): δ 136.9 (*i*-C_6H_5), 134.8 (*m*- or *o*-C_6H_5), 129.5 (*p*-C_6H_5), 128.2 (*o*- or *m*-C_6H_5), 6.6 and 6.5 [$Si(CH_2)_2Si$], −4.4 (CH_3), −6.4 (Me-Al). Anal. Calcd for $C_{94}H_{114}O_2Si_8Al_2$: C, 72.63; H, 7.39. Found: C, 72.23; H, 7.04.

Reaction of $\{MeC[NSi(CH_2CH_2SiMePh_2)_3]_2\}AlMe_2$ (3) with $B(C_6F_5)_3$. Compound **3** (74 mg, 0.051 mmol) and $B(C_6F_5)_3$ (27 mg, 0.051 mmol) were dissolved in C_6D_6 (0.5 mL) in a J-Young NMR tube, and the mixture was stirred at room temperature for 12 h. After this time the sample was assayed by NMR spectroscopy, showing quantitative formation of a 1:1 mixture of $\{MeC[NSi(CH_2CH_2SiMePh_2)_3]_2\}AlMe(C_6F_5)$ (**5**) and $BMe(C_6F_5)_2$.

Synthesis of $\{MeC[NSi(CH_2CH_2SiMePh_2)_3]_2\}AlMe(C_6F_5)$ (5). To a solution of **3** (0.44 g, 0.29 mmol) in toluene (20 mL) was added $B(C_6F_5)_3$ (0.15 g, 0.29 mmol) and the mixture stirred at room temperature for several days until the ^1H NMR spectrum of the solution showed complete transformation into **5**. After evaporation of solvent, the resulting oil was placed under high vacuum at 45 °C overnight to remove the relatively volatile $BMe(C_6F_5)_2$, yielding **5** (0.45 g, 93%) pure by ^1H NMR as a colorless oil. ^1H NMR (300 MHz, C_6D_6): δ 7.46 (m, 24H, C_6H_5), 7.15 (m, 36H, C_6H_5), 1.50 (s, 3H, *Me*-C), 0.91 and 0.68 [A and B part of an A_2B_2 spin system, 24H, $Si(CH_2)_2Si$], 0.45 (s, 18H, Me), −0.04 (br s, 3H, *Me*-Al). ^{13}C NMR (75 MHz, C_6D_6): δ 183.9 (Me-*C*), 136.9 (*i*-C_6H_5), 134.7 (*m*- or *o*-C_6H_5), 129.6 (*p*-C_6H_5), 128.2 (*o*- or *m*-C_6H_5), 23.3 (Me-C), 6.3 and 5.2 [$Si(CH_2)_2Si$], −5.0 (CH_3), −8.7 (Me-Al). ^{19}F NMR (282.3 MHz, C_6D_6): δ −121.8 (*o*-C_6F_5), −153.1 (*p*-C_6F_5), −161.3 (*m*-C_6F_5). Anal. Calcd for $C_{99}H_{108}AlF_5N_2Si_8$: C, 71,09; H, 6,51; N, 1,67. Found: C, 70.91; H, 6.48; N, 1.64.

Reaction of $[(Ph_2MeSiCH_2CH_2)_3SiOAlMe_2]_2$ (4) with 2 Equiv of $B(C_6F_5)_3$. Compound **4** (55 mg, 0.035 mmol) and $B(C_6F_5)_3$ (36 mg, 0.071 mmol) were dissolved in C_6D_6 (0.5 mL) in a J-Young NMR tube. Since no reaction was observed below 80 °C, the solution was heated at 80 °C for 24 h and the sample assayed by NMR spectroscopy, showing the presence of a 1:1:1 mixture of $[(Ph_2MeSiCH_2CH_2)_3SiOAl]_2Me_3(C_6F_5)$ (**6**), $BMe(C_6F_5)_2$, and $B(C_6F_5)_3$.

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(24) Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 476−482.

Data for 6. ^{1}H NMR (300 MHz, C_6D_6): δ 7.44 (m, 24H, C_6H_5), 7.15 (m, 36H, C_6H_5), 0.91−0.68 [complex spin system, 24 H, $Si(CH_2)_2Si$], 0.43 (s, 18H, Me), −0.20 (t, 3H, $^5J_{H-F} = 1.7$ Hz, Me-Al-C_6F_5), −0.46 (t, 3H, $^7J_{H-F} = 1.2$ Hz, Me-Al *cis* to C_6F_5), −0.54 (br, 3H, *Me*-Al *trans* to C_6F_5). ^{13}C NMR (75 MHz, C_6D_6): δ 136.9 (*i*-C_6H_5), 134.7 (*m*- or *o*-C_6H_5), 129.6 (*p*-C_6H_5), 128.2 (*o*- or *m*-C_6H_5), 6.2 and 6.1 [$Si(CH_2)_2Si$], −5.1 (CH_3), −5.8 (Me-Al-C_6F_5), −7.2 (Me-Al *cis* to C_6F_5), −6.2 (Me-Al *trans* to C_6F_5). ^{1}H and ^{13}C NMR data of Me groups were confirmed by 1D ^{1}H NOESY and {^{1}H−^{13}C} HSQC experiments. ^{19}F NMR (282.3 MHz, C_6D_6): δ −119.5 (*o*-C_6F_5), −150.5 (*p*-C_6F_5), *m*-C_6F_5 signal obscured by the mixture of boron complexes.

Synthesis of $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me_2$ (7). To a solution of $Ti(C_5Me_5)Me_3$ (0.7 g, 3.07 mmol) in toluene (40 mL) was added the silanol $(Ph_2MeSiCH_2CH_2)_3SiOH$ (**2**) (2.2 g, 3.07 mmol), and the mixture was stirred at room temperature for 12 h. The solvent was removed at reduced pressure and the product extracted with pentane (30 mL). After filtration of the extracts, the solvent was removed at reduced pressure to give **7** as a yellow oil (2.3 g, 80%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.58 (m, 12H, C_6H_5), 7.18 (m, 18H, C_6H_5), 1.72 (s, 15H, C_5Me_5), 1.24 and 0.94 [A and B part of an A_2B_2 spin system, 12H, $Si(CH_2)_2Si$], 0.56 (s, 9H, Me), 0.53 (s, 6H, Me-Ti). ^{13}C NMR (75 MHz, C_6D_6): δ 137.6 (*i*-C_6H_5), 134.9 (*m*- or *o*-C_6H_5), 129.4 (*p*-C_6H_5), 128.2 (*o*- or *m*-C_6H_5), 121.9 (*C_5*Me_5), 52.1 (Me-Ti), 11.7 (C_5*Me_5*), 7.3 and 6.6 [$Si(CH_2)_2Si$], −4.7 (Me-Si). Anal. Calcd for $C_{57}H_{72}OSi_4Ti$: C, 73.35; H, 7.78. Found: C, 73.01; H, 7.42.

Reaction of $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me_2$ (7) with 1 Equiv of $B(C_6F_5)_3$. Compound **7** (25 mg, 0.027 mmol) and $B(C_6F_5)_3$ (14 mg, 0.027 mmol) were dissolved in C_6D_6 (0.5 mL) at room temperature in a J-Young NMR tube, which was vigorously shaken, resulting in a dark red solution. The tube was maintained at room temperature and the reaction monitored by ^{1}H NMR spectroscopy. The NMR spectra showed that the reaction initially yields the complex {$Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me$}[$BMe(C_6F_5)_3$] (**8**), which is slowly converted to a mixture of $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3][CH_2B(C_6F_5)_2](C_6F_5)$ (**9**) $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me(C_6F_5)$ (**10**) and $BMe(C_6F_5)_2$. Complete conversion was observed after 96 h at room temperature (296 K).

Data for 8. ^{1}H NMR (300 MHz, C_6D_6): δ 7.52 (m, 12H, C_6H_5), 7.18 (m, 18H, C_6H_5), 1.40 (s, 15H, C_5Me_5), 1.11 (s, 3H, Me-Ti), 1.00 and 0.83 [A and B part of an A_2B_2 spin system, 12H, $Si(CH_2)_2Si$], 0.56 (br, 3H, Me-B), 0.54 (s, 9H, Me). ^{13}C NMR (75 MHz, C_6D_6): δ 136.7 (*i*-C_6H_5), 134.8 (*m*- or *o*-C_6H_5), 129.7 (*p*-C_6H_5), $C_{ortho\ or\ meta}$ obscured by the solvent, 129.4 (*C_5*Me_5), 70.8 (Me-Ti), 31.9 (br, Me-B), 12.1 (C_5*Me_5*), 7.0 and 6.7 [$Si(CH_2)_2Si$], −4.9 (Me-Si). ^{19}F NMR (282.3 MHz, C_6D_6): δ −133.4 (*o*-C_6F_5), −158.9 (*p*-C_6F_5), −164.1 (*m*-C_6F_5).

Data for 9. ^{1}H NMR (300 MHz, C_6D_6): δ 7.52 (m, 12H, C_6H_5), 7.18 (m, 18H, C_6H_5), 3.22 (br, 1H, Ti-CH_2), 2.78 (br, 1H, Ti-CH_2), 1.57 (s, 15H, C_5Me_5), 1.07 and 0.89 [A and B part of an A_2B_2 spin system, 12H, $Si(CH_2)_2Si$], 0.56 (s, 9H, Me). ^{13}C NMR (75 MHz, C_6D_6): δ 136.8 (*i*-C_6H_5), 134.8 (*m*- or *o*-C_6H_5), 130.2 (*C_5*Me_5), 129.5 (*p*-C_6H_5), 128.0 (*o*- or *m*-C_6H_5), 102.2 (BCH_2-Ti), 12.4 (C_5*Me_5*), 8.4 and 7.2 [$Si(CH_2)_2Si$], −5.2 (Me-Si). ^{19}F NMR (282.3 MHz, C_6D_6): δ −113.8 (*o*-C_6F_5), −114.5 (*o*-C_6F_5), the rest of the signals obscured by the mixture of complexes.

Reaction of $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me_2$ (7) with 0.5 Equiv of $B(C_6F_5)_3$. Compound **7** (55 mg, 0.589 mmol) and $B(C_6F_5)_3$ (15 mg, 0.295 mmol) were dissolved in C_6D_6 (0.5 mL) at room temperature in a J-Young NMR tube, which was vigorously shaken, resulting in a dark red solution. Initially the reaction afforded a mixture of the ion pair complex **8** and the excess of the dimethyl compound **6**. During the course of 22 h complete decomposition of **8** occurred, giving a mixture of **10** (97%) and **9** (<3%) and the borane species $BMe(C_6F_5)_2$ and $BMe_2(C_6F_5)$.

Synthesis of $Ti(C_5Me_5)[OSi(CH_2CH_2SiMePh_2)_3]Me(C_6F_5)$ (10). Compound **10** was isolated in a synthetic experiment as follows: **7** (0.21 g, 0.22 mmol) and $B(C_6F_5)_3$ (58 mg, 0.11 mmol) were dissolved in toluene (10 mL) at room temperature and stirred several days. The completeness of the reaction was checked by ^{1}H NMR spectroscopy. Volatiles were eliminated under high vacuum at 45 °C, yielding **10** (0.22 g, 90%) as a pure yellow oil, confirmed by ^{1}H NMR. ^{1}H NMR (300 MHz, C_6D_6): δ 7.52 (m, 12H, C_6H_5), 7.18 (m, 18H, C_6H_5), 1.66 (s, 15H, C_5Me_5), 1.07 and 0.89 [A and B part of an A_2B_2 spin system, 12H, $Si(CH_2)_2Si$], 1.10 (br, 3H, Me-Ti), 0.51 (s, 9H, Me). ^{13}C NMR (75 MHz, C_6D_6): δ 137.3 (*i*-C_6H_5), 134.9 (*m*- or *o*-C_6H_5), 129.6 (*p*-C_6H_5), 128.1 (*o*- or *m*-C_6H_5), 126.6 (*C_5*Me_5), 70.3 (Me-Ti), 11.9 (C_5*Me_5*), 7.2 and 6.5 [$Si(CH_2)_2Si$], −4.9 (Me-Si). ^{19}F NMR (282.3 MHz, C_6D_6): δ −115.1 (br, 2F, *o*-C_6F_5), −152.6 (br, 1F, *p*-C_6F_5), −160.0 (br, 2F, *m*-C_6F_5). Anal. Calcd for $C_{62}H_{69}F_5OSi_4Ti$: C, 68.61; H, 6.41. Found: C, 68.34; H, 6.36.

X-ray Structure Determination of 1. White prismatic crystals of **1** were obtained from a saturated pentane solution at room temperature. A summary of crystal data, data collection, and refinement parameters for the structural analysis is given in Tables 1 and 2 (for the last table see the Supporting Information). The crystal was glued to a glass fiber and mounted on Kappa-CCD Bruker-Nonius diffractometer with area detector, and data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was performed at 170(2) K, with an exposure time of 40 s per frame (3 sets; 623 frames). Raw data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods, completed by the subsequent difference Fourier techniques, and refined by full-matrix least squares on F^2 (SHELXL-97).[25] Anisotropic thermal parameters were used in the last cycles of refinement for the non hydrogen atoms. The hydrogen atoms were found in the final Fourier map and were refined with isotropic thermal displacement parameters. All the calculations were made using the WINGX system.[26]

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Supporting Information Available: Selected bond lengths and angles and X-ray crystallographic data as CIF files for **1**. Selected NMR data for **9** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[26] WinGX System: Farrugia, L. J., *J. Appl. Crystallogr.* **1999**, *32*, 837−838.