Cationic Cyclopentadienyl Phenylenediamido Titanium Species Generated by Reaction of $TiCp^R[1,2\text{-}C_6H_4(NCH_2t\text{-}Bu)_2]R$ ($Cp^R = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$; R = CH_3, CH_2Ph) with $B(C_6F_5)_3$. X-ray Molecular Structure of $Ti(\eta^5\text{-}C_5Me_5)[1,2\text{-}C_6H_4(NCH_2t\text{-}Bu)_2][\mu\text{-}MeB(C_6F_5)_3]$†

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The reaction of $TiCp^R[1,2\text{-}C_6H_4(NNp)_2]R$ with the Lewis acid $B(C_6F_5)_3$ in noncoordinating solvent affords the new zwitterionic species $TiCp^R[1,2\text{-}C_6H_4(NNp)_2)][\mu\text{-}RB(C_6F_5)_3]$. When the reaction is performed in dichloromethane, the $[\mu\text{-}RB(C_6F_5)_3]^-$ anion is displaced by solvent molecules, giving ionic products in which the anion is not coordinated. The cyclopentadienyl zwitterionic complexes $TiCp[1,2\text{-}C_6H_4(NNp)_2)][\mu\text{-}RB(C_6F_5)_3]$ decompose via ligand scrambling between boron and titanium to give the neutral titanium complex $TiCp[1,2\text{-}C_6H_4(NNp)_2](C_6F_5)$ along with the byproduct $RB(C_6F_5)_2$. In contrast, the pentamethylcyclopentadienyl analogues $TiCp^*[1,2\text{-}C_6H_4(NNp)_2][\mu\text{-}RB(C_6F_5)_3]$ evolve through C−H activation to yield an unresolved mixture of compounds. The molecular structure of $TiCp^*[1,2\text{-}C_6H_4\text{-}(NNp)_2][\mu\text{-}MeB(C_6F_5)_3]$ has been determined by X-ray diffraction methods.

As part of our interest in complexes bearing ligands that incorporate nitrogen donors, such as cyclopentadienyl-amido,[1−4] diamido,[5,6] and alkoxo-amido,[7] as potential precursors for new olefin polymerization catalysts, we have recently reported the synthesis of the chelating diamido complexes $MCp^R[1,2\text{-}C_6H_4\text{-}(NR)_2]X$ [M = Ti, Zr; Cp^R = Cp, Cp*, $\eta^5\text{-}C_5H_4(SiMe_3)$; R = Np, *n*-Pr; X = Cl, Me, Bz].[5,6] Upon treatment with methylaluminoxane (MAO), these complexes initiate active ethylene polymerization processes, in which the nature of the active species was studied via stoichiometric reactions.[6] The alkyl complexes $MCp[1,2\text{-}C_6H_4(NR)_2]R$ are attacked by MAO at the diamido ligand to give zwitterionic species active for ethylene polymerization. In contrast, these titanium derivatives do not show any catalytic activity in the presence of the widely used boron-based cocatalysts $B(C_6F_5)_3$ and $[CPh_3][B(C_6F_5)_4]$. In probing these observations, we have studied the reaction of the complexes $TiCp^R[1,2\text{-}C_6H_4(NNp)_2]X$ (Cp^R = Cp, Cp*; X = Cl, Me, Bz) with $B(C_6F_5)_3$ and $[CPh_3][B(C_6F_5)_4]$ by NMR spectroscopy in the absence of monomer, and the molecular structure of $TiCp^*[1,2\text{-}C_6H_4(NNp)_2][\mu\text{-}MeB(C_6F_5)_3]$ has been determined by single-crystal X-ray diffraction.

On the basis of our earlier results from the reaction of $MCp\text{-}[1,2\text{-}C_6H_4(NR)_2]R$ with MAO, the question of the determination of the site of boron-based Lewis acid attack arises. Consequently, as a first step, we studied the reaction of the chloro derivate $TiCp[1,2\text{-}C_6H_4(NNp)_2]Cl$ (**1a**) with $B(C_6F_5)_3$. In this reaction, the titanium complex is recovered unaltered regardless of the reaction conditions or solvent used, suggesting that in further reactions with boron reagents the Ti−N bond of these monocyclopentadienyl phenylenediamido alkyl complexes will not be affected.

When C_6D_6 was added to mixtures of $TiCp^R[1,2\text{-}C_6H_4\text{-}(NNp)_2]R$ (Np = CH_2t-Bu; Cp^R = Cp, R = Me, **2a**; Bz, **2b**; Cp^R = Cp*, R = Me, **3a**; Bz, **3b**) and $B(C_6F_5)_3$ in an equimolar ratio at room temperature, dark solutions were formed. This reaction results in the selective abstraction of the alkyl ligand to give the new zwitterionic titanium species $TiCp^R[1,2\text{-}C_6H_4\text{-}(NNp)_2)][\mu\text{-}RB(C_6F_5)_3]$ (Cp^R = Cp, R = Me, **4a**; Bz, **4b**; Cp^R = Cp*, R = Me, **5a**; Bz, **5b**) (Scheme 1), in contrast to the attack observed on the diamido ligand when an aluminum reagent is used.[6] In view of such results, we propose that the difference in selectivity between boron- and aluminum-based reactions causes the difference in polymerization catalytic behavior for compounds in this class.

The NMR spectra recorded after reagent mixing show all signals shifted downfield compared with those found for the corresponding neutral titanium precursors as a consequence of the high Lewis acidity of titanium metal after the formation of the cation. The ^1H NMR spectra of **4a** and **5a** show a broad signal ascribed to the methyl group bonded to boron, supporting the formation of the methylborate anion. Evidence for the

† Dedicated to José Antonio Abad, an excellent chemist and better person.

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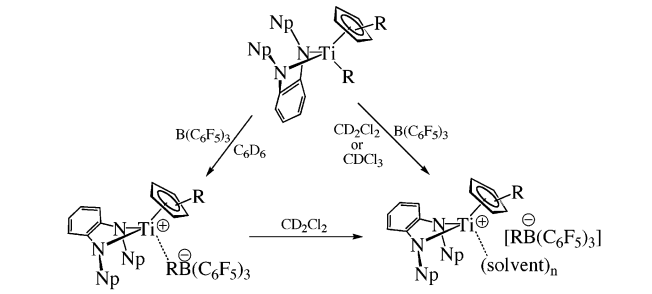
Scheme 1



Cp^R = Cp, R = Me, **4a;** Bz, **4b**
Cp^R = Cp*, R = Me, **5a;** Bz, **5b**
Np = CH_2t-Bu

Cp^R = Cp, R = Me, **6a;** Bz, **6b**
Cp^R = Cp*, R = Me, **7a;** Bz, **7b**

presence of the coordinated $[RB(C_6F_5)_3]^-$ anion is provided by the comparatively large ^{19}F chemical shift difference $\Delta\delta = \delta(m\text{-F}) - \delta(p\text{-F})$[8−10] (3.3, **4a**; 3.5 **4b**; 4.7, **5a**) observed in the ^{19}F NMR spectra. The *Me*-B resonances appear at δ 0.41 for **4a** and δ 0.58 for **5a**. In compound **4b** the $[PhCH_2B(C_6F_5)_3]^-$ anion is coordinated to the metal center via the benzylic phenyl group, as shown by the downfield ^{13}C NMR resonance exhibited by the *ipso*-carbon atom of the phenyl group (δ 159.6).[11,12] The solubility of all of these complexes in benzene is also consistent with their zwitterionic character.

To establish the molecular geometry for this type of species, single crystals of **5a** suitable for X-ray diffraction were obtained by slow evaporation from a benzene solution (Figure 1). The crystal structure of **5a** shows the titanium atom, which is coordinated to the Cp* and the phenylenediamido ligands, interacting with the methyl group of the borate anion. The Ti···B distance of 4.154(1) Å is within the Ti···B distance range (3.991−4.017 Å) found for the four Ti-methylborate zwiterionic species TiCpMe(NP-*t*-Bu_3)[μ-MeB(C_6F_5)$_3$],[13] Ti(NP-*t*-Bu_3)$_2$[μ-MeB(C_6F_5)$_3$]$_2$,[14] TiLMe[μ-MeB(C_6F_5)$_3$] [L = 1,1′-bis(trimethylsilylamido)ferrocene-*N*,*N*′],[15] and Ti(L′)Me[μ-MeB(C_6F_5)$_3$] [L′ = η^5-(3-ethylindenyl-1-dimethylsilyl)-*tert*-butylamido][16] already reported.

The Ti−C(27) distance of 2.489(1) Å found for compound **5a** is slightly longer than those found for the four reported Ti···CH_3−B zwiterionic complexes (2.333−2.404 Å). This could be a consequence of the steric crowding around the titanium center in compound **5a**. The Ti−C−B angle of 170.03(8)° found for compound **5a** lies in the normal range for similar derivatives (Ti···C−B 167.2−175.0°). A structural parameter study for Ti···CH_3−B interactions in the already reported compounds has been made (see Figure 2 and Table 1). The borate methyl group hydrogen atom positions for compound **5a** were located in a difference Fourier synthesis and freely refined. However, the symmetrical or unsymmetrical nature of the Ti···CH_3−B interaction could not be established due to the large uncertainties in the metrical data. The unsymmetrical nature for the Ti···CH_3−B interaction has been reported for compounds TiCpMe(NP-*t*-Bu_3)[μ-MeB(C_6F_5)$_3$][13] and Ti(NP-*t*-Bu_3)$_2$[μ-MeB(C_6F_5)$_3$]$_2$,[14] whose hydrogen atoms have been located in a difference Fourier synthesis and refined. For these compounds one of the three Ti···H interactions is clearly longer and corresponds to the closest Ti···H−C angle (77−81°). On the other hand, the unsymmetrical nature of the Ti···CH_3−B interaction for compounds TiLMe[μ-MeB(C_6F_5)$_3$][15] (L = 1,1′-bis(trimethylsilylamido)ferrocene-*N*,*N*′) and Ti(L′)-Me[μ-MeB(C_6F_5)$_3$][16] (L′ = η^5-(3-ethylindenyl-1-dimethylsilyl)-*tert*-butylamido) cannot be established because it is not clear how the H atom positions were located and the uncertainties in the metrical data are not provided.

The internal structural parameters of the "Ti(1,2-C_6H_4-$(NNp)_2$)" metalacycle are essentially the same as those found in the neutral precursors, which indicates that the phenylenediamido ligand is attached to the metal in a η^2-N,N′-π manner. However, there is a notable structural difference; whereas the neutral precursors exist as the *supine* isomer,[17,18] in **5a** the phenylenediamido ligand adopts a *prono* conformation. This fact

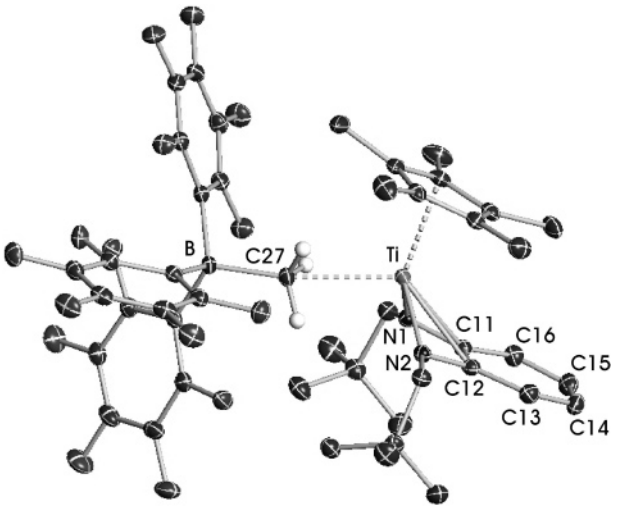


Figure 1. Ellipsoid plot for the crystal structure of compound **5a**. Hydrogen atoms except for the methylborate group have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti−N2 1.912(1), Ti−N1 1.918(1), Ti−C12 2.412(1), Ti−C11 2.419(1), Ti···C27 2.489(1), N1−C11 1.3943(16), N1−C17 1.4688(15), N2−C12 1.3975(16), N2−C22 1.4648(15), C11−C12 1.4457(17), C12−C13 1.4195(17), C13−C14 1.3661(19), C14−C15 1.4039(19), C15−C16 1.3729(19), C11−C16 1.4201(17), B−C27 1.679(18), N2−Ti−N1 90.42(4), N2−Ti−C12 35.37(4), N1−Ti−C11 35.15(4), C11−N1−C17 121.85(10), C11−N1−Ti 92.47(7), C12−N2−C22 121.31(10), C12−N2−Ti 92.25(7), C22−N2−Ti 141.31(8), B−C27···Ti 170.03(8).

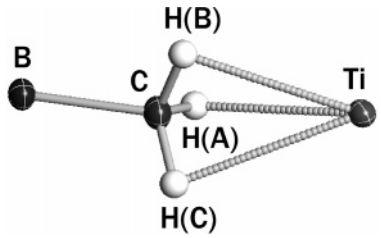


Figure 2. Ellipsoid plot for the B−CH_3···Ti fragment. The hydrogen atoms have been labeled from the shortest to the longest C−H bond as A, B, and C, respectively.

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Table 1. Structural Parameters for the B−CH_3···Ti Agostic Interactions in Compounds 5a, TiCpMe(NP-*t*-Bu_3)[μ-MeB(C_6F_5)$_3$],[13] Ti(NP-*t*-Bu_3)$_2$[μ-MeB(C_6F_5)$_3$]$_2$,[14] (TiLMe(μ-MeB(C_6F_5)$_3$) [L = 1,1′-bis(trimethylsilylamido)ferrocene-*N*,*N*′][15] and Ti(L′)[Me(μ-MeB(C_6F_5)$_3$)] [L′ = η^5-(3-ethylindenyl-1-dimethylsilyl)-*tert*-butylamido][16]

compound	bond	C···Ti (Å)	C−H (Å)	H···Ti (Å)	C−H···Ti (deg)
5a	C−H(A)	2.489(1)	0.976(17)	2.358(17)	86.1(11)
	C−H(B)	2.489(1)	0.987(18)	2.470(18)	79.6(11)
	C−H(C)	2.489(1)	1.002(16)	2.240(16)	92.3(10)
TiCpMe(NP-*t*-Bu_3)[μ-MeB(C_6F_5)$_3$]	C−H(A)	2.404(4)	0.931	2.435(3)	80.8
	C−H(B)	2.404(4)	0.945	2.197(3)	90.8
	C−H(C)	2.404(4)	1.012	2.257(3)	85.8
Ti(NP-*t*-Bu_3)$_2$[μ-MeB(C_6F_5)$_3$]$_2$	C−H(A)	2.333(7)	0.801	2.219	88.1
	C−H(B)	2.333(7)	0.992	2.205	84.8
	C−H(C)	2.333(7)	1.013	2.351	77.0
TiLMe[μ-MeB(C_6F_5)$_3$]	C−H(A)	2.297(4)	0.944	2.122	88.4
	C−H(B)	2.297(4)	0.976	2.321	76.5
	C−H(C)	2.297(4)	0.985	2.198	83.1
Ti(L′)Me[μ-MeB(C_6F_5)$_3$]	C−H(A)	2.333	0.967	2.129	89.65
	C−H(B)	2.333	0.961	2.253	82.6
	C−H(C)	2.333	0.960	2.415	73.6

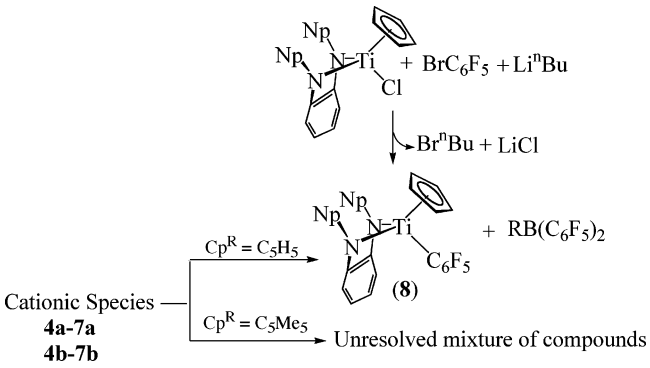
implies a conformational process associated with cationic generation in the reactions of the neutral alkyl compounds with the boron reagents. The presence of the sterically demanding methylborate in the coordination sphere of the metal center forces the phenylenediamido ligand to adopt the *prone* conformation to minimize their steric interactions.

Similar reactions of TiCp^R[1,2-C_6H_4(NNp)$_2$]R and B(C_6F_5)$_3$ in a chlorinated solvent ($CDCl_3$ or CD_2Cl_2) did not lead to the analogous zwitterionc species obtained in C_6D_6 but gave the ionic products {TiCp^R[1,2-C_6H_4(NNp)$_2$](solvent)$_n$}$^+$[RB(C_6F_5)$_3$]$^-$ (Cp^R = Cp, R = Me, **6a**; Bz, **6b**; Cp^R = Cp*, R = Me, **7a**; Bz, **7b**) (Scheme 1), where the anion is displaced by an indeterminate number of solvent molecules. The facile displacement of the alkylborate anion from the coordination sphere by the chlorinated solvent is in contrast to the behavior of TiMe(NP-*t*-Bu_3)$_2$(μ-MeB(C_6F_5)$_3$),[19] which was recrystallized from dichloromethane without exchange of methylborate. This difference is attributed to the effect of the bulky and donating (up to eight electrons) η^4-phenylenediamido ligand. The noncoordinating nature of the anions is deduced from the NMR spectroscopic data. In all cases, the ^{19}F chemical shift difference $\Delta\delta = \delta(m\text{-F}) - \delta(p\text{-F})$ (3.1, **6a**; 2.7, **6b**; 2.5, **7a**, **7b**) is in accordance with a noncoordinated anion. Such free disposition is further confirmed by the upfield shifted *ipso*-carbon resonances of the benzylic groups (i.e., δ 148.6 for compound **6b**). Comparison of the spectroscopic data for the cationic fragment of the compounds **6a**,**b** and **7a**,**b** shows slight changes due to the different solvents and the nature of the counterion.

Treatment of TiCp[1,2-C_6H_4(NNp)$_2$]Me (**2a**) with [CPh_3][B(C_6F_5)$_4$] in CD_2Cl_2 at 25 °C was studied by NMR spectroscopy. The instantaneous generation of Ph_3CCH_3, as judged by NMR spectroscopy,[20] indicates the abstraction of the methyl group initially attached to titanium. The ^{1}H NMR spectrum shows a set of resonances indicative of the formation of the cationic fragment {TiCp[1,2-C_6H_4(NNp)$_2$]}$^+$.

All the cationic species described above are reasonably stable in solution, even in chlorinated solvents, and decomposition at room temperature is observed only very gradually. Reaction of TiCp^R[1,2-C_6H_4(NNp)$_2$]R with B(C_6F_5)$_3$ proceeds in an identical fashion whether C_6D_6 or chlorinated solvents are used, regardless of the nature of the Cp^R ligand. However, the decomposition

Scheme 2



pathway of the cationic species depends on the Cp^R group. Thus, the cyclopentadienyl derivatives decompose to give the neutral pentafluorophenyl complex TiCp[1,2-C_6H_4(NNp)$_2$](C_6F_5) (**8**) along with the corresponding byproduct RB(C_6F_5)$_2$ (Scheme 2).[21] In this decomposition process, the formation of the chloro complex TiCp[1,2-C_6H_4(NCH_2*t*-Bu)$_2$]Cl (**1a**) by chloro abstraction from the solvent was never observed. The ligand redistribution reaction between titanium and boron atoms occurs faster for the methyl than for the benzyl anionic derivative and is clearly influenced by the polarity of the solvent, being accelerated in polar mediums. Similar reactivity has been described for analogous cationic group 4 metal species derived from the reaction of B(C_6F_5)$_3$ with diamido complexes,[22−27] although systems containing diamido and cyclopentadienyl ligands exhibit a higher proclivity for this type of reaction. To confirm the formation of **8**, this compound was synthesized by an alternative procedure using the reaction of the chloro derivative TiCp[1,2-C_6H_4(NNp)$_2$]Cl with Li(C_6F_5) (generated in situ from C_6F_5Br and *n*-BuLi) in hexane at −78 °C (Scheme 2). The permethylated-cyclopentadienyl derivatives evolve through C−H activa-

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tion to yield an unresolved mixture of compounds (Scheme 2). The bulkiness and the electronic properties of the Cp* ring play a decisive role in the decomposition process. Recently, similar conclusions based on theoretical studies have been published, suggesting that the aryl group transfer reaction can be prevented if bulky substituents on the ancillary ligand or methyl substituents on the Cp ring are employed.[28] Our experimental results support these theoretical predictions.

In conclusion, the synthesis and characterization of cationic titanium compounds derived from the reaction of monocyclopentadienyl phenylenediamido alkyl titanium derivatives with boron reagents are described. It has been demonstrated that the existence or absence of anion coordination is a reflection of the solvent polarity used for the reaction. Depending on the nature of the cyclopentadienyl ligand, the cationic complexes decompose, in solution, through different pathways, reflecting the decisive role of the cyclopentadienyl ring in determining the way that the cations evolve. The solution chemistry, solid state structure, and polymerization behavior are self-consistent and afford considerable insight into the nature of potentially active species in the olefin polymerization reactions.

Experimental Section

General Considerations. All manipulations were performed under rigorous exclusion of oxygen and moisture under argon using Schlenk and high-vacuum line techniques or in a glovebox, model MO40-2. Solvents were predried by standing over activated 4 Å molecular sieves and then purified by distillation under argon before use by employing the appropriate drying/deoxygenated agent. Deuterated solvents were degassed by several freeze−thaw cycles and stored in ampules equipped with Young's Teflon valves over activated 4 Å molecular sieves. C, H, and N microanalyses were performed on a Perkin-Elmer 2400 microanalyzer. NMR spectra, measured at 25 °C, were recorded on a Varian Unity FT-300 (^{1}H NMR at 300 MHz, ^{13}C NMR at 75 MHz) spectrometer, and chemical shifts were referenced to $SiMe_4$ via the ^{13}C resonances and the residual protons (^{1}H) of the deuterated solvent. Li^{n}Bu (1.6 M in hexane solution) was purchased from Aldrich and Br(C_6F_5) was purchased from ABCR. B(C_6F_5)$_3$ and [Ph_3C][B(C_6F_5)$_4$] were synthesized following established procedures.[29−31] Alkyl compounds TiCp^R[1,2-C_6H_4(NCH_2t-Bu)$_2$]R (Cp^R = η^5-C_5H_5, η^5-C_5Me_5, R = Me, Bz) were prepared as described in previous work.[5,6]

TiCp[1,2-C_6H_4(NNp)$_2$][μ-PhCH$_2$B(C_6F_5)$_3$] (4b). Compound **2b** (0.010 g, 0.022 mmol) and B(C_6F_5)$_3$ (0.011 g, 0.022 mmol) were loaded in a Teflon-valved NMR tube. C_6D_6 was charged, causing the formation of a red solution. All operations described were carried out in the drybox at room temperature. NMR data were recorded at 25 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.38 (m, 2H, Ph), 6.97 (m, 2H, Ph), 6.18, 5.96, 5.87 (br, 5H, CH_2*Ph*), 5.59 (s, 5H, C_5H_5), 4.04 (d, J = 14.1 Hz, 2H, CH_2), 3.75 (d, J = 14.1 Hz, 2H, CH_2), 2.87 (br, 2H, BC*H*$_2$Ph), 0.42 (s, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ 159.6 (*ipso*-CH_2*Ph*), 128.8, 119.9 (Ph), 131.6, 129.9, 128.8 (BCH_2*Ph*), 118.2 (C_5H_5), 69.2 (CH_2), 38.5 (B*C*H$_2$Ph), 36.0 (*ipso*-*t*-Bu), 28.5 (*t*-Bu), 150.3, 147.2, 140.2, 139.1, 137.0, 135.6 (C_6F_5), C*ipso* for Ph group not observed. ^{19}F NMR (282 MHz, C_6D_6, 25 °C): δ −131.1 (br, *o*-C_6F_5), −162.5 (br, *p*-C_6F_5), −166.0 (br, *m*-C_6F_5), $\Delta\delta$ (*p, m*-F) = 3.5 ppm.

TiCp*[1,2-C_6H_4(NNp)$_2$][μ-CH$_3$B(C_6F_5)$_3$] (5a). C_6D_6 was added to a mixture of **3a** (0.010 g, 0.022 mmol) and B(C_6F_5)$_3$ (0.011 g, 0.022 mmol). The solution darkened, and an oily product along with black crystals was soon observed. Checking the sample before total precipitation of the product allowed us to obtain NMR data for the desired cationic species. Anal. Calcd for $C_{45}H_{44}N_2TiBF_{15}$ (956.13 g/mol): C, 56.52; H, 4.60; N, 2.93. Found: C, 56.41; H, 4.33; N, 2.79. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.11 (m, 2H, Ph), 7.03 (m, 2H, Ph), 4.20 (br, 2H, CH_2), 3.91 (br, 2H, CH_2), 1.17 (s, 15H, C_5Me_5), 0.63 (s, 18H, *t*-Bu), 0.58 (s, 3H, BC*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ 128.6, 119.6 (Ph), 115.5 (*ipso*-C_5Me_5), 62.5 (CH_2), 36.1 (*ipso*-*t*-Bu), 28.9 (*t*-Bu), 11.7 (B*C*H$_3$), 10.5 (C_5Me_5), 150.7, 147.7, 140.7, 139.0, 136.0, (C_6F_5), C*ipso* for Ph not observed. ^{19}F NMR (282 MHz, C_6D_6, 25 °C): δ −132.4 (br, *o*-C_6F_5), −161.1 (br, *p*-C_6F_5), −165.8 (br, *m*-C_6F_5), $\Delta\delta$ (*p, m*-F) = 4.7 ppm.

{TiCp[1,2-C_6H_4(NNp)$_2$](solvent)$_n$}$^+$[CH$_3$B(C_6F_5)$_3$]$^-$ (6a). A mixture of the methyl complex **2a** (0.010 g, 0.027 mmol) and B(C_6F_5)$_3$ (0.013 g, 0.027 mmol) was dissolved in CD_2Cl_2 at room temperature in the drybox to give dark solution. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.60 (m, 2H, Ph), 7.40 (m, 2H, Ph), 6.60 (s, 5H, C_5H_5), 4.18 (d, J = 13.5 Hz, 2H, CH_2), 3.95 (d, J = 13.5 Hz, 2H, CH_2), 0.77 (s, 18H, *t*-Bu), 0.41 (br, 3H, BC*H*$_3$). ^{19}F NMR (282 MHz, CD_2Cl_2, 25 °C): δ −134.5 (br, *o*-C_6F_5), −161.1 (br, *p*-C_6F_5), −164.2 (br, *m*-C_6F_5), $\Delta\delta$ (*p, m*-F) = 3.1 ppm.

{TiCp[1,2-C_6H_4(NNp)$_2$](solvent)$_n$}$^+$[PhCH$_2$B(C_6F_5)$_3$]$^-$ (6b). Compound **6b** was obtained in a manner similar to **4b** using 0.010 g (0.022 mmol) and 0.011 g of B(C_6F_5)$_3$ (0.022 mmol). The addition of $CDCl_3$ produces a dark solution. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.66 (m, 2H, Ph), 7.36 (m, 2H, Ph), 6.88−6.78 (br, 5H, CH_2*Ph*), 6.25 (s, 5H, C_5H_5), 4.30 (d, J = 13.8 Hz, 2H, CH_2), 4.04 (d, J = 13.8 Hz, 2H, CH_2), 2.89 (br, 2H, C*H*$_2$Ph), 0.67 (s, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 148.6 (*ipso*-CH_2*Ph*), 126.7, 119.4 (Ph), 129.2−128.5 (BCH_2*Ph*), 118.1 (C_5H_5), 69.3 (CH_2), 38.0 (B*C*H$_2$Ph), 36.0 (*ipso*-*t*-Bu), 28.5 (*t*-Bu), 149.7, 146.4, 139.0, 137.7, 135.7, 134.7 (C_6F_5), C*ipso* for Ph group not observed. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ −131.2 (m, *o*-C_6F_5), −164.5 (m, *p*-C_6F_5), −167.2 (m, *m*-C_6F_5), $\Delta\delta$ (*p, m*−F) = 2.7 ppm.

{TiCp*[1,2-C_6H_4(NNp)$_2$](solvent)$_n$}$^+$[CH$_3$B(C_6F_5)$_3$]$^-$ (7a). C_6D_6 was added to a mixture of 0.010 g (0.022 mmol) of **3a** and 0.011 g (0.022 mmol) of B(C_6F_5)$_3$ in a Young tube; an oily product was precipitated. After 12 h the solvent was removed by decantation, the residue was dried in vacuo, and CD_2Cl_2 was added to give a dark red solution. All operations were performed in the drybox. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.62 (m, 2H, Ph), 7.56 (m, 2H, Ph), 4.59 (d, J = 14.1 Hz, 2H, CH_2), 4.09 (d, J = 14.1 Hz, 2H, CH_2), 2.17 (s, 15H, C_5Me_5), 0.77 (s, 18H, *t*-Bu), 0.50 (br, 3H, BC*H*$_3$). ^{19}F NMR (282 MHz, CD_2Cl_2, 25 °C): δ −131.5 (br, *o*-C_6F_5), −163.7 (br, *p*-C_6F_5), −166.2 (br, *m*-C_6F_5), $\Delta\delta$ (*p, m*-F) = 2.5 ppm.

{TiCp*[1,2-C_6H_4(NNp)$_2$](solvent)$_n$}$^+$[PhCH$_2$B(C_6F_5)$_3$]$^-$ (7b). C_6D_6 was added to a mixture of 0.010 g (0.019 mmol) of **3b** and 0.010 g (0.019 mmol) of B(C_6F_5)$_3$ in a Young tube, and an oily product was precipitated. After 10 h the solvent was removed by decantation, the residue was dried in vacuo, and CD_2Cl_2 was added to give a dark red solution. All operations were performed in the drybox. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.62 (m, 2H, Ph), 7.56 (m, 2H, Ph), 4.59 (d, J = 14.4 Hz, 2H, CH_2), 4.09 (d, J = 14.4 Hz, 2H, CH_2), 2.81 (br, 2H, BC*H*$_2$Ph), 2.17 (s, 15H, C_5Me_5), 0.77 (s, 18H, *t*-Bu). ^{19}F NMR (282 MHz, CD_2Cl_2, 25 °C): δ −131.5 (br, *o*-C_6F_5), −163.7 (br, *p*-C_6F_5), −166.2 (br, *m*-C_6F_5), $\Delta\delta$ (*p, m*-F)- = 2.5 ppm.

TiCp[1,2-C_6H_4(NNp)$_2$](C_6F_5) (8). LiB(C_6F_5) was prepared in situ by the usual procedure, allowing 0.11 mL (0.867 mmol) of Br(C_6F_5) and 0.54 mL (0.87 mmol) of Li^{n}Bu to react in hexane at −78 °C. Then 0.34 g (0.87 mmol) of **1a** was added dropwise to the stirring reaction mixture, which was maintained at low temperature. After the addition was completed, the reaction mixture

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was warmed to room temperature and stirred for 12 h. The white precipitate formed was filtered, and the resulting solution was cooled to −40 °C. Compound **8** was obtained as a red oil in good yield, 60% (0.27 g, 0.52 mmol). Anal. Calcd for $C_{27}H_{31}N_2TiF_5$ (526.43 g/mol): C, 61.60; H, 5.94; N, 5.32. Found: C, 59.90; H, 6.04; N, 4.98. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.09 (m, 2H, Ph), 7.00 (m, 2H, Ph), 6.22 (s, 5H, C_5H_5), 4.14 (d, J = 13.5 Hz, 2H, CH_2), 3.99 (d, J = 13.5 Hz, 2H, CH_2), 0.64 (s, 18H, *t*-Bu). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.34 (m, 2H, Ph), 7.23 (m, 2H, Ph), 6.51 (s, 5H, C_5H_5), 4.39 (d, J = 13.5 Hz, 2H, CH_2), 4.19 (d, J = 13.5 Hz, 2H, CH_2), 0.78 (s, 18H, *t*-Bu). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ 127.5, 120.4 (Ph), 114.8 (C_5H_5), 67.1 (CH_2), 35.6 (*ipso*-*t*-Bu), 28.7 (*t*-Bu), C*ipso* for Ph not observed. ^{19}F NMR (282 MHz, C_6D_6, 25 °C): δ −119.1 (br, *o*-C_6F_5), −158.5 (br, *p*-C_6F_5), −162.7 (br, *m*-C_6F_5). ^{19}F NMR (282 MHz, CD_2Cl_2, 25 °C): δ −119.9 (br, *o*-C_6F_5), −160.2 (br, *p*-C_6F_5), −164.0 (br, *m*-C_6F_5).

X-ray data for compound 5a: dark red prism, 0.49 × 0.23 × 0.17 mm size, triclinic, $P\bar{1}$, a = 11.1096(4) Å, b = 12.2344(4) Å, c = 17.8694(6) Å, α = 86.356(1)°, β = 75.321(1)°, γ = 63.958(1)°, V = 2107.8(1) Å^3, Z = 2, ρ_{calcd} = 1.507 g cm^{-3}, θ_{max} = 28.05, Mo Kα, λ = 0.71073 Å, ω-scan, diffractometer Siemens Smart APEX CCD, T = 100(2) K, 30 724 reflections were collected, of which 10 308 were independent (R_{int} = 0.018), absorption correction based on multiscans, T_{min}/T_{max} 0.887/0.949, direct primary solution and refinement on F^2 (SHELXS-97 and SHELXL-97, G. M. Sheldrick, University of Göttingen, 1997), 600 refined parameters, hydrogen atoms refined as free for the mehtyl borate, rigid for the rest of the methyl groups, and *riding* for any other hydrogen atom, $R_1[I > 2\sigma(I)]$ = 0.0363, wR_2(all data) = 0.097.

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Supporting Information Available: Crystallographic data for **5a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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