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Group 4 Zwitterionic Metallocenes Based upon the Bridged Amido-Cyclopentadienyl Ligand and Coordinated Dienes

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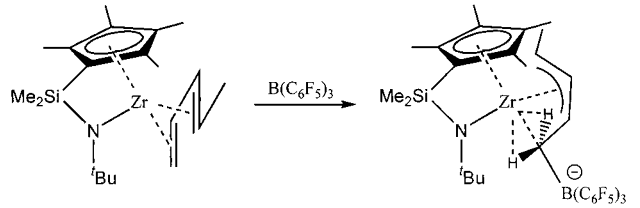
The reaction of (η^5-$C_5Me_4SiMe_2N^tBu$)Zr(1,3-pentadiene) with $B(C_6F_5)_3$ results in the formation of the zirconium borate zwitterion complex (η^5-$C_5Me_4SiMe_2N^tBu$)Zr(η^3-$CH_3(CH)_3CH_2B(C_6F_5)_3$) (**1**). Furthermore, reaction of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(2,4-hexadiene), (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(2-methyl-1,3-butadiene), (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(1,3-butadiene), and (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(2,3-dimethylbutadiene) with either $B(C_6F_5)_3$ or $Al(C_6F_5)_3$ results in the formation of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_3CH_2(CH)_3CH_2B(C_6F_5)_3$) (**2**), ($\eta^5$-$C_5Me_4SiMe_2N^tBu$)Ti($\eta^3$-$CH_2C(CH_3)CHCH_2Al(C_6F_5)_3$) (**3**), ($\eta^5$-$C_5Me_4SiMe_2N^tBu$)Ti($\eta^3$-$CH_2(CH)_2CH_2B(C_6F_5)_3$) (**4**), and ($\eta^5$-$C_5Me_4SiMe_2N$-$^tBu$)Ti($\eta^3$-$CH_2C(CH_3)C(CH_3)CH_2B(C_6F_5)_3$) (**5**). The X-ray crystal structures of **1**−**4** have been determined.

Introduction

Group 4 metallocene complexes have attracted considerable interest due to their ability to function as highly active Ziegler−Natta type catalysts for the polymerization of olefins. Of particular interest are catalysts based upon the bridged amido-cyclopentadienyl ligand or "constrained geometry" ligand, [($C_5Me_4SiMe_2NR$)MX_2], originally developed by Bercaw for the formation of single component scandium catalysts.[1] This has led to a number of patents for the use of the bridged amido-cyclopentadienyl ligand with group 4 metals.[2] As a method of controlling cation−anion interactions in metallocene systems, zwitterionic catalysts in which the cation and anion are separated have attracted considerable attention. A number of zwitterionic catalysts have been prepared to date. One of the first ones was prepared by Turner et al. by the reaction of dialkylmetallocenes with ammonium borate salts.[3] An important factor in the stabilization of this zwitterion was the presence of an agostic interaction between an ortho C−H group and the Zr center.

A number of zwitterionic catalysts have been prepared from group 4 metallocene diene complexes. In general, the diene ligand is transformed into an η^3-allyl unit by the electrophilic addition of Lewis acids such as $B(C_6F_5)_3$ or $Al(C_6F_5)_3$[4] to a methylene carbon of the diene. In 1995, Erker et al.[5] reported a zwitterionic catalyst by reaction of Cp_2Zr(butadiene) with $B(C_6F_5)_3$. The zirconium center is protected by a weak interaction with an ortho fluorine atom on one of the C_6F_5 groups. Upon reaction with an olefin monomer, this weak interaction (~8.5 kcal/mol)[6] is easily broken leading to rapid polymerization of the olefin. In 1995, Marks et al.[7] prepared the first examples of bridged amido-cyclopentadienyl titanium diene complexes. The reaction of (η^5-$C_5Me_4SiMe_2NR$)$TiCl_2$ (R = Ph, ^tBu) with 2 equiv of n-BuLi in the presence of an excess of the diene resulted in the formation of complexes of the type (η^5-$C_5Me_4SiMe_2NR$)Ti(diene). We have recently described the preparation of several zwitterionic catalysts by activation of ($C_5Me_4SiMe_2NtBu$)Ti(1,3-pentadiene) with $B(C_6F_5)_3$ and the related aluminum complex, $Al(C_6F_5)_3(C_6H_6)$.[8] We report here the synthesis and characterization of a series of zwitterionic compounds based upon the bridged amido-cyclopentadienyl ligand (η^5-$C_5Me_4SiMe_2N^tBu$) and coordinated dienes which have been activated by $B(C_6F_5)_3$ and $Al(C_6F_5)_3$.

Scheme 1. Preparation of **1**



Results and Discussion

Synthesis of (η^5-$C_5Me_4SiMe_2N^tBu$)Zr(η^3-$CH_3(CH)_3CH_2B(C_6F_5)_3$) (1). The treatment of (η^5-$C_5Me_4SiMe_2N^tBu$)Zr(1,3-pentadiene) with 1 equiv of $B(C_6F_5)_3$ in hexane at 25 °C leads to an immediate color change from red to bright orange and the isolation of a bright orange crystalline complex of composition (η^5-$C_5Me_4SiMe_2N^tBu$)Zr(1,3-pentadiene)$B(C_6F_5)_3$(hexane) (**1**) (Scheme 1). The $B(C_6F_5)_3$ group is bound to the terminal methylene carbon atom of the original pentadiene ligand, which may now be regarded as an η^3-allyl fragment. The spectroscopic data for **1** are in accord with the solid-state structure as determined by X-ray crystallography. Thus, the allylic protons were identified at δ 5.04, 3.63, and 2.44. The signal for the allyl CH_3 group is obscured by the presence of hexane which crystallizes with **1**; however, this resonance can be detected in the COSY spectrum at δ 1.31. The CH_2 protons next to the $B(C_6F_5)_3$ group are observed at δ 0.84 and 0.00. The ^{11}B NMR

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[1] Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

[2] See, for example: Stevens, J. C.; Timmers, F. J.; Rosen, G. W.; Knight, G. W.; Lai, S. Y. European Patent Application, EP 0 416 815 A2, 1991. Canich, J. A. European Patent Application, EP 0 420 436 A1, **1991**.

[3] Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728.

[4] Hair, G. S.; Cowley, A. H.; Jones, R. A.; McBurnett, B. G.; Voigt, *J. Am. Chem. Soc.* **1999**, *121*, 4922.

[5] Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755.

[6] Karl, J.; Erker, G.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165.

[7] Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132.

[8] Cowley, A. H.; Hair, G. S.; McBurnett, B. G.; Jones, R. A. *Chem. Commun.* **1999**, 437.

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Table 1. Crystal Data and Structure Refinement for **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{44}H_{49}BF_{15}N$ SiZr	$C_{39}H_{37}BF_{15}N$ SiTi	$C_{38}H_{35}AlF_{15}NSiTi$	$C_{43}H_{44}BF_{15}NSiTi$
formula weight	1006.96	891.50	893.64	946.59
temperature	153(2) K	153(2) K	173(2) K	153(2) K
space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P\bar{1}$
unit cell dimensions				
a, Å	10.5910(6)	12.0450(7)	12.090(2)	10.451(3)
b, Å	13.0810(7)	12.3810(6)	17.785(3)	12.995(3)
c, Å	16.9690(9)	15.2330(1)	36.379(13)	16.921(5)
α, deg	81.281(3)	73.468(4)	90	80.372(2)
β, deg	86.746(3)	69.220(3)	90	86.946(2)
γ, deg	74.504(3)	65.407(3)	90	75.287(2)
volume, $Å^3$	2238.9(2)	1906.0(2)	7822(3)	2191.25(10)
Z	2	2	8	2
density (calcd) mg/m^3	1.49	1.55	1.518	1.435
absorption coefficient, mm^{-1}	0.368	0.361	0.373	0.319
final *R* indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0753$	$R_1 = 0.0665$	$R_1 = 0.0708$	$R_1 = 0.0729$
	$wR_2 = 0.146$	$wR_2 = 0.109$	$wR_2 = 0.1511$	$wR_2 = 0.179$
R indices (all data)	$R_1 = 0.131$	$R_1 = 0.141$	$R_1 = 0.1252$	$R_1 = 0.0881$,
	$wR_2 = 0.167$	$wR_2 = 0.141$	$wR_2 = 0.1818$	$wR_2 = 0.186$
largest diff peak and hole, e $Å^{-3}$	0.48 and −0.57	0.39 and −0.40	0.740 and −0.512	0.74 and −0.37

$^a R_1 = \sum|F_o| - |F_c|/\sum|F_o|$. $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

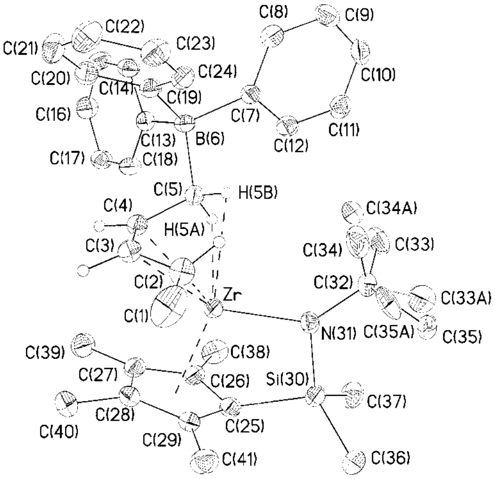

Figure 1. Molecular structure and atom numbering scheme for (η^5-$C_5Me_4SiMe_2N^tBu$)Zr(η^3-$CH_3(CH)_3CH_2B(C_6F_5)_3$) (**1**). The thermal ellipsoids are scaled to the 30% probability level. The fluorine atoms and methyl hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) for **1**

Zr−N(31)	2.079(3)	C(5)−B(6)	1.685(7)
Zr−C(2)	2.342(5)	B(6)−C(7)	1.649(7)
Zr−C(4)	2.401(5)	B(6)−C(19)	1.654(7)
Zr−C(3)	2.476(5)	B(6)−C(13)	1.650(7)
Zr−H(5A)	2.32(4)	C(25)−Si(30)	1.874(5)
Zr−H(5B)	2.45(4)	Si(30)−N(31)	1.752(4)
C(1)−C(2)	1.494(8)	Si(30)−C(37)	1.859(5)
C(2)−C(3)	1.414(7)	Si(30)−C(36)	1.869(5)
C(3)−C(4)	1.378(7)	N(31)−C(32)	1.495(6)
C(4)−C(5)	1.495(6)	C(32)−C(34)	1.511(6)

Table 3. Selected Bond Angles (deg) for **1**

N(31)−Zr−C(2)	105.9(2)	C(3)−C(4)−C(5)	126.8(5)
N(31)−Zr−C(4)	140.9(2)	C(3)−C(4)−Zr	76.6(3)
C(2)−Zr−C(4)	63.1(2)	C(5)−C(4)−Zr	76.2(3)
N(31)−Zr−C(3)	137.1(2)	C(4)−C(5)−B(6)	114.5(4)
C(2)−Zr−C(3)	34.0(2)	C(4)−C(5)−Zr	68.4(3)
C(4)−Zr−C(3)	32.8(2)	B(6)−C(5)−Zr	176.4(3)
N(31)−Zr−C(5)	108.50(14)	C(7)−B(6)−C(19)	113.9(4)
C(2)−Zr−C(5)	80.1(2)	C(7)−B(6)−C(13)	105.3(4)
C(4)−Zr−C(5)	35.4(2)	C(19)−B(6)−C(13)	113.6(4)
C(3)−Zr−C(5)	62.1(2)	C(7)−B(6)−C(5)	109.8(4)
C(3)−C(2)−C(1)	121.0(5)	C(19)−B(6)−C(5)	101.3(4)
C(3)−C(2)−Zr	78.2(3)	C(13)−B(6)−C(5)	113.2(4)
C(1)−C(2)−Zr	133.5(4)	N(31)−Si(30)−C(25)	94.5(2)
C(4)−C(3)−C(2)	125.6(5)	C(32)−N(31)−Si(30)	122.2(3)
C(4)−C(3)−Zr	70.6(3)	C(32)−N(31)−Zr	135.7(3)
C(2)−C(3)−Zr	67.8(3)	Si(30)−N(31)−Zr	102.1(2)

spectrum revealed a singlet at δ −10.4 which falls in the region observed for four-coordinate boron species. The ^{19}F NMR spectrum exhibited resonances at δ −129.4, −158.2, and −163.1 ppm for the *ortho*, *para*, and *meta* fluorine atoms, respectively. No upfield resonances (∼200 ppm) that would be indicative of Zr−F interactions were detected.[9] Moreover, no spectral changes were apparent upon cooling the ^{19}F NMR sample to −70 °C. The IR spectrum of **1** revealed a weak band at 2609 cm^{-1} that was tentatively assigned as an agostic C−H stretch.

To gain more insight into the structure of **1** and to determine whether agostic Zr−H interaction persisted in the solid state, an X-ray crystallographic study was undertaken.

X-ray Crystal Structure of (η^5-$C_5Me_4SiMe_2N^tBu$)Zr(η^3-$CH_3(CH)_3CH_2B(C_6F_5)_3$) (1). Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. Figure 1 shows the molecular geometry and atom numbering scheme, and the crystal data are presented in Table 1. A listing of bond lengths and angles appears in Tables 2 and 3, respectively. The hydrogen atoms on the diene fragment were located and refined isotropically. The *tert*-butyl group on the nitrogen atom was disordered about two orientations. As shown in Scheme 1, the $B(C_6F_5)_3$ group is bound to the terminal methylene carbon (C(5)) to form a zwitterionic structure. The coordination about the zirconium atom is very similar to that previously observed for compounds of this type.[8] The bond distances between the zirconium atom and the η^3-allyl terminal carbons (Zr−C(2) = 2.342(5) Å and Zr−C(4) = 2.401(5) Å) are shorter than those between the zirconium atom and the central carbon atom (Zr−C(3) = 2.476(5) Å). This observation is very common for early transition metal allyl complexes, while this trend is reversed in late transition metal allyl complexes.[10] The $C(sp^2)$−$C(sp^2)$ bonds of the allyl unit (C(2)−C(3) = 1.414(7) Å and C(3)−C(4) = 1.378(7) Å) are similar to those of other π-allyl complexes.[8]

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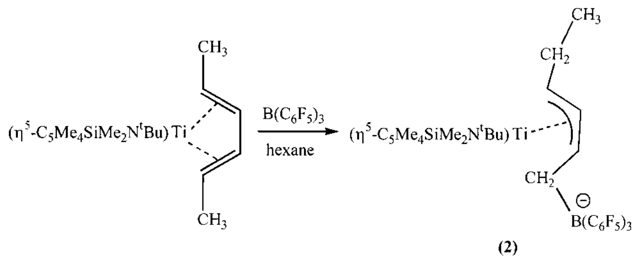
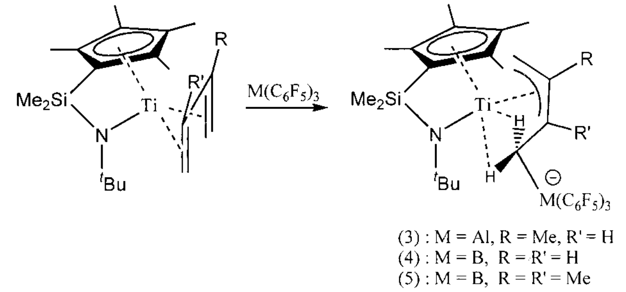
[9] Pindado, G. J.; Pett, M. T.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 3115.

[10] Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723.

Scheme 2. Synthesis of **2**



Scheme 3. Synthesis of Complexes **3**−**5**



The geometry about the boron atom can best be described as pseudo-tetrahedral with C−B−C bond angles ranging from 105.3(4)° to 113.9(4)°. The B−C(5) bond length of 1.685(7) Å is slightly longer than the other three B−C bond lengths (av. B−C = 1.651(7) Å). The η^3-$CH_3(CH)_3CH_2B(C_6F_5)_3$ group exhibits a *Z*-configuration with respect to the π bond of C(3)−C(4). This *Z* configuration brings C(5) into the correct position for agostic interactions to occur between the hydrogen atoms (H5A and H5B) of C(5) and the zirconium atom.[11] The Zr−C(5)−B bond angle of 176.4° is almost linear, again suggesting agostic interactions. The hydrogen atoms on C(5) were located and found to have close interactions with the zirconium atom. The Zr−H distances (Zr−H(5A) = 2.32(4) Å and Zr−H(5B) = 2.45(4) Å) are very similar to those observed in $[1,3\text{-}(SiMe_3)_2\text{-}C_5H_3]Zr(\eta^3\text{-}C_3H_5)(\eta^3\text{-}CH_2CMeCMeCH_2B(C_6F_5)_3)$ (Zr−H = 2.30(5) Å and 2.29(5) Å).[12] No intramolecular Zr−F interactions are observed in the crystal structure of **1**.

Synthesis of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_3CH_2(CH)_3CH_2B(C_6F_5)_3$) (2). We have also studied the effects of diene substitution on the structures of related, titanium zwitterions. The dienes used in this study were 2,4-hexadiene, 2-methyl-1,3-butadiene, 1,3-butadiene, and 2,3-dimethyl-1,3-butadiene. The corresponding titanium complexes were prepared and treated with 1 equiv of $B(C_6F_5)_3$ (**2**,**4**, and **5**) or $Al(C_6F_5)_3(C_6H_6)$ (**3**) in either toluene or hexane solution (Schemes 2 and 3). The new complexes were isolated and characterized by spectroscopic and crystallographic methods. Of particular interest is the structure of the zwitterion **2** prepared from the 2,4-hexadiene derivative. This compound may be isolated as a dark green crystalline material with an empirical composition of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(2,4-hexadiene)$B(C_6F_5)_3$(hexane) (**2**). The allylic protons of **2** were identified at δ 4.89, 3.96, and 3.26 and the allyl CH_3 group was detected at δ 0.66. On the basis of the COSY spectrum it was determined that the $B(C_6F_5)_3$ moiety in the ^1H NMR spectrum was located on a newly created terminal CH_2 group (formerly CH_3) of the allyl ligand, instead of on one of the CH groups as would be expected from the standpoint of an electrophilic addition (Scheme 2). The CH_2 protons adjacent to the $B(C_6F_5)_3$ group are observed at δ 0.50 and −0.11. The foregoing observations are likely a result of the migration of the $B(C_6F_5)_3$ group and a concomitant hydrogen shift, although a similar type of hydrogen shift was observed by Erker for the $Cp_2Hf(\eta^3\text{-}CH_2CHCHCH_2B(C_6F_5)_3$ zwitterion after a solution of this compound had been allowed to stand for 2 days at ambient temperature.[5] In addition, the IR spectrum of **2** revealed a weak band at 2680 cm^{-1} that was tentatively assigned as an agostic C−H stretch. ^{19}F and ^{11}B NMR shifts for **2**−**5** are listed in Table 10. To confirm the unusual structural rearrangement found for **2** an X-ray crystal structure analysis was undertaken.

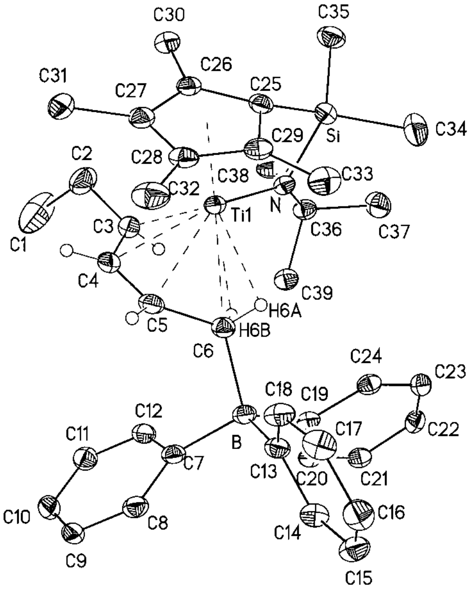


Figure 2. Molecular structure and atom labeling scheme for (η^5-C_5-$Me_4SiMe_2N^tBu$)Zr(η^3-$CH_3(CH)_3CH_2B(C_6F_5)_3$) (**2**). Thermal ellipsoids are scaled to the 30% probability level. The fluorine atoms and most hydrogen atoms have been omitted for clarity.

X-ray Crystal Structure of (η^5-$C_5Me_4SiMe_2N^tBu$) Ti(η^3-$CH_3CH_2(CH)_3CH_2B(C_6F_5)_3$) (2). Compound **2** crystallizes in the triclinic space group *P*$\bar{1}$ with two molecules per unit cell (Figure 2). Crystallographic details are given in Table 1, and selected bond lengths and angles are presented in Tables 4 and 5, respectively. The hydrogen atoms on the diene fragment were located and refined isotropically. The $B(C_6F_5)_3$ group is attached to a terminal CH_2 group, C(6), which was undoubtedly a CH_3 group in the original hexadiene ligand. The resulting structure is a zwitterionic metal−allyl complex similar to **1**, with the $B(C_6F_5)_3$ group at the end of the allyl unit and the titanium atom symmetrically bound to the η^3-allyl unit. The bond distances between the Ti atom and the η^3-allyl terminal carbons (Ti(1)−C(3) = 2.227(4) Å and Ti(1)−C(5) = 2.306(3) Å) are slightly shorter than that between the titanium atom and the central carbon atom (Ti(1)−C(4) = 2.340(4) Å).

Compound **2** features Ti−H distances of 2.21(3) Å (Ti(1)−H(6A)) and 2.28(3) Å (Ti(1)−H(6B)). The Ti(1)−C(6)−B fragment is almost linear (170.1(2)°), with a Ti(1)−C(6) bond length of 2.348(3) Å. The geometry about the boron atom is pseudo-tetrahedral with C−B−C bond angles ranging from 103.9(3)° to 115.4(3)°. The B−C(6) bond length of 1.711(5) Å is slightly elongated compared to the other three B−C bond lengths (av. B−C = 1.652(5) Å). No intramolecular Ti−F interactions are observed in **2**.

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(11) Karl, J.; Erker, G.; Fröhlich, R.; Zippel, F.; Bickelhaupt, F.; Goedheijt, S.; Akkerman, O.; Binger, P.; Stannek, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2771.

(12) Pindado, G. J.; Pett, M. T.; Bouwkamp, M.; Meetsma, A.; Hessen, B.; Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2358.

Table 4. Selected Bond Lengths (Å) for **2**

Ti(1)−N	1.961(3)	N−C(36)	1.509(4)
Ti(1)−C(3)	2.227(4)	C(1)−C(2)	1.478(6)
Ti(1)−C(5)	2.306(3)	C(2)−C(3)	1.538(5)
Ti(1)−C(4)	2.340(4)	C(3)−C(4)	1.403(6)
Ti(1)−C(6)	2.348(3)	C(4)−C(5)	1.380(5)
Ti(1)−H(6A)	2.21(3)	C(5)−C(6)	1.490(5)
Ti(1)−H(6B)	2.28(3)	C(6)−B	1.711(5)
Si−N	1.763(3)	C(7)−B	1.654(5)
Si−C(34)	1.854(4)	C(13)−B	1.646(5)
Si−C(35)	1.861(4)	C(19)−B	1.655(5)
Si−C(25)	1.866(3)		

Table 5. Selected Bond Angles (deg) for **2**

N−Ti(1)−C(3)	100.41(13)	C(2)−C(3)−Ti(1)	131.4(3)
N−Ti(1)−C(5)	135.95(12)	C(5)−C(4)−C(3)	126.4(4)
C(3)−Ti(1)−C(5)	66.42(14)	C(5)−C(4)−Ti(1)	71.4(2)
N−Ti(1)−C(4)	132.39(13)	C(3)−C(4)−Ti(1)	67.7(2)
C(3)−Ti(1)−C(4)	35.66(14)	C(4)−C(5)−C(6)	126.6(4)
C(5)−Ti(1)−C(4)	34.54(13)	C(4)−C(5)−Ti(1)	74.1(2)
N−Ti(1)−C(6)	103.16(11)	C(6)−C(5)−Ti(1)	72.9(2)
C(3)−Ti(1)−C(6)	85.59(13)	C(5)−C(6)−B	119.9(3)
C(5)−Ti(1)−C(6)	37.32(12)	C(5)−C(6)−Ti(1)	69.8(2)
C(4)−Ti(1)−C(6)	66.30(13)	B−C(6)−Ti(1)	170.1(2)
N−Si−C(25)	92.77(13)	C(13)−B−C(7)	113.4(3)
C(36)−N−Si	120.1(2)	C(13)−B−C(19)	103.9(3)
C(36)−N−Ti(1)	139.6(2)	C(7)−B−C(19)	114.0(3)
Si−N−Ti(1)	100.21(13	C(13)−B−C(6)	115.4(3)
C(1)−C(2)−C(3)	116.4(4)	C(7)−B−C(6)	104.9(3)
C(4)−C(3)−C(2)	123.1(4)	C(19)−B−C(6)	105.2(3)
C(4)−C(3)−Ti(1)	76.6(2)		

Table 6. Selected Bond Lengths (Å) for **3**

Ti(1)−N(1)	1.964(3)	Al(1)−C(1)	2.043(3)
Ti(1)−C(4)	2.223(4)	Si(1)−N(1)	1.752(3)
Ti(1)−C(2)	2.274(4)	Si(1)−C(19)	1.858(6)
Ti(1)−C(1)	2.310(3)	Si(1)−C(6)	1.864(4)
Ti(1)−C(3)	2.389(3)	Si(1)−C(20)	1.874(7)
Ti(1)−H(1A)	2.31(4)	N(1)−C(15)	1.512(4)
Ti(1)−H(1B)	2.47(4)	C(1)−C(2)	1.480(5)
Al(1)−C(21)	1.990(4)	C(2)−C(3)	1.388(5)
Al(1)−C(27)	2.009(4)	C(3)−C(4)	1.417(5)
Al(1)−C(33)	2.010(3)	C(3)−C(5)	1.501(5)

Table 7. Selected Bond Angles (deg) for **3**

N(1)−Ti(1)−C(4)	95.53(13)	C(15)−N(1)−Si(1)	120.5(2)
N(1)−Ti(1)−C(2)	135.09(12)	C(15)−N(1)−Ti(1)	137.9(2)
C(4)−Ti(1)−C(2)	65.98(14)	Si(1)−N(1)−Ti(1)	101.09(14)
N(1)−Ti(1)−C(1)	104.02(12)	C(2)−C(1)−Al(1)	110.1(2)
C(4)−Ti(1)−C(1)	85.08(14)	C(2)−C(1)−Ti(1)	69.8(2)
C(2)−Ti(1)−C(1)	37.65(13)	Al(1)−C(1)−Ti(1)	165.0(2)
N(1)−Ti(1)−C(3)	128.30(12)	C(3)−C(2)−C(1)	128.4(3)
C(4)−Ti(1)−C(3)	35.55(13)	C(3)−C(2)−Ti(1)	77.3(2)
C(2)−Ti(1)−C(3)	34.53(13)	C(1)−C(2)−Ti(1)	72.5(2)
C(1)−Ti(1)−C(3)	66.63(13)	C(2)−C(3)−C(4)	121.6(3)
C(21)−Al(1)−C(27)	104.26(14)	C(2)−C(3)−C(5)	118.7(4)
C(21)−Al(1)−C(33)	112.7(2)	C(4)−C(3)−C(5)	119.1(4)
C(27)−Al(1)−C(33)	114.1(2)	C(2)−C(3)−Ti(1)	68.2(2)
C(21)−Al(1)−C(1)	109.8(2)	C(4)−C(3)−Ti(1)	65.8(2)
C(27)−Al(1)−C(1)	111.0(2)	C(5)−C(3)−Ti(1)	136.0(3)
C(33)−Al(1)−C(1)	105.13(14)	C(3)−C(4)−Ti(1)	78.6(2)
N(1)−Si(1)−C(6)	92.91(14)		

Syntheses of other Zwitterions: (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_2C(CH_3)CHCH_2Al(C_6F_5)_3$) (3), $CH_2C(CH_3)CHCH_2$-$Al(C_6F_5)_3$) (3), (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_2(CH)_2CH_2B$-$(C_6F_5)_3$) (4) and (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_2C(CH_3)C$-$(CH_3)CH_2B(C_6F_5)_3$) (5). Compounds **3**−**5** were prepared and isolated as dark red crystalline complexes in an analogous fashion to that described for **1** and **2**. The spectroscopic data for these complexes are straightforward; relevant ^{11}B and ^{19}F NMR data are presented in Table 10. The X-ray crystal structures of **3** and **4** were determined and are discussed below.

Table 8. Selected Bond Lengths (Å) for **4**

Ti(1)−N(1)	1.954(3)	Si(2)−C(34)	1.879(4)
Ti(1)−C(1)	2.237(4)	N(1)−C(29)	1.507(4)
Ti(1)−C(3)	2.292(3)	C(1)−C(2)	1.377(6)
Ti(1)−C(2)	2.353(4)	C(2)−C(3)	1.355(5)
Ti(1)−C(4)	2.393(3)	C(3)−C(4)	1.493(5)
Ti(1)−H(4A)	2.32(4)	C(4)−B(5)	1.700(5)
Ti(1)−H(4B)	2.26(4)	B(5)−C(18)	1.647(5)
Si(2)−N(1)	1.760(3)	B(5)−C(12)	1.651(5)
Si(2)−C(24)	1.859(3)	B(5)−C(6)	1.659(5)
Si(2)−C(33)	1.861(4)		

Table 9. Selected Bond Angles (deg) for **4**

N(1)−Ti(1)−C(1)	104.0(2)	C(3)−C(2)−Ti(1)	70.6(2)
N(1)−Ti(1)−C(3)	136.52(12)	C(1)−C(2)−Ti(1)	68.0(2)
C(1)−Ti(1)−C(3)	64.7(2)	C(2)−C(3)−C(4)	127.6(4)
N(1)−Ti(1)−C(2)	135.17(14)	C(2)−C(3)−Ti(1)	75.5(2)
C(1)−Ti(1)−C(2)	34.8(2)	C(4)−C(3)−Ti(1)	75.1(2)
C(3)−Ti(1)−C(2)	33.90(14)	C(3)−C(4)−B(5)	111.8(3)
N(1)−Ti(1)−C(4)	102.63(11)	C(3)−C(4)−Ti(1)	67.8(2)
C(1)−Ti(1)−C(4)	82.91(14)	B(5)−C(4)−Ti(1)	178.0(2)
C(3)−Ti(1)−C(4)	37.10(11)	C(18)−B(5)−C(12)	104.2(3)
C(2)−Ti(1)−C(4)	65.18(12)	C(18)−B(5)−C(6)	113.0(3)
C(29)−N(1)−Si(2)	121.4(2)	C(12)−B(5)−C(6)	114.6(3)
C(29)−N(1)−Ti(1)	138.0(2)	C(18)−B(5)−C(4)	113.7(2)
Si(2)−N(1)−Ti(1)	100.49(13)	C(12)−B(5)−C(4)	110.6(3)
C(2)−C(1)−Ti(1)	77.2(2)	C(6)−B(5)−C(4)	101.1(2)
C(3)−C(2)−C(1)	124.8(4)	N(1)−Si(2)−C(24)	92.84(14)

Table 10. ^{19}F and ^{11}B NMR Data for Compounds **1**−**5**[a]

compd	^{19}F NMR	^{11}B NMR
1	δ −129.4 (m, *o*-F, 6F), 158.2 (m, *p*-F, 3F), 163.1 (m, *m*-F, 6F)	δ −10.4 (s)
2	δ −126.9 (m, *o*-F, 6F), 155.9 (m, *p*-F, 3F), 160.9 (m, *m*-F, 6F)	δ −15.3 (s)
3	δ −121.6 (m, *o*-F, 6F), 154.0 (m, *p*-F, 3F), 162.0 (m, *m*-F, 6F)	N/A
4	δ −127.4 (m, *o*-F, 6F), 154.7 (m, *p*-F, 3F), 160.8 (m, *m*-F, 6F)	δ −14.9 (s)
5	δ −127.0 (m, *o*-F, 6F), 155.6 (m, *p*-F, 3F), 160.8 (m, *m*-F, 6F)	δ −15.5 (s)

[a] Spectra were obtained at room temperature in C_6D_6 at 282 MHz (^{19}F) and 96 MHz (^{11}B), ^{19}F spectra were referenced to C_6F_6 (δ −162.9), and ^{11}B spectra were referenced to $BF_3 \cdot Et_2O$ (δ 0.0).

X-ray Crystal Structures of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_2C(CH_3)CHCH_2Al(C_6F_5)_3$) (3) and ($\eta^5$-$C_5Me_4SiMe_2N^tBu$)-Ti($\eta^3$-$CH_2(CH)_2CH_2B(C_6F_5)_3$) (4). Compound **3** (Figure 3) crystallizes in the orthorhombic space group *Pbca* with eight molecules per unit cell. Compound **4** (Figure 4) crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. Selected bond lengths and angles for **3** and **4** are given in Tables 6−9. The hydrogen atoms of the diene fragments were located and refined isotropically. In **3**, the $Al(C_6F_5)_3$ moiety is bound to the least sterically hindered, terminal CH_2 group of the isoprene ligand to form a zwitterionic metal allyl complex. In **4**, the $B(C_6F_5)_3$ is bound in a similar fashion. The coordination geometry about the Ti in **3** and **4** is very similar to that found in the other zwitterions **1** and **2**, with the titanium atom symmetrically bound to an η^3-allyl unit. The bond distances between the Ti atom and the η^3-allyl terminal carbons [(Ti(1)−C(2) = 2.274(4) Å and Ti(1)−C(4) = 2.223(4) Å for **3** and (Ti(1)−C(1) = 2.237(4) Å and Ti(1)−C(3) = 2.292(3) Å for **4**] are slightly shorter than the bond distance between the titanium atom and the central carbon atom [Ti(1)−C(3) = 2.389(3) Å for **3** and (Ti(1)−C(2) = 2.353(4) Å) for **4**].

Again, the allyl groups exhibit a *Z*-configuration with respect to the π bond of the allyl unit, which allows for agostic interactions to occur between the hydrogen atoms and the

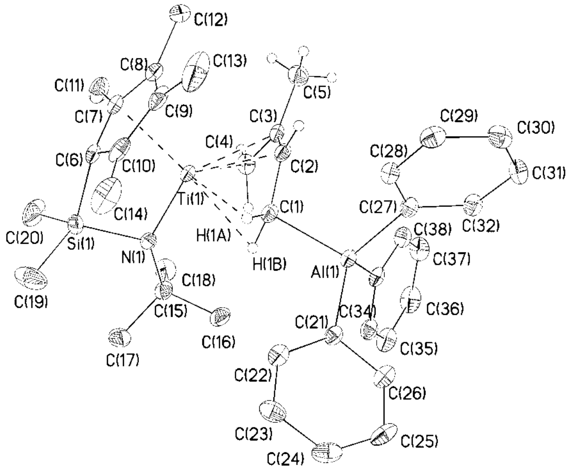

Figure 3. Molecular structure and atom numbering scheme for (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_2C(CH_3)CHCH_2Al(C_6F_5)_3$) (**3**). Thermal ellipsoids are scaled to the 30% probability level. The fluorine atoms and most hydrogen atoms have been omitted for clarity.

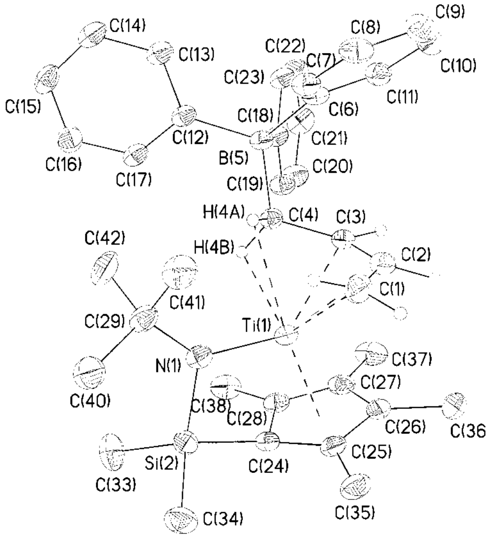

Figure 4. Molecular structure and atom labeling scheme for (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_2(CH)_2CH_2B(C_6F_5)_3$) (**4**). The thermal ellipsoids are scaled to the 30% probability level. The F atoms and methyl hydrogen atoms have been omitted for clarity.

titanium atom. Surprisingly, the related compound, Cp_2Zr(η^3-$CH_2(CH)_2CH_2B(C_6F_5)_3$),[5] exhibits an *E*-configuration, thus allowing for intramolecular Zr−F coordination. Compound **3** features Ti−H distances of 2.31(4) Å (Ti(1)−H(1A)) and 2.47(4) Å (Ti(1)−H(1B)), while **4** features Ti−H distances of 2.32(4) Å (Ti(1)−H(4A)) and 2.26(4) Å (Ti(1)−H(4B)). The Ti−C−Al/B fragments are almost linear (165.0(2)° **3** and 178.0(2)° **4**), with Ti(1)−C bond lengths of 2.310(3) Å **3** and 2.393(3) Å **4**. Again, no intramolecular Ti−F interactions are evident in the solid states of either **3** or **4**.

Experimental Section

Synthesis. All reactions were performed under a dry, oxygen-free nitrogen atmosphere or under vacuum using standard Schlenk line and drybox techniques, unless otherwise indicated. All solvents were dried prior to use by distillation from molten sodium or sodium benzophenone ketyl under nitrogen. $B(C_6F_5)_3$,[13] $Al(C_6F_5)_3(C_6H_6)$,[4] (η^5-$C_5Me_4SiMe_2N^tBu$)$ZrCl_2$,[14] (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(2,4-hexadiene),[7] (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(2-methyl-1,3-butadiene),[15] and (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(2,3-dimethylbutadiene)[15] were prepared as described in the literature. All other reagents were purchased from commercial suppliers and used without further purification.

NMR measurements were performed at room temperature on either a Varian Inova-500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) or a General Electric QE300 (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{11}B, 96 MHz; ^{19}F, 282 MHz) spectrometer. Chemical shifts are reported in ppm with positive values corresponding to downfield shifts from the standard. Chemical shifts are reported relative to tetramethylsilane (TMS, $\delta = 0.00$) and are referenced to the residual protons of C_6D_6 (^{1}H, $\delta = 7.15$, ^{13}C, $\delta = 128.0$) or CD_2Cl_2 (^{1}H, $\delta = 5.32$; ^{13}C, $\delta = 54.0$).

IR measurements were performed with a Digilab FTS-40 spectrometer as Nujol mulls with KBr plates. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. High and low resolution mass spectra were obtained with a VG Analytical ZAB2-E mass spectrometer in chemical ionization mode with CH_4 as the ionizing gas.

Synthesis of (η^5-$C_5Me_4SiMe_2N^tBu$)Zr(η^3-$CH_3(CH)_3CH_2B(C_6F_5)_3$) (1). To a solution of (η^5-$C_5Me_4SiMe_2N^tBu$)$ZrCl_2$ (1.00 g, 2.43 mmol) in hexane (30 mL) was added 1,3-pentadiene (1.25 mL, 12.5 mmol) and n-BuLi (3.04 mL, 4.87 mmol, 1.6 M in hexane) at 25 °C with stirring. The mixture was refluxed for 30 min and upon cooling to room temperature, the solution was filtered. The solution was then added to a solution of $B(C_6F_5)_3$ (1.25 g, 2.44 mmol) in hexane (30 mL) at 25 °C with stirring. The mixture was stirred for 2 h and was then concentrated to ca. 15 mL, filtered, and stored at −30 °C. X-ray quality crystals of **1** formed over several days. For **1**: mp 145−147 °C; isolated yield: 1.85 g, 83%.

^{1}H NMR (500 MHz, d_8-toluene): δ 0.00 (broad s, CH_2-diene, 1H), 0.39 (s, SiCH_3, 3H), 0.51 (s, SiCH_3, 3H), 0.84 (broad m, CH_2-diene, 1H), 0.94 (s, N^{t}Bu, 9H), 1.30 (s, CpCH_3, 3H), 1.31 (d, CH_3-diene, 3H, $^3J = 5$ Hz), 1.33 (s, CpCH_3, 3H), 1.53 (s, CpCH_3, 3H), 1.94 (s, CpCH_3, 3H), 2.44 (m, MeCH-diene, 1H), 3.63 (broad t, CH-diene, 1H), 5.04 (dd, CH-diene, 1H, $^3J = 10.5$, 12.5 Hz). ^{13}C {^{1}H} NMR (125 MHz, d$_8$-toluene): δ 6.84 (s, SiCH$_3$), 7.01 (s, SiCH$_3$), 10.08 (s, CpCH$_3$), 11.51 (s, CpCH$_3$), 12.88 (s, CpCH$_3$), 13.91 (s, CpCH$_3$), 17.04 (s, CH$_3$-diene), 34.87 (s, CH$_3$-^{t}Bu), 60.92 (s, C-^{t}Bu), 77.70 (s, CH-diene), 101.72 (s, CH-diene), 113.38 (s, C(Cp)), 131.62 (s, CMe(Cp)), 134.21 (s, CMe(Cp)), 136.55 (m, C_6F_5), 136.89 (s, CH-diene), 138.52 (m, C_6F_5), 140.52 (m, C_6F_5), 147.82 (m, C_6F_5), 149.71 (m, C_6F_5). ^{19}F NMR (282 MHz, C_6D_6): δ −129.4 (m, *o*-F, 6F), −158.2(m, *p*-F, 3F), −163.1 (m, *m*-F, 6F). ^{11}B NMR (96.3 MHz, C_6D_6): δ −10.4. IR (cm^{-1}, Nujol): 2985 (s), 2923 (s), 2851 (s), 2729 (w), 2609 (w), 2390 (w), 1645 (s), 1602 (w), 1561 (m), 1520 (s), 1455 (s), 1379 (s), 1366 (m), 1349 (w), 1309 (m), 1280 (m), 1260 (m), 1255 (m), 1231 (w), 1217 (w), 1183 (m), 1089 (s), 1017 (w), 984 (s), 966 (s), 950 (m), 925 (m), 909 (w), 882 (w), 846 (s), 817 (m), 796 (m), 788 (m), 778 (m), 764 (m), 751 (s), 732 (m), 684 (m), 663 (m), 649 (w), 621 (w), 606 (m). MS-CI (CH_4): *m*/*z* = 920. Microanalysis found: C, 50.21; H, 4.21; N, 1.62%; calcd: C, 49.56; H, 3.84; N, 1.52%.

Synthesis of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_3CH_2(CH)_3CH_2B(C_6F_5)_3$) (2). A solution of ($\eta^5$-$C_5Me_4SiMe_2N^tBu$)Ti(2,4-hexadiene) (0.51 g, 1.34 mmol) in hexane (20 mL) was added to a solution of $B(C_6F_5)_3$ (0.69 g, 1.35 mmol) in hexane (50 mL) at 25 °C with stirring. The mixture was stirred for 2 h and was then concentrated to ca. 10 mL, filtered, and stored at −30 °C. X-ray quality crystals of **2** formed over several days. For **2**: mp 133−135 °C. Isolated yield: 0.941 g, 79%. ^{1}H NMR (500 MHz, C_6D_6): δ −0.11 (broad s, CH_2−B, 1H), 0.35 (s, SiCH_3, 3H), 0.50 (s, CH_2-diene, 1H), 0.56 (s, SiCH_3, 3H), 0.66 (t, CH_3-diene, 3H, $^3J = 7.25$ Hz), 0.81 (m, CH_2−B, 1H), 1.06 (s, N^{t}Bu, 9H), 1.17 (m, CH_2-diene, 1H), 1.25 (s, CpCH_3, 3H), 1.26 (s, CpCH_3, 3H), 1.36 (s, CpCH_3, 3H), 1.83 (s, CpCH_3, 3H), 3.26 (broad t, CH-diene, 1H), 3.96 (broad t, CH-diene, 1H), 4.89 (dd, CH-diene, 1H, $^3J = 10.0$, 13.4 Hz). ^{13}C {^{1}H} (125 MHz, C_6D_6): δ 6.61 (s, SiCH$_3$), 6.79 (s, SiCH$_3$), 10.97 (s, CpCH$_3$), 12.37 (s, CpCH$_3$), 14.40 (s, CpCH$_3$), 14.51 (s, CpCH$_3$), 17.47 (s, CH$_3$-diene), 27.71 (s, CH$_2$-diene), 33.80 (s, CH$_3$-^{t}Bu), 61.40 (s, C-^{t}Bu), 99.58 (s, CH-diene), 110.78 (s, C(Cp)), 112.90 (s, CH-diene), 129.56 (s, CH-diene), 133.23 (s, CMe(Cp)),

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(13) Karl, J.; Erker, G.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165.

(14) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572.

(15) Devore, D.; Timmers, F. J.; Stevens, J. C.; Rosen, R. K. US Patent 5,486,632, 1996.

135.19 (s, *C*Me(Cp)), 136.52 (m, C_6F_5), 136.67 (s, *C*Me(Cp)), 138.26 (s, *C*Me(Cp)), 138.44 (m, C_6F_5), 140.42 (m, C_6F_5), 147.60 (m, C_6F_5), 149.51 (m, C_6F_5). ^{19}F NMR (282 MHz, C_6D_6): δ −126.9 (m, *o*-F, 6F), −155.9 (m, *p*-F, 3F), −160.9 (m, *m*-F, 6F). ^{11}B NMR (96.3 MHz, C_6D_6): δ −15.3. IR (cm^{-1}, Nujol): 2956 (s), 2854 (s), 2725 (w), 1642 (m), 1515 (m), 1461 (s), 1377 (s), 1310 (m), 1278 (m), 1255 (m), 1174 (m), 1088 (s), 976 (s), 917 (w), 844 (m), 814 (m), 797 (m), 775 (m), 765 (m), 740 (s), 728 (s), 722 (s), 682 (m), 660 (m), 642 (w). MS-CI (CH_4): *m*/*z* = 891 HRMS (CI): for $C_{39}H_{36}BF_{15}NSiTi$ ($M^+ - H$): *m*/*z* (calcd) = 890.19500; *m*/*z* (obsvd.) = 890.19501. Microanalysis found: C, 52.89; H, 4.37; N, 1.60%; calcd: C, 52.56; H, 4.19; N, 1.57%.

Synthesis of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_2C(CH_3)CHCH_2Al(C_6F_5)_3$) (3). A solution of ($\eta^5$-$C_5Me_4SiMe_2N^tBu$)Ti(2-methyl-1,3-butadiene) (0.64 g, 1.75 mmol) in toluene (20 mL) was added to a solution of $Al(C_6F_5)_3(C_6H_6)$ (1.06 g, 1.74 mmol) in toluene (75 mL) at 25 °C with stirring. The mixture was stirred for 2 h and was then concentrated to 15 mL, filtered, and stored at −30 °C. X-ray quality crystals of **3** formed over several days. Isolated yield: 1.18 g, 77%.

^{1}H NMR (500 MHz, C_6D_6): δ 0.15 (bs, C*H*$_2$−Al, 1H), 0.46 (s, SiC*H*$_3$, 3H), 0.60 (s, SiC*H*$_3$, 3H), 0.76 (bd, C*H*$_2$−Al, 1H), 1.03 (s, N^{t}Bu, 9H), 1.22 (s, CpC*H*$_3$, 3H), 1.37 (s, CpC*H*$_3$, 3H),), 1.43 (s, C*H*$_3$-diene, 3H), 1.45 (s, CpC*H*$_3$, 3H), 1.84 (s, CpC*H*$_3$, 3H), 2.25 (bd, C*H*$_2$-diene, 1H), 2.34 (bd, C*H*$_2$-diene, 1H), 4.41 (bd, C*H*-diene, 1H). ^{13}C {^{1}H} (125 MHz, C_6D_6): δ 6.70 (s, Si*C*H$_3$), 7.25 (s, Si*C*H$_3$), 10.70 (s, Cp*C*H$_3$), 11.81 (broad s, *C*H$_2$−Al), 12.26 (s, Cp*C*H$_3$), 15.17 (s, Cp*C*H$_3$), 15.36 (s, Cp*C*H$_3$), 26.62 (s, *C*H$_3$-diene), 33.75 (s, *C*H$_3$-^{t}Bu), 74.68 (s, *C*-^{t}Bu), 110.23 (s, *C*(Cp)), 110.82 (s, *C*H-diene), 124.80 (m, C_6F_5), 129.28 (s, *C*-diene), 131.25 (s, *C*Me(Cp)), 135.21 (m, C_6F_5), 136.16 (m, C_6F_5), 136.80 (s, *C*Me(Cp)), 137.12 (s, *C*Me(Cp)), 138.10 (m, C_6F_5), 138.36 (s, *C*Me(Cp)), 149.45 (m, C_6F_5), 151.23 (m, C_6F_5). ^{19}F NMR (282 MHz, C_6D_6): δ −121.6 (m, *o*-F, 6F), δ −154.0 (m, *p*-F, 3F), δ −162.0 (m, *m*-F, 6F). Microanalysis found: C, 50.17; H, 3.59; N, 1.60%; calcd: C, 51.07; H, 3.95; N, 1.57%.

Synthesis of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_2(CH)_2CH_2B(C_6F_5)_3$) (4). A solution of ($\eta^5$-$C_5Me_4SiMe_2N^tBu$)Ti(1,3-butadiene) (0.31 g, 0.88 mmol) in hexane (20 mL) was added to a solution of $B(C_6F_5)_3$ (0.46 g, 0.90 mmol) in hexane (30 mL) at 25 °C with stirring. The mixture was stirred for 2 h and was then concentrated to ca. 15 mL, filtered, and stored at −30 °C. X-ray quality crystals of **4** formed over several days. For **4**: mp 131−133 °C. Isolated yield: 0.325 g, 43%.

^{1}H NMR (500 MHz, C_6D_6): δ −0.08 (bs, C*H*$_2$−B, 1H), 0.41 (s, SiC*H*$_3$, 3H), 0.60 (s, SiC*H*$_3$, 3H), 0.75 (m, C*H*$_2$−B, 1H), 1.00 (s, N^{t}Bu, 9H), 1.19 (s, CpC*H*$_3$, 3H), 1.29 (s, CpC*H*$_3$, 6H), 1.87 (s, CpC*H*$_3$, 3H), 2.20 (dd, C*H*$_2$-diene, 1H, ^2J = 9.8 Hz, ^3J = 6.8 Hz), 2.64 (m, C*H*$_2$-diene, 1H), 4.24 (m, C*H*-diene, 1H), 5.14 (q, C*H*-diene, 1H, ^3J = 10.3 Hz). ^{13}C {^{1}H} NMR (125 MHz, C_6D_6): δ 6.52 (s, Si*C*H$_3$), 6.58 (s, Si*C*H$_3$), 10.75 (s, Cp*C*H$_3$), 12.10 (s, Cp*C*H$_3$), 14.28 (s, Cp*C*H$_3$), 15.70 (s, Cp*C*H$_3$), 33.69 (s, *C*H$_3$-^{t}Bu), 61.69 (s, *C*-^{t}Bu), 74.43 (s, *C*H$_2$-diene), 110.77 (s, *C*(Cp)), 115.43 (s, *C*H-diene), 130.07 (s, *C*H-diene), 133.12 (s, *C*Me(Cp)), 135.37 (s, *C*Me(Cp)), 136.54 (m, C_6F_5), 137.93 (s, *C*Me(Cp)), 138.16 (s, *C*Me(Cp)), 138.51 (m, C_6F_5), 140.49 (m, C_6F_5), 147.62 (m, C_6F_5), 149.52 (m, C_6F_5). ^{19}F NMR (282 MHz, C_6D_6): δ −127.4 (m, *o*-F, 6F), −154.7 (m, *p*-F, 3F), −160.8 (m, *m*-F, 6F). ^{11}B NMR (96.3 MHz, C_6D_6): δ −14.9. IR (cm^{-1}, Nujol): 2954 (s), 2923 (s), 2854 (s), 2725 (w), 1643 (m), 1515 (m), 1462 (s), 1377 (s), 1313 (m), 1280 (m), 1260 (m), 1254 (m), 1181 (m), 1087 (s), 1013 (w), 976 (s), 915 (w), 879 (w), 842 (m), 819 (m), 796 (m), 773 (m), 760 (m), 744 (s), 683 (m), 662 (m). MS-CI (CH_4): *m*/*z* = 863. Microanalysis found: C, 51.70; H, 4.70; N, 1.58%; calcd: C, 51.46; H, 4.09; N, 1.62%.

Synthesis of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(η^3-$CH_2C(CH_3)C(CH_3)CH_2B(C_6F_5)_3$) (5). A solution of ($\eta^5$-$C_5Me_4SiMe_2N^tBu$)Ti(2,3-dimethylbutadiene) (0.43 g, 1.13 mmol) in toluene (20 mL) was added to a solution of $B(C_6F_5)_3$ (0.58 g, 1.13 mmol) in toluene (30 mL) at 25 °C with stirring. The mixture was stirred for 2 h and was then concentrated to 3 mL, filtered, and stored at −30 °C. Dark red/brown crystals of **5** formed overnight. For **5**: mp 140−142 °C. Isolated yield: 0.623 g, 62%.

^{1}H NMR (500 MHz, C_6D_6): δ 0.07 (bs, C*H*$_2$−B, 1H), 0.47 (s, SiC*H*$_3$, 3H), 0.63 (s, SiC*H*$_3$, 3H), 0.85 (s, N^{t}Bu, 9H), 0.94 (m, C*H*$_2$−B, 1H), 1.20 (s, C*H*$_3$-diene, 3H), 1.25 (s, CpC*H*$_3$, 3H), 1.35 (s, C*H*$_3$-diene, 3H), 1.46 (s, CpC*H*$_3$, 3H), 1.47 (s, CpC*H*$_3$, 3H), 2.07 (s, CpC*H*$_3$, 3H), 2.36 (d, C*H*$_2$-diene, 1H, ^3J = 8.5 Hz), 2.77 (d, C*H*$_2$-diene, 1H, ^3J = 8.4 Hz). ^{13}C {^{1}H} NMR (125 MHz, C_6D_6): δ 6.40 (s, Si*C*H$_3$), 7.15 (s, Si*C*H$_3$), 11.21 (s, Cp*C*H$_3$), 12.40 (s, Cp*C*H$_3$), 14.81 (s, Cp*C*H$_3$), 15.87 (s, Cp*C*H$_3$), 31.93 (s, *C*H$_3$-^{t}Bu), 62.07 (s, *C*-^{t}Bu), 80.99 (s, *C*H$_2$-diene), 112.75 (s, *C*(Cp)), 113.61 (s, *C*Me-diene), 132.82 (s, *C*Me(Cp)), 134.23 (s, *C*Me-diene), 134.36 (s, *C*Me(Cp)), 136.54 (m, C_6F_5), 136.59 (s, *C*Me(Cp)), 137.49 (s, *C*Me(Cp)), 138.51 (m, C_6F_5), 140.49 (m, C_6F_5), 147.62 (m, C_6F_5), 149.52 (m, C_6F_5). ^{19}F NMR (282 MHz, C_6D_6): δ −127.0 (m, *o*-F, 6F), −155.6 (m, *p*-F, 3F), −160.8 (m, *m*-F, 6F). ^{11}B NMR (96.3 MHz, C_6D_6): δ −15.5. IR (cm^{-1}, Nujol): 2954 (s), 2923 (s), 2854 (s), 2725 (w), 1643 (m), 1515 (m), 1462 (s), 1377 (s), 1313 (m), 1280 (m), 1260 (m), 1254 (m), 1181 (m), 1087 (s), 1013 (w), 976 (s), 915 (w), 879 (w), 842 (m), 819 (m), 796 (m), 773 (m), 760 (m), 744 (s), 683 (m), 662 (m). MS-CI (CH_4): *m*/*z* = 891. HRMS (CI): for $C_{39}H_{37}BF_{15}NSiTi$ (M^+): *m*/*z* (calcd) = 891.2028; *m*/*z* (obsvd) = 891.2047. Microanalysis found: C, 52.59; H, 4.17; N, 1.64%; calcd: C, 52.56; H, 4.19; N, 1.57%.

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Supporting Information Available: Details of the X-ray structure determinations in CIF format of the structures of **1**, **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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