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[(Allylsilyl)(η-amidosilyl)-η^5-cyclopentadienyl] Group 4 Metal Complexes: Synthesis, Reactivity, and Olefin Polymerization

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Reaction of the dilithium salts $Li_2\{C_5H_3[1\text{-}SiMe_2(NR)][3\text{-}SiMe_2(CH_2CH{=}CH_2)]\}$ with $TiCl_3(THF)_3$ and further oxidation with $PbCl_2$ gave the allylsilyl-substituted η^1-amidosilyl-η^5-cyclopentadienyltitanium(IV) complexes $[Ti\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}NR)[SiMe_2(CH_2CH{=}CH_2)]\}Cl_2]$ (R = *t*Bu, **1**; 2,6-$Me_2C_6H_3$, **2**). Complex **1** was reacted with MeMgCl and $(CH_2Ph)MgCl$ to give the dialkyl complexes $[Ti\{\eta^5\text{-}C_5H_3\text{-}(SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)[SiMe_2(CH_2CH{=}CH_2)]\}R_2]$ (R = Me, **3**; CH_2Ph, **4**). Reaction of **1** and related monocyclopentadienyl zirconium and hafnium complexes with $Na(C_5H_5)$ gave the η-amidosilyl metallocene derivatives $[M(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)[SiMe_2(CH_2CH{=}CH_2)]\}Cl]$ (M = Ti, **5**; Zr, **6**; Hf, **7**), which were further methylated with MeMgCl and MeLi to give the methyl derivatives $[M(\eta^5\text{-}C_5H_5)\text{-}\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)[SiMe_2(CH_2CH{=}CH_2)]\}Me]$ (M = Ti, **8**; Zr, **9**). Insertion of $CN(2,6\text{-}Me_2C_6H_3)$ into the Zr−Me bond of complex **9** afforded the iminoacyl derivative $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)[SiMe_2(CH_2CH{=}CH_2)]\}\{\eta^1\text{-}CMe[N(2,6\text{-}Me_2C_6H_3)]\}]$, **10**. Methyl abstraction by reaction of the amidosilyl−metallocene compounds **8** and **9** with $B(C_6F_5)_3$ gave the ionic species $[M(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_3\text{-}(SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)[SiMe_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2)]\}]^+[MeB(C_6F_5)_3]^-$ (M = Ti, **11**; Zr, **12**) stabilized by coordination of the allyl olefinic moiety, whereas similar benzyl abstraction reactions from the dibenzyl−amidosilyl−monocyclopentadienyl compounds produced further benzyl-migratory insertion of the η^2-coordinated olefinic moiety to give the cyclic alkyl complexes $[M\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)[SiMe_2{-}CH_2{-}CH(CH_2Ph){-}CH_2]\}]^+[(CH_2Ph)B(C_6F_5)_3]^-$ (M = Zr, **13**; Hf, **14**). The new compounds were characterized by elemental analysis and NMR spectroscopy, and the molecular structures of complexes **2**, **6**, and **7** were determined by X-ray diffraction methods. The chloro complexes **1** and **5**−**7** were studied as catalyst precursors in the polymerization of different olefins and the copolymerization of ethylene/1-hexene, after activation with MAO.

Introduction

Many studies related to single-site metallocene catalysts have reported[1,2] the structure, dynamic behavior, and reactivity of the active cationic species in olefin polymerization processes, providing insights that facilitate catalyst and cocatalyst modifications designed to control the tacticity, molecular weight, chain branching, and other desirable properties in the derived polymeric materials.

Substitution of one cyclopentadienyl ring in silyl-bridged *ansa*-metallocenes by an alkylamido ligand provided new types of coordinatively unsaturated and sterically open “constrained geometry (CGC) catalysts” that can polymerize long-chain α-olefins and produce long-chain branching and ethylene copolymers with a high content of different α-olefins.[3−7]

Further studies were extended to related compounds obtained by changing the bridging silyl groups for different methylene[8] and boron bridges[9] and the amido group by other ligands with different O- (phenolate)[10] and P-donor atoms.[8d,h,11] The active species in all of these homogeneous Ziegler−Natta catalysts is

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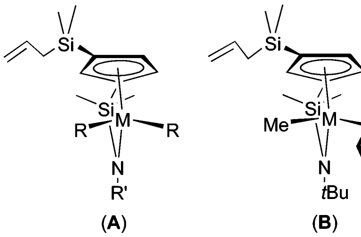
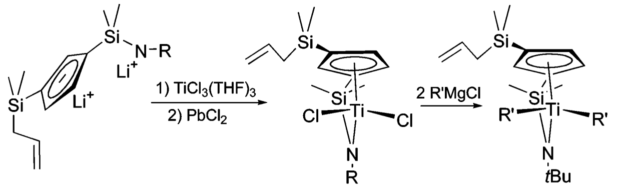
a cationic coordinatively unsaturated 12-electron d^0 alkyl compound.[5h,12] Coordination of the olefin to this unsaturated metal cation followed by migratory insertion of the alkyl group is assumed to be the initiation step of the polymerization process.

We reported[13] that the doubly silylamido-bridged cyclopentadienyl zirconium cation $[Zr\{(\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}NtBu)_2\}]^+$ polymerizes ethene despite being free from the alkyl group required for insertion. Similar results were also reported[14] for silylamido−zirconocenium cations $[Zr\{(\eta^5\text{-}C_5Me_4(SiMe_2\text{-}\eta^1\text{-}NtBu)\}(\eta^5\text{-}C_5H_5)]$ and for imino cobalt(I) $[Co\{2,6\text{-}(CR'{=}NAr)_2C_5H_3N\}R]^+$ compounds,[15] for which different activation mechanisms, involving coordination of the olefin and nucleophilic attack by the alkyl group abstracted by the Lewis acid cocatalyst, through formation of a bimetallic complex[16] and activation by Li^+ [17] have been proposed.

Scheme 1



Scheme 2



R = *t*Bu **1**; 2,6-$Me_2C_6H_3$ **2**   R' = Me **3**; CH_2Ph **4**

We were interested in studying the formation of catalytically active group 4 metal cationic species stabilized by coordination of the ring-tethered silylallyl olefinic moiety of η-amidosilyl−cyclopentadienyl and −metallocene compounds. We have recently reported[18] the synthesis of dialkyl zirconium and hafnium compounds of the type represented in Scheme 1 (A) as precursors of the η-amidosilyl−cyclopentadienyl cations. In this paper we report the synthesis of the related titanium compounds, new η-amidosilyl−metallocene derivatives of the type represented in Scheme 1 (B) and the behavior of both types of compound in reactions with $B(C_6F_5)_3$ and as catalysts for olefin polymerization processes following activation with MAO.

Results and Discussion

The method based on the reaction of the metal(IV) chlorides with the dilithium salt of the disilylated cyclopentadienyl ring was initially used to transfer this ligand in order to synthesize the zirconium and hafnium derivatives reported recently.[18] However similar reaction with $TiCl_4$ led to a mixture containing reduction products from which the desired compound could be isolated only in very low yields.

As shown in Scheme 2, the most convenient method was direct access to the titanium(III) complex by reaction of the dilithium salt $Li_2\{C_5H_3[1\text{-}SiMe_2(NR)][3\text{-}SiMe_2(CH_2CH{=}CH_2)]\}$ (R = *t*Bu) with $[TiCl_3(THF)_3]$ and further oxidation with $PbCl_2$ to give the η-amidosilyl complex $[Ti\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}NtBu)\text{-}[SiMe_2(CH_2CH{=}CH_2)]\}Cl_2]$, **1**, in high yield. Complex **1** is highly soluble in hexane and could not be recrystallized and

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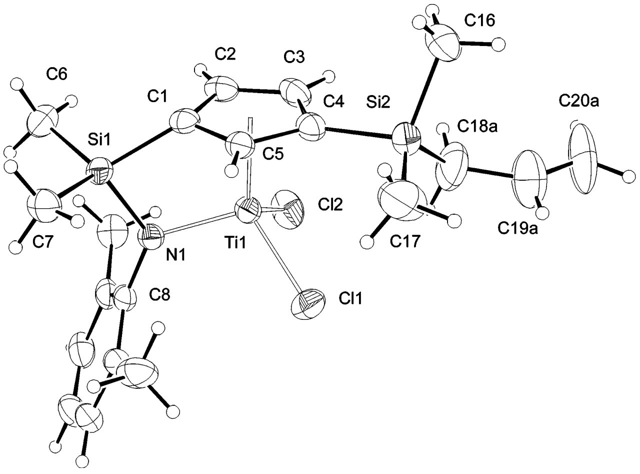

Figure 1. ORTEP drawing of the molecular structure of **2** in the solid state. Thermal ellipsoids are drawn at the 30% probability level. Only one of the two disordered allyl groups is represented.

was isolated as a dark oily product characterized by elemental analysis and NMR spectroscopy. We reported[18] that the X-ray diffraction analysis of the related zirconium complex showed a dinuclear structure with two bridging chloro ligands that alleviate the electron deficiency of the otherwise monomeric 14-electron compound, which would be the more favorable disposition expected for the smaller titanium atom. Nevertheless the spectroscopic data for this type of asymmetric molecule did not allow the two structural assignments to be distinguished. For this reason, in the hope of obtaining improved crystallinity[19] we decided to prepare the analogous (2,6-dimethylphenyl)amido compound using the same method with the appropriate dilithium salt (R = 2,6-$Me_2C_6H_3$). The new silylamido complex [Ti{(η^5-C_5H_3[$SiMe_2$-η^1-N(2,6-$Me_2C_6H_3$)][$SiMe_2(CH_2CH{=}CH_2)$]}Cl_2], **2**, was isolated as a solid characterized by elemental analysis and NMR spectroscopy and was recrystallized from a hexane solution cooled to −35 °C to give yellow crystals appropriate for X-ray diffraction studies.

As expected, the molecular structure of **2** corresponds to a monomeric complex where the titanium atom is in a pseudo-tetrahedral environment defined by two chlorine atoms, the centroid of the cyclopentadienyl ring, and the nitrogen atom of the silylamido group (Figure 1). From a comparison of 13 structures[20] of $TiCl_2$ complexes containing a linked amidosilylcyclopentadienyl ligand, all the metrical parameters of **2** are within the expected range (Table 1). The complex shows a chirality plane (the disubstituted Cp ring), and in the structure both the *M* and *P* isomers are present.

As shown in Scheme 2, the synthesis of the alkyl titanium derivatives was carried out by the reaction of **1** with 2 equiv of alkylating agents such as MeLi, MeMgCl, $(CH_2Ph)MgCl$, and $(CH_2Ph)_2Mg(THF)_2$. The dialkyl complexes [Ti{η^5-$C_5H_3(SiMe_2$-η^1-N*t*Bu)[$SiMe_2(CH_2CH{=}CH_2)$]}R_2] (R = Me, **3**; CH_2Ph, **4**) are highly soluble in hexanes and were isolated as black or red, oily products in 60% yield after purification and characterized by elemental analyses and NMR spectroscopy.

Several features of the ^1H and ^{13}C NMR spectra of the dichloro and dialkyl complexes **1**−**4** are worthy of note. The enantiotopic faces of the 1,3-disilylated cyclopentadienyl ligand with two different silyl groups are responsible for the asymmetry in these molecules, all of which probably show the same molecular structure found for complex **2** by X-ray diffraction studies. Therefore four occasionally overlapped methyl signals (^1H and ^{13}C) attributed to the bridging η-amidosilyl and to the allylsilyl groups are observed, together with an ABC spin system for the cyclopentadienyl ring protons and five ^{13}C resonances for the ring carbon atoms (see Experimental Section). In addition, all of the complexes show the signals typical of the allyl moiety and the N-bonded *t*Bu or 2,6-$Me_2C_6H_3$ groups.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Compounds 2, 6, and 7[a]

	M = Ti	M = Zr	M = Hf
M−Cl(1)	2.2620(14)	2.4628(14)	2.433(2)
M−Cl(2)	2.2552(16)		
M-CE(1)	2.026(4)	2.208(3)	2.199(10)
M-CE(2)		2.256(4)	2.241(16)
M−N	1.912(3)	2.116(2)	2.099(6)
C(1)−C(2)	1.426(5)	1.413(3)	1.433(12)
C(2)−C(3)	1.406(5)	1.409(3)	1.396(11)
C(3)-C4)	1.410(5)	1.414(3)	1.414(12)
C(4)−C(5)	1.428(4)	1.416(3)	1.457(11)
C(1)−C(5)	1.405(5)	1.418(3)	1.427(11)
Si(1)−C(1)	1.864(4)	1.863(3)	1.858(9)
Si(1)-N	1.760(3)	1.736(2)	1.732(6)
Si(1)−C(6)	1.852(4)	1.866(3)	1.866(10)
Si(1)−C(7)	1.848(4)	1.856(3)	1.858(11)
N−C(8)	1.434(4)	1.500(3)	1.527(11)
Si(2)−C(4)	1.867(4)	1.874(2)	1.876(8)
Cl(1)−M−Cl(2)	101.49(5)		
Cl(1)−M−CE(2)		106.07(9)	106.0(3)
Cl(1)−M−CE(1)	117.85(10)	107.81(7)	107.9(2)
Cl(2)−M−CE(1)	117.01(11)		
CE(2)−M−CE(1)		125.45(14)	125.2(5)
Cl(1)−M−N	106.12(8)	100.25(7)	99.6(2)
N−M−CE(1)	105.46(14)	100.12(9)	100.7(3)
N−M−CE(2)		114.33(11)	114.6(3)
Cl(2)−M−N	108.23(9)		
Si(1)−N−M	107.34(14)	105.12(10)	104.9(3)
Si(1)−N−C(8)	126.3(2)	121.79(15)	122.1(5)
C(8)−N−M	126.29(19)	132.90(15)	132.8(5)

[a] CE(1) and CE(2) are the centroids of the Cp rings C(1),C(2),C(3),C(4),C(5) and C(17),C(18),C(19),C(20),C(21), respectively.

The ^{13}C resonance due to the bridge-bonded ring C_{ipso} is shifted highfield (δ 110.2−112.6), as reported[5c] for chelate "constrained geometry" compounds. The π-bonding contribution of the bridging *tert*-butylamido ligand measured by the $\Delta\delta$ = (δ $C_{tert}-C_{Me}$) values[21] is higher in the more acidic titanium complexes **1**−**4** (32.0−24.7) than in related zirconium and hafnium compounds (24.7−19.9), which are in the known range for this type of cyclopentadienylsilyl-η^1-amido complex, ranging from 24.7 (R = CH_2Ph) for the more donating to 32.0 (R = Cl) for the less donating substituents.

As illustrated in Scheme 2 the dialkyl complexes **3** and **4** show two nonequivalent alkyl groups, one of which is located under the allylsilyl ring substituent. The two ^1H NMR singlets observed for the titanium-bonded methyl groups of **3** are shifted lowfield (δ 0.68, 0.74) with respect to the values observed for related zirconium and hafnium compounds ($<\delta$ 0.15), and similar displacement was observed for the ^{13}C NMR signals (Ti: δ 51.9, 59.1; Zr: δ 35.1, 35.7; Hf: δ 47.1, 48.0). Similar behavior was observed for the dibenzyl complex **4**, where the ^1H NMR spectrum shows four doublets for the methylenic protons of two nonequivalent benzyl groups. The value of the

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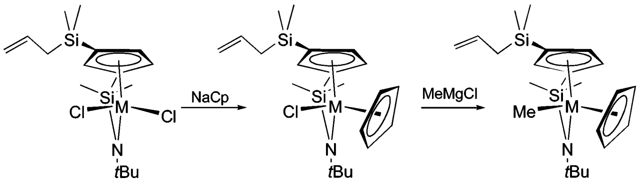
(19) Humphries, M. J.; Green, M. L. H.; Douthwaite, R. E.; Rees, L. H. *J. Chem. Soc., Dalton Trans.* **2000**, 4555−4562.

(20) Retrieved from CCDC data bank (ConQuest 1.8, 2006).

(21) (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123−175. (b) Wigley, D. E. Prog. *Inorg. Chem.* **1994**, *42*, 239. (c) Humphries, M. J.; Green, M. L. H.; Leech, M. A.; Gibson, V. C.; Jolly, M.; Williams, D. N.; Elsegood, M. R. J.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **2000**, 4044−4051.

Scheme 3



M = Ti **5**, Zr **6**, Hf **7**

M = Ti **8**, Zr **9**

geminal coupling constant[22] ($^2J_{H-H}$ = 9.5−10.8 Hz) and the lowfield-shifted signal due to the phenyl C_{ipso} atom (δ 149.3, 149.9) are consistent with the η^1-coordination of the benzyl ligand.[5h,22]

The reactivity of these cyclopentadienyl silyl-η-amido titanium complexes is remarkably different from that observed for the related zirconium and hafnium compounds. Products of insertion into the Ti−alkyl groups and of further C−C coupling reactions similar to those reported for methyl and benzyl zirconium and hafnium compounds could not be isolated when complexes **3** and **4** were treated with $CN(2,6\text{-}Me_2C_6H_3)$, although reactions do occur to give mixtures that could not be resolved. Similarly **3** and **4** reacted when a 1:1 molar ratio of the boron Lewis acid $B(C_6F_5)_3$ was added to their CD_2Cl_2 or C_6D_5Br solutions to give a mixture of compounds, which could not be identified by NMR spectroscopy.

As shown in Scheme 3, metathesis reactions of **1** and related monocyclopentadienyl zirconium and hafnium complexes with 1 equiv of sodium cyclopentadienide gave the η-amidosilyl-metallocene compounds $[M(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}NtBu)[SiMe_2(CH_2CH{=}CH_2)]\}Cl]$ (M = Ti, **5**; Zr, **6**; Hf, **7**), which were isolated as red (Ti) and yellow (Zr, Hf) solids in 70−80% yield and characterized by elemental analysis, NMR spectroscopy, and X-ray diffraction methods (**6** and **7**). These coordinatively saturated complexes are asymmetric molecules, which in addition to the enantiotopic face of the disilylated cyclopentadienyl ring show the metal as a second stereogenic center, which would be expected to give an enantiomeric pair of diastereomers. However their ^{1}H and ^{13}C NMR spectra demonstrated the presence of one unique isomer, indicating that the metathesis is a highly diastereoselective reaction that takes place at the nonprotected chloro ligand to give the more stable isomer in which the more bulky Cp ligand is distant from the allyl−silyl substituent. The ^{1}H NMR spectra showed the expected ABC spin system for the cyclopentadienyl ring protons, and the ^{13}C NMR spectrum showed the C_{ipso} signal of the η^1-amidosilyl chelate shifted highfield (δ 113.4−111.8) and a π-bonding contribution slightly lower ($\Delta\delta$ = 31.2, 23.7, 22.6) than those observed[18] for the dichloro compounds.

Compounds **6** and **7** are isostructural, and the metal atoms are tetrahedrally coordinated by a chlorine atom, the centroid of a Cp ring, the nitrogen atom, and the centroid of the amidosilylcyclopentadienyl ligand (Figure 2). The complexes are chiral due to a chirality plane as in **2** and a chirality center (the metal atoms); in the structure both the isomers are present. Bond distances and angles for the two compounds are comparable, and the coordination bond distances of Hf are systematically shorter than those of Zr (Table 1). The N atom shows sp^2 hybridization and the Si−N distances in **6** and **7** are shorter than in **2**, indicative of less delocalization in the double bond in the Si−N−M system.

The titanium complex **5** reacted slowly with 1 equiv of a 3 M THF solution of MeMgCl, affording the methyl derivative $[M\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}NtBu)[SiMe_2(CH_2CH{=}CH_2)]\}(\eta^5\text{-}C_5H_5)\text{-}Me]$ (M = Ti, **8**) as a light orange solid in 70% yield after purification, whereas LiMe was required with the zirconium complex **6** to give the methyl derivative (M = Zr, **9**) as a yellow, oily product, and no reaction was observed with either alkylating agent with the hafnium derivative **7**. The related benzyl complexes could not be obtained when the same reactions were carried out with alkylating agents such as $(CH_2Ph)MgCl$ and $(CH_2Ph)_2Mg$, probably due to the steric demands of the bulky (allylsilyl)metallocene−amido ligands with the comparatively small titanium center and the less reactive chloro−zirconium and −hafnium bonds. The methyl compounds **8** and **9** were identified by elemental analysis and NMR spectroscopy. Their spectroscopic NMR behavior is analogous to that described for **5** and **6** with one additional resonance at δ 0.13, 0.12 (^{1}H) and δ 29.7, 20.0 (^{13}C) for the titanium- and zirconium-bonded methyl group, respectively.

We reported[18] that $CN(2,6\text{-}Me_2C_6H_3)$ was easily inserted into the metal−methyl bonds of the dimethyl amidosilyl−cyclopentadienyl zirconium and hafnium complexes at room temperature to give the corresponding di(iminoacyl) compounds, which were further transformed into the C−C coupled metalladiazacyclopentene derivatives. In contrast, no reaction was observed when toluene solutions of the methyl complexes **5**−**7** were treated with excess isocyanides at room temperature, as expected for 18-electron molecules if the amido group is considered as a three-electron donor ligand. However, the zirconium complex **6** reacted slowly with 1 equiv of $CN(2,6\text{-}Me_2C_6H_3)$ when the toluene solution was heated to 85 °C, and the transformation into the iminoacyl complex $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}NtBu)[SiMe_2(CH_2-CH{=}CH_2)]\}\{\eta^1\text{-}CMe[N(2,6\text{-}Me_2C_6H_3)]\}]$, **10**, was complete after 4 days. Under similar conditions an unidentified mixture of decomposition products was obtained for the titanium complex **5** and the unreacted starting compound was recovered for the related hafnium derivative **7**. The ν(C=N) IR absorption band at 1580 cm^{-1} and the ^{13}C NMR resonance at δ 247.5 observed for complex **10** are consistent with the proposed η^1-coordination of the iminoacyl ligand (see Scheme 4), although appropriate crystals for a molecular structure determination could not be obtained to confirm a definitive structural assignment.

Formation of Cationic Complexes. When C_6D_6/C_6D_5Br (4:1) solutions of complexes **8** and **9** in Teflon-valved NMR tubes were treated with 1 equiv of $B(C_6F_5)_3$, formation of the salts $[M(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}NtBu)[SiMe_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2)]\}]^+[(CH_3)B(C_6F_5)_3]^-$ (M = Ti, **11**; Zr, **12**) was immediately observed (Scheme 4). These salts contained the 18-electron cations, and the presence of the free methylborate anion was demonstrated by the small $\Delta\delta = \delta_{para} - \delta_{meta}$ difference of 2.5 and 2.7, respectively, observed in the ^{19}F NMR spectrum,[23] despite the broad lowfield-shifted boron−methyl signal at δ 1.27 observed in the ^{1}H NMR spectrum, which could suggest the presence of the titanium-coordinate anion.

In addition to the stereogenic centers described above for the unique isomer of the neutral complexes **8** and **9**, coordination of the enantiotopic face of the silylallyl olefinic moiety introduces a new stereogenic principle which does not modify the NMR behavior of the cationic species, as the dynamic olefin coordination−decoordination process is in rapid exchange at room temperature.[1d] The asymmetry of the unique isomer observed for the cationic complexes **11** and **12** is consistent with the four Si−Me singlets and the ring protons ABC spin system observed in their ^{1}H NMR spectra. All of these

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[22] Crowther, D. J.; Jordan, R. F.; Baenziger, N. C.; Verma, A. *Organometallics* **1990**, *9*, 2574−2580.

[23] Horton, A. D. *Organometallics* **1996**, *15*, 2675−2677.

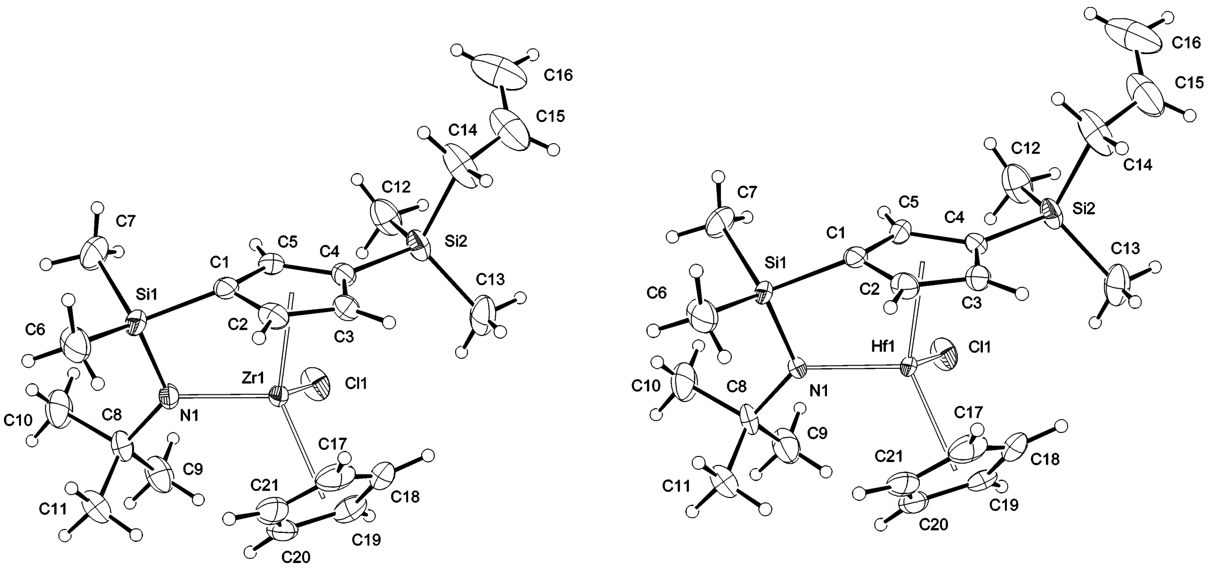
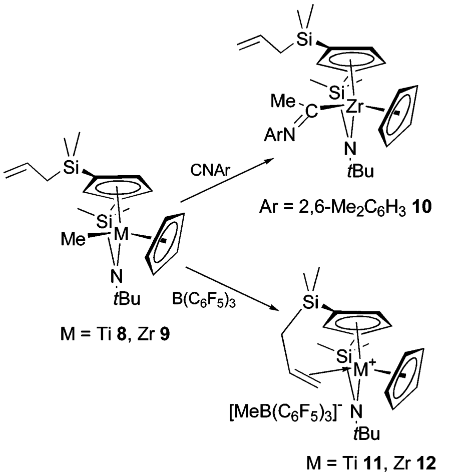


Figure 2. 2. ORTEP drawing of the molecular structures of complexes **6** and **7**. Thermal ellipsoids are drawn at the 30% probability level.

Scheme 4



resonances are shifted highfield with respect to values found for the related neutral methyl compounds. The difference $\Delta\delta = (\delta C_{tert} - \delta C_{Me})$ found in the ^{13}C NMR spectra for the two resonances of the *t*Bu amido group indicated a metal−amido π-bonding contribution which was lower in the titanium complex **11** (23.6) than in the zirconium compound **12** (27.6), whereas the reverse behavior was observed[18] for the related neutral compounds **8** and **9**.

The most remarkable spectroscopic feature found in the ^1H NMR spectra was that the cationic complexes **11** and **12** did not show the typical signals of the silyl−allylic moiety but rather five new multiplets studied by TOCSY-1D, HMQC-2D, and HMBC-2D were observed, with the protons bound to the external alkenic carbon shifted highfield (δ 3.73, 3.80 for **11**, δ 4.07, 4.34 for **12**), whereas the proton bound to the internal carbon was shifted lowfield to δ 6.10 (**11**) and δ 6.67 (**12**). The ^{13}C NMR spectrum was consistent with the known asymmetric coordination of the olefin to the metal center.[1d]

Similar reactions were carried out by addition of 1 equiv of $B(C_6F_5)_3$ to C_7D_8 solutions of the dibenzyl complexes $[M(\eta^5\text{-}C_5Me_4SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)(CH_2Ph)_2]$ (M = Zr, Hf) previously reported,[18] using Teflon-valved NMR tubes, and monitored by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. An immediate reaction occurred at 25 °C to give the new ionic species $[M\{\eta^5\text{-}C_5H_3\text{-}(SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)[SiMe_2{-}CH_2{-}CH(CH_2Ph)\text{-}\eta^1\text{-}CH_2]\}]^+[(CH_2\text{-}Ph)B(C_6F_5)_3]^-$ (M = Zr, **13**; Hf, **14**), which were characterized by NMR spectroscopy as compounds containing metallacyclic alkyl cations, analogous to the hafnocenium cation reported previously[24] (see Scheme 5). This behavior may be explained by considering that benzyl abstraction following addition of the Lewis acid is a stereoselective reaction that affords one single diastereomer, either by abstraction of the benzyl group located under the silylallyl substituent that occupies the vacant coordination site directly or after epimerization. The enantiotopic face of the olefinic moiety is a new stereogenic center which could give two *exo*- and *endo*-diastereoisomers, although the behavior observed indicates that only the *endo*-isomer facilitates olefin insertion to give the metallacyclic cation, resulting from the migratory insertion of the alkene into the metal−benzyl bond of the *endo*-isomer through bonding the metal to the terminal methylenic group and the remaining benzyl group to the *endo* position of the internal carbon atom. Formation of the cationic species is consistent with the presence of two broad resonances in the ^1H NMR spectra between δ 3.20 and 3.35 due to the B-benzyl methylenic protons. The most relevant feature of these spectra is the absence of the low-field signal for the internal olefinic CH group, whereas signals [δ 1.80 (**13**) and 1.90 (**14**) (^1H) and δ 41.4 (**13**) and 41.3 (**14**) (^{13}C)] are observed for a tertiary CH group. Complexes **13** and **14** were characterized by DEPT, HOMO-DEC, TOCSY-1D, NOESY-1D, and HMQC-2D NMR techniques as one single diastereoisomer that shows the expected seven signals of the cyclic alkyl system. A slight stabilization produced by interaction of the coordinatively unsaturated 12-electron cation with the benzyl borate anion is consistent with the ^{19}F NMR spectra, which show values of $\Delta\delta(F_{meta} - F_{para}) = 4.2$ (**13**) and 4.1 (**14**).

Polymerization Studies. The chloro complexes **1** and **5**−**7** were studied as catalysts for polymerization of different olefins. Complex **1** activated with MAO (molar ratio [Al]:[Ti] = 500) was investigated for ethylene polymerization in toluene solution using 27.0 μmol of the catalyst precursor **1** under 3 atm of ethylene at 30 °C for 30 min. The catalytic activity found under these conditions (6.9 kg PE·Ti $mol^{-1}\cdot atm^{-1}\cdot h^{-1}$) was comparable to that measured for $[Ti(\eta^5\text{-}C_5Me_4SiMe_2\text{-}\eta^1\text{-}N\mathit{t}Bu)Cl_2]$ (8.6 kg PE·Ti $mol^{-1}\cdot atm^{-1}\cdot h^{-1}$) used as a reference under the same conditions. Thermal analysis of the resulting polymer studied by DSC showed a unimodal melting peak at 133 °C with ΔH

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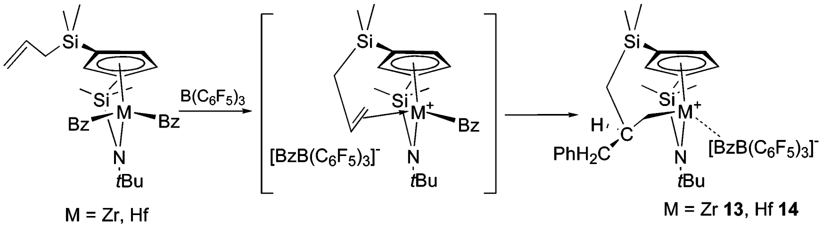
[24] Martínez, G.; Royo, P. *Organometallics* **2005**, *24*, 4782−4787.

Scheme 5



= 158 J•g^{-1}. The molecular weight determined by GPC gave a M_w value of 1.50 × 10^5 g•mol^{-1} with a rather narrow value of polydispersity (M_w/M_n = 2.2). These physical properties are consistent with the formation of HDPE in the presence of a single-site active species. We did not observe any catalytic activity when we used the resulting polyethylene as a self-immobilized heterogeneous catalyst[25] assumed to contain the incorporated active catalyst.

Complex **1** was also studied as an ethylene/1-hexene copolymerization catalyst. The catalytic activity (50 kg polymer•Ti mol^{-1}•atm^{-1}•h^{-1}) measured after addition of 5 mL of 1-hexene to the toluene solution of **1** using the same conditions described above was higher than that observed for the polymerization of ethylene due to the known comonomer effect.[26] In addition, the resulting copolymer showed a higher molecular weight M_w of 2.58 × 10^5 g•mol^{-1} with a narrow polydispersity of 2.7 determined by GPC and a much lower melting point of 102 °C determined by DSC; both features are consistent with the incorporation of 1-hexene and polymeric chain branching.

In contrast to the typical Ziegler−Natta catalyst precursor dichloro complex **1**, the metallocenes **5**−**7** are monoalkyl complexes that should follow a different polymerization mechanism, as the active species does not contain the alkyl−metal cation required for the migratory insertion. It would be expected that activation of **5**−**7** with MAO should give alkyl-free cationic species like those obtained when $B(C_6F_5)_3$ was used as the Lewis acid. Similar monoalkyl precursors have been reported previously[13,14,15a,17] and their catalytic activities explained by assuming that alkyl transfer from the counteranion to the coordinated olefin and from the metal to the Lewis acid are the steps responsible for the polymerization process. It has also been reported[17] that the cobalt(I)−Me complexes gave active catalysts upon activation with Li$^+$. For comparison, we studied the behavior of complexes **5**−**7** in the polymerization and copolymerization of ethylene. Complex **5**, activated with MAO and used under the conditions described above for **1**, displayed a very high activity with rapid precipitation of polyethylene. In order to reduce the total mass of insoluble material by producing a smaller amount of polyethylene to ensure that the homogeneity of the reaction system was maintained, shorter reaction times and lower temperatures were used. The activity measured at 30 °C and 3 atm of ethylene after 5 min was on the order of 100 times higher (604 kg PE•Ti mol^{-1}•atm^{-1}•h^{-1}) than that observed for **1**, whereas it decreased to almost one-half (326 kg PE•Ti mol^{-1}•atm^{-1}•h^{-1}) at 10 °C after 5 min. The much higher molecular weight (M_w = 1.241 × 10^6 g•mol^{-1} for PE at 30 °C and 7.297 × 10^6 g•mol^{-1} for PE at 10 °C) of the resulting polyethylenes with narrow polydispersities (M_w/M_n = 1.9−4.0) measured by GPC and their significantly higher melting points (134 and 137 °C, respectively) determined by DSC are the typical characteristics of HDPE. Lower activities were found for the zirconium **6** (95 kg PE•Zr mol^{-1}•atm^{-1}•h^{-1}) and hafnium **7** (32 kg PE•Hf mol^{-1}•atm^{-1}•h^{-1}) complexes at 30 °C and 3 atm of ethylene after 10 min.

Complex **5** was also studied as catalyst precursor to copolymerize ethylene and 1-hexene when 5 mL of the monomers was added to toluene solutions of **5** activated with MAO under the conditions described above. It was observed not only that the catalytic activity was decreased (99 kg•mol^{-1}) but also that the molecular weight of the polymer product was lower (M_w = 30,184) with a broad polydispersity of 5.5 and lower melting point (123 °C).

Both complexes **1** and **5** show similar rather low catalytic activities for propylene (14.0 kg PE•Ti mol^{-1}•atm^{-1}•h^{-1} for **1** and 20.0 kg PE•Ti mol^{-1}•atm^{-1}•h^{-1} for **5**) and styrene (73.0 kg PE•Ti mol^{-1}•h^{-1} for **1** and 27.0 kg PE•Ti mol^{-1}•h^{-1} for **5**) polymerization, which were essentially independent of the temperature and gave atactic PP and PS. Thermal analysis studied by DSC gave T_g values of 104 and 111 °C for **1** and **5**, respectively, although these polymers were not further characterized.

Conclusions

New dichloro (**1**, **2**) and dialkyl (**3**, **4**) titanium(IV) complexes ligated by chelating η^1-amidosilyl-η^5-(allylsilyl) cyclopentadienyl ligands were synthesized and characterized. The metathesis reactions of the titanium complex **1** and related dichloro zirconium and hafnium complexes with sodium cyclopentadienide were highly *diastereoselective* reactions that gave one unique isomer characterized as the chloro-η^1-amidosilylmetallocenes (**5**−**7**), in which the chloro ligand and the ring-substituted allylsilyl group are located in an eclipsed orientation, whereas the bulky unsubstituted cyclopentadienyl ligand is staggered with respect to the allylsilyl substituent. The same structural disposition is preserved in the subsequent methylation (**8**, **9**), isocyanide insertion (**10**), and methyl abstraction reactions (**11**, **12**) in which the methyl or iminoacyl groups and the coordinated alkene moiety occupy the coordination site of the substituted chloro ligand.

We have demonstrated that abstraction of the methyl group by reaction of the η^1-amidosilylmetallocene compounds **5**−**7** with the Lewis acid $B(C_6F_5)_3$ afforded cationic species that were saturated by η^2-coordination of the silylallyl ring-substituent olefinic moiety to the metal. The saturated character of this cationic complex is consistent with the highfield-shifted resonances observed in its ^{1}H NMR spectrum, the lower π-bonding participation observed for the silyl−η^1-amido ligand in the ^{13}C NMR spectrum, and the presence of $[MeB(C_6F_5)_3]^-$ as a free counteranion observed in the ^{19}F NMR spectrum. More reactive were the related electron-deficient cationic compounds generated when the dibenzyl cyclopentadienyl amido zirconium and hafnium complexes were treated with $B(C_6F_5)_3$ to give similar alkene-coordinate complexes that immediately are transformed into metallacyclic alkyl complexes (**13**, **14**) by alkene insertion into the metal−benzyl bond.

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[25] Alt, H. G. *Dalton Trans.* **2005**, *32713276*.

[26] Chien, J. C. W.; Nozaki, T. *J. Polym. Sci. A: Polym. Chem.* **1993**, *31*, 227−237.

The dichloro η^1-amidosilyl-η^5-(allylsilyl)cyclopentadienyl titanium complex **1** activated with MAO showed a reasonable catalytic activity for ethylene polymerization and for ethylene/1-hexene copolymerization; the properties of the resulting polymers were consistent with the presence of a single-site active species. The most remarkable feature was the considerably higher catalytic activity found when the chloro η^1-amidosilyltitanocene **5** precursor was activated with MAO, which, despite giving a methyl-free active species, showed a catalytic activity 100 times higher than that observed for the typically Z-N catalyst **1**, to give polyethylene of very high molecular weight (10 times higher than that obtained with **1**). It was also more active than **1** for copolymerization of ethylene/1-hexene, although the activity was much lower than that observed for polymerization of ethylene. Compared with the titanium complex (**5**), the catalytic activity of the related zirconium (**6**) and hafnium (**7**) complexes for ethylene polymerization was lower and both catalysts **1** and **5** also showed rather low activities for propylene and styrene polymerization.

Experimental Section

General Comments. All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques, and solvents were distilled from appropriate drying agents prior to use. NMR spectra were recorded at 300.13 (^{1}H), 188.31 (^{19}F), and 75.47 (^{13}C) MHz at ambient probe temperature (23 °C) on a Varian Unity 300 (^{1}H, ^{13}C, ^{19}F) spectrometer. Chemical shifts (δ) are given in ppm, relative to internal TMS (^{1}H and ^{13}C) or external $CFCl_3$ (^{19}F), and all coupling constants are given in hertz. Deuterated solvents were stored over activated 4 Å molecular sieves in Teflon-valved flasks and previously degassed by several freeze−pump−thaw cycles. Elemental analyses were performed on a Perkin-Elmer 240C microanalyzer. Compounds $TiCl_3(THF)_3$[27] $B(C_6F_5)_3$,[28] dilithium salts $Li_2\{C_5H_3[1\text{-}SiMe_2(NR)][3\text{-}SiMe_2(CH_2CH{=}CH_2)]\}$ (R = *t*Bu; 2,6-$Me_2C_6H_3$),[18] and complexes $[M(\eta^5\text{-}C_5Me_4SiMe_2\text{-}\eta^1\text{-}N{t}Bu)(CH_2Ph)_2]$ (M = Zr, Hf)[18] were prepared by literature methods. $TiCl_4$ (Aldrich), MgClMe (Aldrich), and $MgCl(CH_2Ph)$ (Aldrich) were purchased from commercial sources and used without further purification. Polyethylene molecular weights were determined by gel permeation chromatography on a Waters Alliance GPCV 2000 using trichlorobenzene as solvent. DSC measurements were performed on a Perkin-Elmer DSC6 calorimeter.

$[Ti\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N{t}Bu)[SiMe_2(CH_2CH{=}CH_2)]\}Cl_2]$ (1). THF (50 mL) was added to a mixture of the dilithium salt $Li_2\{C_5H_3[1\text{-}SiMe_2(N{t}Bu)][3\text{-}SiMe_2(CH_2CH{=}CH_2)]\}$[18] (1.65 g, 5.40 mmol) and $TiCl_3(THF)_3$ (2.00 g, 5.40 mmol) cooled to −78 °C. The reaction mixture was stirred while it was warmed to room temperature, and then it was treated with $PbCl_2$ (1.50 g, 5.40 mmol) and stirred for 8 h. The solvent was removed under reduced pressure, and the residue was extracted into hexanes (2 × 25 mL). After filtration the solvent was removed under vacuum to give a black, oily residue identified as compound **1** (1.73 g, 4.2 mmol, 78%).

Data for **1**: ^{1}H NMR ($CDCl_3$): 0.32 (s, 3H, Si*Me*$_2$), 0.34 (s, 3H, Si*Me*$_2$), 0.60 (s, 3H, Si*Me*$_2$), 0.62 (s, 3H, Si*Me*$_2$), 1.44 (s, 9H, *tBu*), 1.78 (m, 2H, SiC*H*$_2$), 4.89 (m, 2H, CH=C*H*$_2$), 5.78 (m, 1H, C*H*=CH$_2$), 6.47 (t, 1H, C$_5$*H*$_3$), 6.60 (t, 1H, C$_5$*H*$_3$), 7.17 (t, 1H, C$_5$*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): −3.4 (Si*Me*$_2$), −3.0 (Si*Me*$_2$), 0.1 (Si*Me*$_2$), 0.7 (Si*Me*$_2$), 24.0 (Si*C*H$_2$), 32.2 (C*Me*$_3$), 64.2 (*C*Me$_3$), 112.6 (C_{ipso}, C$_5$H$_3$), 114.0 (CH=*C*H$_2$), 129.5, 131.3, 132.6 (*C*$_5$H$_3$), 134.0 (*C*H=CH$_2$), 139.6 (C_{ipso}, C$_5$H$_3$). Anal. Calcd for $C_{16}H_{29}Cl_2NSi_2Ti$ (410.37): C 46.83, H 7.12, N 3.41. Found: C 46.86, H 7.31, N 3.49.

$[Ti\{\eta^5\text{-}C_5H_3[SiMe_2\text{-}\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)][SiMe_2(CH_2CH{=}CH_2)]\}Cl_2]$ (2). The procedure used for **1**, but starting from $Li_2[C_5H_3\{1\text{-}SiMe_2[N(2,6\text{-}Me_2C_6H_3)]\}\{3\text{-}SiMe_2(CH_2CH{=}CH_2)\}]$[18] (2.00 g, 5.66 mmol), $TiCl_3(THF)_3$ (2.10 g, 5.66 mmol), and $PbCl_2$ (1.57 g, 5.66 mmol), gave **2** as a crystalline yellow solid after concentration and cooling to −35 °C (0.78 g, 1.70 mmol, 30%).

Data for **2**: ^{1}H NMR ($CDCl_3$): 0.35 (s, 3H, Si*Me*$_2$), 0.39 (s, 3H, Si*Me*$_2$), 0.55 (s, 3H, Si*Me*$_2$), 0.58 (s, 3H, Si*Me*$_2$), 1.80 (m, 2H, SiC*H*$_2$), 1.99 (s, 3H, *Me*$_2$C$_6$H$_3$), 2.04 (s, 3H, *Me*$_2$C$_6$H$_3$), 4.90 (m, 2H, CH=C*H*$_2$), 5.77 (m, 1H, C*H*=CH$_2$), 6.74 (t, 1H, C$_5$*H*$_3$), 6.88 (t, 1H, C$_5$*H*$_3$), 7.00 (t, 1H, C$_5$*H*$_3$), 6.90−7.10 (m, 3H, C$_6$*H*$_5$). ^{13}C-{^{1}H} NMR ($CDCl_3$): −2.9 (Si*Me*$_2$), −2.6 (Si*Me*$_2$), −0.2 (Si*Me*$_2$), −0.1 (Si*Me*$_2$), 20.1 (*Me*$_2$C$_6$H$_3$), 20.2 (*Me*$_2$C$_6$H$_3$), 24.4 (Si*C*H$_2$), 114.6 (CH{^{1}H}*C*H$_2$), 115.3 (C_{ipso}, C$_5$H$_3$), 126.3, 129.2, 129.3 (*C*$_5$H$_3$), 129.9, 130.2, 130.5 (*C*$_6$H$_3$), 134.3 (*C*H=CH$_2$), 139.6 (C_{ipso}, C$_5$H$_3$), 131.7, 131.9, 148.3 (C_{ipso}, C$_6$H$_3$). Anal. Calcd for $C_{20}H_{29}Cl_2NSi_2Ti$ (458.41): C 52.40, H 6.38, N 3.06. Found: C 52.02, H 6.51, N 2.88.

$[Ti\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N{t}Bu)[SiMe_2(CH_2CH{=}CH_2)]\}Me_2]$ (3). A solution of compound **1** (1.50 g, 3.60 mmol) in hexane (50 mL) was cooled at −78 °C and then treated with a 3 M THF solution of MgClMe (2.40 mL, 7.30 mmol). The reaction mixture was stirred while it was warmed to room temperature, and stirring was continued for an additional 16 h. The solution was filtered and the solvent was removed under vacuum to give an oily, black residue, which after being cooled at −35 °C and dried under vacuum was identified as **3** (0.80 g, 2.20 mmol, 60%).

Data for **3**: ^{1}H NMR (C_6D_6): 0.29 (s, 9H, Si*Me*$_2$), 0.31 (s, 3H, Si*Me*$_2$), 0.68 (s, 3H, Ti*Me*$_2$), 0.74 (s, 3H, Ti*Me*$_2$), 1.52 (s, 9H, *tBu*), 1.74 (m, 2H, SiC*H*$_2$), 4.97 (m, 2H, CH=C*H*$_2$), 5.85 (m, 1H, C*H*=CH$_2$), 6.03 (t, 1H, C$_5$*H*$_3$), 6.15 (t, 1H, C$_5$*H*$_3$), 6.98 (t, 1H, C$_5$*H*$_3$), ^{13}C{^{1}H} NMR (C_6D_6): −2.9 (Si*Me*$_2$), −2.7 (Si*Me*$_2$), 0.9 (Si*Me*$_2$), 1.6 (Si*Me*$_2$), 25.0 (Si*C*H$_2$), 34.4 (C*Me*$_3$), 51.9 (Ti*Me*$_2$), 59.1 (*C*Me$_3$), 107.3 (C_{ipso}, C$_5$H$_3$), 113.9 (CH=*C*H$_2$), 126.3, 126.9, 127.3 (*C*$_5$H$_3$), 131.1 (C_{ipso}, C$_5$H$_3$), 134.7 (*C*H=CH$_2$). Anal. Calcd for $C_{18}H_{35}NSi_2Ti$ (369.53): C 58.51, H 9.55, N 3.79. Found: C 58.72, H 9.46, N 3.85.

$[Ti\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N{t}Bu)[SiMe_2(CH_2CH{=}CH_2)]\}(CH_2C_6H_5)_2]$ (4). The same procedure described for **3** was followed using a 2 M THF solution of $MgCl(CH_2C_6H_5)$ (3.70 mL, 7.30 mmol) to give **4** as a red residue after being dried under vacuum (1.10 g, 2.10 mmol, 60%).

Data for **4**: ^{1}H NMR (C_6D_6): 0.22 (s, 3H, Si*Me*$_2$), 0.24 (s, 3H, Si*Me*$_2$), 0.26 (s, 3H, Si*Me*$_2$), 0.27 (s, 3H, Si*Me*$_2$), 1.42 (s, 9H, *tBu*), 1.65 (m, 2H, SiC*H*$_2$), 2.38 (d, 1H, ^2J = 10.8, C*H*$_2$Ph), 2.52 (d, 1H, ^2J = 9.5, C*H*$_2$Ph), 2.83 (d, 1H, ^2J = 9.5, C*H*$_2$Ph), 2.89 (d, 1H, ^2J = 10.8, C*H*$_2$Ph), 4.91 (m, 2H, CH=C*H*$_2$), 5.75 (m, 1H, C*H*=CH$_2$), 5.79 (t, 1H, C$_5$*H*$_3$), 6.07 (t, 1H, C$_5$*H*$_3$), 6.75 (t, 1H, C$_5$*H*$_3$), 6.86−7.04 (m, 10H, C$_6$*H*$_5$). ^{13}C{^{1}H} NMR (C_6D_6): −2.6 (Si*Me*$_2$), −2.3 (Si*Me*$_2$), 0.8 (Si*Me*$_2$), 1.6 (Si*Me*$_2$), 25.0 (Si*C*H$_2$), 34.4 (C*Me*$_3$), 61.6 (*C*Me$_3$), 79.3 (Ti*C*H$_2$), 84.4 (Ti*C*H$_2$), 110.2 (C_{ipso}, C$_5$H$_3$), 114.0 (CH=*C*H$_2$), 122.1, 122.7, 125.9 (*C*$_5$H$_3$), 127.8, 128.3, 128.7, 129.5, 132.1 (*C*$_6$H$_5$), 134.4 (C_{ipso}, C$_5$H$_3$), 134.5 (*C*H=CH$_2$), 149.3, 149.9 (C_{ipso}, C$_6$H$_5$). Anal. Calcd for $C_{30}H_{43}NSi_2Ti$ (521.73): C 69.06, H 8.31, N 2.68. Found: C 68.87, H 8,09, N 2.65.

$[Ti(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N{t}Bu)[SiMe_2(CH_2CH{=}CH_2)]\}Cl]$ (5). THF (50 mL) was added to a mixture of complex **1** (1.00 g, 2.40 mmol) and $Na(C_5H_5)$ (0.23 g, 2.60 mmol) at room temperature. After stirring this mixture for 18 h the solvent was removed under reduced pressure, the residue was extracted into hexanes (2 × 25 mL), and the NaCl was separated by filtration. The resulting solution was concentrated to 3 mL and then cooled to −35 °C to give a red solid, which after filtration and drying under vacuum was identified as complex **5** (0.74 g, 1.70 mmol, 70%).

Data for **5**: ^{1}H NMR (C_6D_6): 0.21 (s, 3H, Si*Me*$_2$), 0.28 (s, 3H, Si*Me*$_2$), 0.42 (s, 3H, Si*Me*$_2$), 0.59 (s, 3H, Si*Me*$_2$), 1.32 (s, 9H, *tBu*),

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1.77 (m, 2H, SiC*H*$_2$), 4.95 (m, 2H, CH═C*H*$_2$), 5.45 (t, 1H, C$_5$*H*$_3$), 5.83 (m, 1H, C*H*═CH$_2$), 5.95 (s, 5H, C$_5$*H*$_5$), 6.20(t, 1H, C$_5$*H*$_3$), 7.20 (t, 1H, C$_5$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): −2.4 (Si*Me*$_2$), −2.1 (Si*Me*$_2$), 1.8 (Si*Me*$_2$), 4.8 (Si*Me*$_2$), 24.9 (Si*C*H$_2$), 34.3 (C*Me*$_3$), 65.5 (*C*Me$_3$), 113.4 (*C*$_{\mathrm{ipso}}$, C$_5$H$_3$), 113.7 (CH═*C*H$_2$), 113.9 (*C*$_5$H$_5$), 128.3, 135.0 (*C*$_5$H$_3$), 134.4 (*C*$_{\mathrm{ipso}}$, C$_5$H$_3$), 135.8 (*C*H═CH$_2$). Anal. Calcd for C$_{21}$H$_{34}$ClNSi$_2$Ti (440.01): C 57.32, H 7.79, N 3.18. Found: C 57.56, H 7.95, N 3.08.

[Zr(η^5-C$_5$H$_5$){η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH═CH$_2$)]}Cl] (6). The same procedure described for **5** was followed using THF (40 mL), [Zr{η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH═CH$_2$)]}Cl$_2$] (1.00 g, 2.20 mmol), and Na(C$_5$H$_5$) (0.21 g, 2.40 mmol) to give a light yellow crystalline solid identified as complex **6** (0.85 g, 1.76 mmol, 80%).

Data for **6**: ^{1}H NMR (C$_6$D$_6$): 0.29 (s, 3H, Si*Me*$_2$), 0.33 (s, 3H, Si*Me*$_2$), 0.42 (s, 3H, Si*Me*$_2$), 0.58 (s, 3H, Si*Me*$_2$), 1.26 (s, 9H, *tBu*), 1.75 (m, 2H, SiC*H*$_2$), 4.96 (m, 2H, CH═C*H*$_2$), 5.65 (t, 1H, C$_5$*H*$_3$), 5.80 (m, 1H, C*H*═CH$_2$), 6.02 (s, 5H, C$_5$*H*$_5$), 6.18 (t, 1H, C$_5$*H*$_3$), 6.89 (t, 1H, C$_5$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): −2.6 (Si*Me*$_2$), −2.0 (Si*Me*$_2$), 2.2 (Si*Me*$_2$), 4.9 (Si*Me*$_2$), 24.9 (Si*C*H$_2$), 35.0 (C*Me*$_3$), 58.7 (*C*Me$_3$), 113.8 (*C*$_{\mathrm{ipso}}$, C$_5$H$_3$), 114.3 (CH═*C*H$_2$), 112.3 (*C*$_5$H$_5$), 124.4, 128.3, 130.3 (*C*$_5$H$_3$), 130.1 (*C*$_{\mathrm{ipso}}$, C$_5$H$_3$), 134.8 (*C*H═CH$_2$). Anal. Calcd for C$_{21}$H$_{34}$ClNSi$_2$Zr (483.35): C 52.18, H 7.09, N 2.90. Found: C 52.22, H 7.31, N 2.84.

[Hf(η^5-C$_5$H$_5$){η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH═CH$_2$)]}Cl] (7). The same procedure described for **5** was followed using THF (45 mL), [Hf{η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH═CH$_2$)]}Cl$_2$] (1.50 g, 2.80 mmol), and Na(C$_5$H$_5$) (0.26 g, 2.90 mmol) to give a yellow crystalline solid identified as complex **7** (1.20 g, 2.20 mmol, 80%).

Data for **7**: ^{1}H NMR (C$_6$D$_6$): 0.30 (s, 3H, Si*Me*$_2$), 0.34 (s, 3H, Si*Me*$_2$), 0.41 (s, 3H, Si*Me*$_2$), 0.58 (s, 3H, Si*Me*$_2$), 1.26 (s, 9H, *tBu*), 1.75 (m, 2H, SiC*H*$_2$), 4.96 (m, 2H, CH═C*H*$_2$), 5.58 (t, 1H, C$_5$*H*$_3$), 5.81 (m, 1H, C*H*═CH$_2$), 5.96 (s, 5H, C$_5$*H*$_5$), 6.16 (t, 1H, C$_5$*H*$_3$), 6.77 (t, 1H, C$_5$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): −2.6 (Si*Me*$_2$), −2.0 (Si*Me*$_2$), 2.4 (Si*Me*$_2$), 5.1 (Si*Me*$_2$), 25.0 (Si*C*H$_2$), 35.3 (C*Me*$_3$), 57.9 (*C*Me$_3$), 112.5 (*C*$_{\mathrm{ipso}}$, C$_5$H$_3$), 113.8 (CH═*C*H$_2$), 111.5 (*C*$_5$H$_5$), 124.8, 128.3, 129.0 (*C*$_5$H$_3$), 134.9 (*C*H═CH$_2$). Anal. Calcd for C$_{21}$H$_{34}$ClNSi$_2$Ti (570.62): C 44.20, H 6.01, N 2.45. Found: C 44.24, H 6.12, N 2.42.

[Ti(η^5-C$_5$H$_5$){η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH═CH$_2$)]}Me] (8). A solution of complex **5** (1.00 g, 2.44 mmol) in diethyl ether (50 mL) at room temperature was treated with a 3 M THF solution of MgClMe (0.80 mL, 2.44 mmol) and the mixture stirred for 18 h. The solvent was removed from the resulting suspension, and the residue was extracted into hexanes (2 × 30 mL). Following filtration, the solution was concentrated and cooled to −35 °C to give a light orange solid, which was separated by filtration and dried under vacuum to be identified as complex **8** (0.72 g, 1.71 mmol, 70%).

Data for **8**: ^{1}H NMR (C$_6$D$_6$): 0.13 (s, 3H, Ti*Me*), 0.23 (s, 3H, Si*Me*$_2$), 0.39 (s, 3H, Si*Me*$_2$), 0.48 (s, 3H, Si*Me*$_2$), 0.59 (s, 3H, Si*Me*$_2$), 1.23 (s, 9H, *tBu*), 1.64 (m, 2H, SiC*H*$_2$), 4.93 (m, 2H, CH═C*H*$_2$), 5.56 (t, 1H, C$_5$*H*$_3$), 5.75 (s, 5H, C$_5$*H*$_5$), 5.77 (m, 1H, C*H*═CH$_2$), 5.78 (t, 1H, C$_5$*H*$_3$), 6.82 (t, 1H, C$_5$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): −2.5 (Si*Me*$_2$), −2.4 (Si*Me*$_2$), 3.0 (Si*Me*$_2$), 3.7 (Si*Me*$_2$), 25.0 (Si*C*H$_2$), 29.7 (Ti*Me*), 35.0 (C*Me*$_3$), 62.1 (*C*Me$_3$), 109.3 (*C*$_{\mathrm{ipso}}$, C$_5$H$_3$), 110.5 (*C*$_5$H$_5$), 113.8 (CH═*C*H$_2$), 127.1, 132.5 (*C*$_5$H$_3$), 134.8 (*C*H═CH$_2$). Anal. Calcd for C$_{22}$H$_{37}$NSi$_2$Ti (419.59): C 62.98, H 8.89, N 3.34. Found: C 62.86, H 8.97, N 3.23.

[Zr(η^5-C$_5$H$_5$){η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH═CH$_2$)]}Me] (9). The same procedure described for **8** was followed using complex **6** (1.20 g, 2.48 mmol) in diethyl ether (40 mL) and a 1.6 M diethyl ether solution of LiMe (1.50 mL, 2.48 mmol) to give a yellow solid identified as complex **9** (0.80 g, 1.74 mmol, 70%).

Data for **9**: ^{1}H NMR (C$_6$D$_6$): 0.12 (s, 3H, Zr*Me*), 0.14 (s, 3H, Si*Me*$_2$), 0.26 (s, 3H, Si*Me*$_2$), 0.42 (s, 3H, Si*Me*$_2$), 0.57 (s, 3H, Si*Me*$_2$), 1.17 (s, 9H, *tBu*), 1.63 (m, 2H, SiC*H*$_2$), 4.96 (m, 2H, CH═C*H*$_2$), 5.77 (t, 1H, C$_5$*H*$_3$), 5.83 (m, 1H, C*H*═CH$_2$), 5.85 (t, 1H, C$_5$*H*$_3$), 5.87 (s, 5H, C$_5$*H*$_5$), 6.75 (t, 1H, C$_5$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): −2.7 (Si*Me*$_2$), −2.3 (Si*Me*$_2$), 2.3 (Si*Me*$_2$), 2.6 (Si*Me*$_2$), 20.0 (Zr*Me*), 25.1 (Si*C*H$_2$), 35.4 (C*Me*$_3$), 57.1 (*C*Me$_3$), 109.7 (*C*$_5$H$_5$), 111.8 (*C*$_{\mathrm{ipso}}$, C$_5$H$_3$), 113.7 (CH═*C*H$_2$), 121.7, 128.8 (*C*$_5$H$_3$), 134.8 (*C*H═CH$_2$). Anal. Calcd for C$_{22}$H$_{37}$NSi$_2$Zr (462.93): C 57.08, H 8.06, N 3.03. Found: C 56.88, H 8.15, N 2.87.

[Zr(η^5-C$_5$H$_5$){η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$CH═CH$_2$)]}{CMe[N(2,6-Me$_2$C$_6$H$_3$)]}] (10). A toluene (30 mL) solution containing a mixture of **9** (0.70 g, 1.51 mmol) and CN(2,6-Me$_2$C$_6$H$_3$) 0.20 g, 1.51 mmol) was heated at 85 °C for 4 days in a Teflon-valved Schlenk vessel, and the solvent was then removed under vacuum. The residue was extracted into pentane (30 mL), and the solvent was removed under vacuum to give compound **10** as an orange, oily solid (0.67 g, 1.13 mmol, 75%).

Data for **10**: ^{1}H NMR (C$_6$D$_6$): 0.32 (s, 3H, Si*Me*$_2$), 0.35 (s, 3H, Si*Me*$_2$), 0.63 (s, 3H, Si*Me*$_2$), 0.67 (s, 3H, Si*Me*$_2$), 1.20 (s, 9H, *tBu*), 1.68 (m, 2H, SiC*H*$_2$), 1.86 (s, 3H, *Me*$_2$C$_6$H$_3$), 1.89 (s, 3H, *Me*$_2$C$_6$H$_3$), 2.02 (s, 3H, *Me*C═N), 4.95 (m, 2H, CH═C*H*$_2$), 5.83 (m, 1H, C*H*═CH$_2$), 5.92 (s, 5H, C$_5$*H*$_5$), 5.95 (m, 1H, C$_5$*H*$_3$), 6.33 (m, 1H, C$_5$*H*$_3$), 6.43 (m, 1H, C$_5$*H*$_3$), 6.80−7.00 (m, 3H, C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): −2.9 (Si*Me*$_2$), −2.4 (Si*Me*$_2$), 3.1 (Si*Me*$_2$), 7.0 (Si*Me*$_2$), 18.5 (*Me*$_2$C$_6$H$_3$), 20.2 (*Me*C═N), 24.5 (*Me*$_2$C$_6$H$_3$), 25.7 (Si*C*H$_2$), 35.5 (C*Me*$_3$), 55.7 (*C*Me$_3$), 108.7 (*C*$_5$H$_5$), 113.8 (CH═*C*H$_2$), 117.6 (*C*$_{\mathrm{ipso}}$, C$_5$H$_3$), 118.9, 120.9, 126.2 (*C*$_5$H$_3$), 125.2−129.0 (C$_6$H$_3$), 134.8 (*C*H═CH$_2$), 146.7 (N*C*), 247.5 (η^1-*C*Me). Anal. Calcd for C$_{31}$H$_{46}$N$_2$Si$_2$Zr (594.11): C 62.67, H 7.80, N 4.72. Found: C 62.84, H 7.41, N 4.72.

[Ti(η^5-C$_5$H$_5$){η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$-η^2-CH═CH$_2$)]}]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (11). An equimolar mixture of complex **8** (20.00 mg, 0.048 mmol) and B(C$_6$F$_5$)$_3$ (24.00 mg, 0.048 mmol) was added to a Teflon-valved NMR tube to which a mixture of C$_6$D$_6$/BrC$_6$D$_5$ (4:1) was transferred under vacuum at 25 °C to give a red solution, in which the presence of complex **11** was confirmed by the following NMR data.

Data for **11**: ^{1}H NMR (C$_6$D$_6$/BrC$_6$D$_5$, 4:1): 0.02 (s, 6H, Si*Me*$_2$), 0.08 (s, 3H, Si*Me*$_2$), 0.47 (s, 3H, Si*Me*$_2$), 1.01 (s, 9H, *tBu*), 1.27 (br, 3H, B*Me*), 1.43 (m, 1H, SiC*H*$_2$), 1.70 (m, 1H, SiC*H*$_2$), 3.73 (m, 1H, *J* = 8.7, ═C*H*$_{\mathrm{cis}}$), 3.80 (m, 1H, *J* = 17.1, ═C*H*$_{\mathrm{trans}}$), 4.85 (t, 1H, C$_5$*H*$_3$), 5.68 (s, 5H, C$_5$*H*$_5$), 6.10 (m, 1H, ═C*H*$_{\mathrm{int}}$), 6.48 (t, 1H, C$_5$*H*$_3$), 6.56 (t, 1H, C$_5$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$/BrC$_6$D$_5$, 4:1): −4.7 (Si*Me*$_2$), 0.1 (Si*Me*$_2$), 1.0 (Si*Me*$_2$), 4.7 (Si*Me*$_2$), 11.0 (B*Me*), 26.7 (Si*C*H$_2$), 34.2 (C*Me*$_3$), 57.8 (*C*Me$_3$), 93.6 (═*C*$_{\mathrm{ext}}$H$_2$), 113.7 (*C*$_5$H$_5$), 113.3, 133.3, 134.4 (*C*$_5$H$_3$), 135.6, 147.5, 150.8 (*C*$_6$F$_5$), 165.5 (═*C*H$_{\mathrm{int}}$). ^{19}F NMR (C$_6$D$_6$/BrC$_6$D$_5$, 4/1): −132.1 (*o*-C$_6$F$_5$), −164.4 (*p*-C$_6$F$_5$), −166.9 (*m*-C$_6$F$_5$).

[Zr(η^5-C$_5$H$_5$){η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$(CH$_2$-η^2-CH═CH$_2$)]}]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (12). The same procedure described for **11** was followed using complex **9** (40.00 mg, 0.086 mmol) and B(C$_6$F$_5$)$_3$ (44.00 mg, 0.086 mmol) to give an orange solution in which the presence of complex **12** was confirmed by the following NMR data.

Data for **12**: ^{1}H NMR (C$_6$D$_6$/BrC$_6$D$_5$, 4:1): 0.02 (s, 3H, Si*Me*$_2$), 0.10 (s, 3H, Si*Me*$_2$), 0.16 (s, 3H, Si*Me*$_2$), 0.44 (s, 3H, Si*Me*$_2$), 0.94 (s, 9H, *tBu*), 1.15 (br, 3H, B*Me*), 1.63 (m, 1H, SiC*H*$_2$), 1.92 (m, 1H, SiC*H*$_2$), 4.07 (d, 1H, *J* = 8.1, ═C*H*$_{\mathrm{cis}}$), 4.34 (d, 1H, *J* = 16.8, ═C*H*$_{\mathrm{trans}}$), 5.31 (t, 1H, C$_5$*H*$_3$), 5.81 (s, 5H, C$_5$*H*$_5$), 6.36 (m, 2H, C$_5$*H*$_3$), 6.67 (m, 1H, ═C*H*$_{\mathrm{int}}$). ^{13}C{^{1}H} NMR (C$_6$D$_6$/BrC$_6$D$_5$, 4:1): −4.3 (Si*Me*$_2$), 0.9 (Si*Me*$_2$), 1.3 (Si*Me*$_2$), 4.7 (Si*Me*$_2$), 11.6 (B*Me*), 28.9 (Si*C*H$_2$), 35.0 (C*Me*$_3$), 57.8 (*C*Me$_3$), 97.8 (═*C*$_{\mathrm{ext}}$H$_2$), 112.7 (*C*$_5$H$_5$), 113.7, 130.3, 131.1 (*C*$_5$H$_3$), 135.7, 138.9, 147.7, 151.0 (*C*$_6$F$_5$), 168.1 (═*C*H$_{\mathrm{int}}$). ^{19}F NMR (C$_6$D$_6$/BrC$_6$D$_5$, 4:1): −132.8 (*o*-C$_6$F$_5$), −163.9 (*p*-C$_6$F$_5$), −166.6 (*m*-C$_6$F$_5$).

[Zr{η^5-C$_5$H$_3$(SiMe$_2$-η^1-N*t*Bu)[SiMe$_2$−CH$_2$−CH(CH$_2$Ph)-η^1-CH$_2$]}][(CH$_2$Ph)B(C$_6$F$_5$)$_3$] (13). The same procedure described for **11** was followed using [Zr(η^5-C$_5$Me$_4$SiMe$_2$-η^1-N*t*Bu)(CH$_2$Ph)$_2$]

Table 2. Crystallographic Data for 2, 6, and 7

	2	6	7
empirical formula	$C_{20}H_{29}Cl_2NSi_2Ti$	$C_{21}H_{34}ClNSi_2Zr$	$C_{21}H_{34}ClNSi_2Hf$
fw	458.42	483.34	570.61
temp (K)	293(2)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst, space group	monoclinic, $P2_1/c$	monoclinic, $C2/c$	monoclinic, $C2/c$
a (Å)	13.118(6)	25.800(12)	25.784(12)
b (Å)	12.472(5)	11.597(8)	11.589(6)
c (Å)	15.820(8)	20.893(10)	20.647(10)
α (deg)	90	90	90
β (deg)	111.22(2)	128.79(2)	127.95(2)
γ (deg)	90	90	90
volume (Å^3)	2412.8(19)	4873(5)	4865(4)
Z, calcd density [Mg m^{-3}]	4, 1.262	8, 1.318	8, 1.558
absorp coeff (mm^{-1})	0.680	0.665	4.502
F(000)	960	2016	2272
cryst size (mm)	0.30 × 0.25 × 0.20	0.45 × 0.35 × 0.25	0.30 × 0.27 × 0.25
θ range for data collection (deg)	3.00 to 25.00	3.00 to 30.00	3.00 to 24.00
index ranges	$-15 \leq h \leq 14$, $0 \leq k \leq 14$, $0 \leq l \leq 18$	$-36 \leq h \leq 28$, $0 \leq k \leq 16$, $0 \leq l \leq 29$	$-29 \leq h \leq 23$, $0 \leq k \leq 13$, $0 \leq l \leq 23$
no. of reflns collected/unique	4317/4186 [R(int) = 0.0895]	7294/7123 [R(int) = 0.0236]	3735/3623 [R(int) = 0.0314]
no. of data/restraints/params	4186/6/269	7123/0/242	3623/0/242
goodness-of-fit on F^2	0.981	0.913	1.015
final R indices [$I > 2\sigma(I)$] (R_1, wR_2)[a]	0.0572, 0.1497	0.0334, 0.0707	0.0351, 0.0767
R indices (all data) (R_1, wR_2)[a]	0.0818, 0.1650	0.0770, 0.0807	0.0542, 0.0858
largest diff peak and hole (e Å^{-3})	0.470 and −0.693	0.580 and −0.462	1.308 and −0.806

[a] GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

(20.00 mg, 0.035 mmol) and $B(C_6F_5)_3$ (18.00 mg, 0.035 mmol) in C_7D_8 to give an orange solution, in which the presence of complex **13** was confirmed by the following NMR data.

Data for **13**: ^{1}H NMR (C_7D_8): −0.03 (s, 3H, SiMe_2), 0.04 (s, 3H, SiMe_2), 0.07 (s, 3H, SiMe_2), 0.14 (s, 3H, SiMe_2), 0.16 (m, 1H, SiCH_2), 0.47 (m, 1H, ZrCH_2), 0.58 (s, 9H, *tBu*), 0.63 (m, 1H, ZrCH_2), 0.79 (m, 1H, SiCH_2), 1.80 (m, 1H, *CH*), 2.16 (m, 1H, CH_2Ph), 2.54 (m, 1H, CH_2Ph), 3.20 (br, 1H, BCH_2Ph), 3.34 (br, 1H, BCH_2Ph), 5.36 (m, 1H, C_5H_3), 5.69 (m, 1H, C_5H_3), 6.03 (m, 1H, C_5H_3), 5.87 (m, 1H, p-BCH_2Ph), 6.09 (m, 1H, *m*-BCH_2Ph), 6.18 (m, 1H, *m*-BCH_2Ph), 6.71 (m, 1H, o-BCH_2Ph), 6.89 (m, 1H, *o*-BCH_2Ph), 6.96−7.14 (m, 5H, C_6H_5). ^{13}C{^{1}H} NMR (C_7D_8): −1.7 (SiMe_2), −0.1 (SiMe_2), 1.0 (SiMe_2), 4.1 (SiMe_2), 24.3 (SiCH_2), 33.8 (CMe_3), 35.0 (BCH_2Ph), 41.4 (*C*H), 51.6 (CH_2Ph), 59.2 (CMe_3), 63.5 (ZrCH_2), 117.6 (C_5H_3), 118.0 ($C_{ipso,}$ C_5H_3), 120.3, 121.8 (C_5H_3), 124.5−131.1 (C_6H_5), 134.9, 139.6, 146.3, 150.9 (C_6F_5), 141.4 ($C_{ipso,}$ CH_2Ph), 158.8 ($C_{ipso,}$ BCH_2Ph). ^{19}F NMR (C_7D_8): −131.1 (*o*-C_6F_5), −161.0 (*p*-C_6F_5), −165.2 (*m*-C_6F_5).

[Hf{η^5-C_5H_3($SiMe_2$-η^1-N*t*Bu)[$SiMe_2$−CH_2−CH(CH_2Ph)-η^1-CH_2]}][(CH_2Ph)B(C_6F_5)$_3$] (14). The same procedure described for **11** was followed using [Hf(η^5-$C_5Me_4SiMe_2$-η^1-N*t*Bu)(CH_2Ph)$_2$] (80.00 mg, 0.120 mmol) and $B(C_6F_5)_3$ (60.00 mg, 0.120 mmol) in C_7D_8 to give an orange solution, in which the presence of complex **14** was confirmed by the following NMR data.

Data for **14**: ^{1}H NMR (C_7D_8): −0.03 (s, 3H, SiMe_2), 0.02 (s, 3H, SiMe_2), 0.10 (s, 3H, SiMe_2), 0.16 (s, 3H, SiMe_2), 0.17 (m, 1H, SiCH_2), 0.24 (m, 1H, HfCH_2), 0.36 (m, 1H, HfCH_2), 0.58 (s, 9H, *tBu*), 0.82 (m, 1H, SiCH_2), 1.90 (m, 1H, *CH*), 2.23 (m, 1H, CH_2Ph), 2.55 (m, 1H, CH_2Ph), 3.20 (br, 1H, BCH_2Ph), 3.35 (br, 1H, BCH_2Ph), 5.30 (m, 1H, C_5H_3), 5.71 (m, 1H, C_5H_3), 5.91 (m, 1H, p-BCH_2Ph), 5.99 (m, 1H, C_5H_3), 6.16 (m, 2H, m-BCH_2Ph), 6.75 (m, 1H, o-BCH_2Ph), 6.83 (m, 1H, o-BCH_2Ph), 6.92−7.16 (m, 5H, C_6H_5). ^{13}C{^{1}H} NMR (C_7D_8): −1.7 (SiMe_2), −0.1 (SiMe_2), 1.1 (SiMe_2), 4.2 (SiMe_2), 24.2 (SiCH_2), 34.1 (CMe_3), 35.0 (BCH_2Ph), 41.3 (*C*H), 53.0 (CH_2Ph), 58.5 (CMe_3), 64.8 (HfCH_2), 117.0 (C_5H_3), 117.5 ($C_{ipso,}$ C_5H_3), 119.9, 121.9 (C_5H_3), 124.8−131.2 (C_6H_5), 135.8, 139.2, 147.0, 150.1 (C_6F_5), 141.6 (C_{ipso}, CH_2Ph), 159.4 ($C_{ipso,}$ BCH_2Ph). ^{19}F NMR (C_7D_8): −131.0 (*o*-C_6F_5), −161.1 (*p*-C_6F_5), −165.2 (*m*-C_6F_5).

X-ray Structure Determination for Complexes [Ti{η^5-C_5H_3-[$SiMe_2$-η^1-N(2,6-$Me_2C_6H_3$)][$SiMe_2$($CH_2CH{=}CH_2$)]}Cl_2] (2), [Zr(η^5-C_5H_5){η^5-C_5H_3($SiMe_2$-η^1-N*t*Bu)[$SiMe_2$ ($CH_2CH{=}CH_2$)]}Cl] (6), and [Hf(η^5-C_5H_5){η^5-C_5H_3($SiMe_2$-η^1-N*t*Bu)[$SiMe_2$ ($CH_2CH{=}CH_2$)]}Cl] (7). Crystals of compounds **2**, **6**, and **7** were obtained by crystallization from hexane, and suitable sized crystals in a Lindemann tube were mounted on a Philips PW 1100 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystallographic and experimental details are summarized in Table 2. Compound **7**, which is isostructural with **6**, underwent partial decomposition during data collection. The structures were solved by direct methods (SIR92)[29] and refined by least-squares against F_o^2 (SHELXL-97).[30] All the non-hydrogen atoms for the three compounds were refined anisotropically. For **2** the allyl group (C(18)−C(19)−C(20)) was found to be disordered in two positions and refined with GOF of 0.53 and 0.47, respectively. All the hydrogen atoms were introduced from geometrical calculations and refined using a riding model. The programs PARST[31] ad ORTEP[32] were also used.

Polymerization Procedures. A Büchi glass reactor was employed for the polymerization of ethylene and propylene and for the copolymerization of ethylene/1-hexene (5 mL). In a typical example, dry toluene (50 mL) was added to a 500 mL glass reactor, which was then pressurized with the olefins (at 3 atm). The solution was maintained with stirring and a thermostat used to determine the polymerization temperature (30 °C). The required amount of MAO (Witco, 10% solution in toluene) was added. Polymerization was started by adding a toluene solution of the required amount of catalyst. After a determined time (2−30 min) acidified methanol was added to terminate the polymerization and the olefin feed was stopped. The resulting polymer was collected by filtration, washed with methanol, and dried in vacuo at 50 °C for 10 h.

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A small reactor of 100 mL was used for the polymerization of styrene. In a typical example, toluene (40 mL) was added to a 100 mL argon-purged glass reactor equipped with a stirrer, and then styrene (5 mL) was added at 1 atm. This solution was maintained at a determined polymerization temperature (30 °C) using a thermostat, and the required amount of MAO (Witco, 10% solution in toluene) was added. Polymerization was started by adding a toluene solution of the required amount of catalyst. After a determined time, acidified methanol was added to terminate the polymerization. The resulting polymer was collected by filtration, washed with methanol, and dried in vacuo at 50 °C for 10 h.

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Supporting Information Available: Crystallographic data for **2**, **6**, and **7** in .cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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