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Synthetic and NMR Studies of Neutral and Cationic Dinuclear Fulvalene Zirconium Complexes Containing the "$Zr_2(\mu\text{-}CN^tBu)$" Unit

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Methylation of the previously described isocyanide-bridged complex $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ with 2 equiv of MgClMe in toluene at 80 °C afforded the dinuclear dimethyl complex $[\{Zr(\eta^5\text{-}C_5H_5)(CH_3)\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, **1**. The same reaction with 1 or 2 equiv of MgClMe at room temperature gave a mixture of compounds containing the dimethyl derivative **1** and two isomers of the monomethyl derivative $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(CH_3)(Cl)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, **2a**, **2b**, identified by NMR spectroscopy. Analogous methylation of the related compound $[\{Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, **3**, isolated by reaction of the zirconium(III) derivative $[\{Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ with 1 equiv of CN^tBu in toluene, gave a mixture of unidentified compounds. Treatment of the dimethyl complex $[\{Zr(\eta^5\text{-}C_5H_5)(CH_3)\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, **1**, with 1 equiv of the Lewis acid $B(C_6F_5)_3$ in dichloromethane at −78 °C affords the new yellow crystalline zirconium cationic derivative $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$, **4**. Hydrolysis of the μ-methyl compound **4** led to the μ-hydroxo cationic derivative $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}OH)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$, **5**. Compound **4** reacts with an excess of isocyanides CNR in dichloromethane at −78 °C to give the cationic species $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(CH_3)(CNR)(\mu\text{-}CNR)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ ($R = {}^tBu$, **6**; 2,6-$Me_2C_6H_3$, **7**). All of the reported compounds were characterized by the usual analytical and NMR spectroscopic methods, which are discussed.

Introduction

Mononuclear 14-electron cationic d^0 species $[MCp_2R]^+$ (M = Ti, Zr, Hf; Cp = substituted or unsubstituted cyclopentadienyl ring) are generally accepted to be the catalytically active species in the polymerization of olefins.[1] Extensive studies of their reactivity with CO, RNC, olefins, acetylenes, and allenes leading to cationic acyl and iminoacyl,[2] alkyl, alkenyl, and allyl derivatives have been reported.[3,4] Insertions of carbon monoxide and nitriles into the titanium−methyl bonds of $[TiCp_2R]^+$ have been described as models for the insertion step in soluble titanium polymerization catalysts;[2a,5] these reactions are remarkably sensitive to the steric requirement of both the organic reagent and the cyclopentadienyl ligand. Group 4 homo- and heterodinuclear cationic derivatives have attracted less attention,[6] despite the importance of these systems in the alkene polymerization process.[6,7] The deactivation of electrophilic d^0 catalysts by the formation of dinuclear com-

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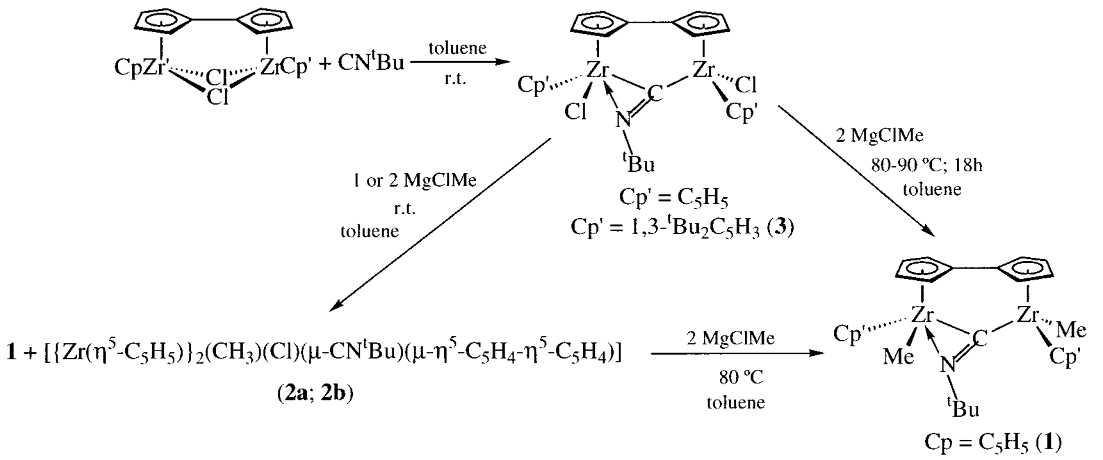
Scheme 1



pounds has been proposed as an important step in alkene polymerization catalysis.[8] Novel dinuclear zirconium cationic complexes, prepared from bisalkynylmetallocene zirconium derivatives, show interesting properties when used as stoichiometric or catalytic reagents.[6f,g]

The bridging fulvalene ligand provides short contacts between two metal centers, and their group 4 electron-deficient metal compounds, greatly developed in the past few years,[9] provide potential models to evaluate the varying reactivity exhibited by dinuclear compounds compared with the corresponding mononuclear compounds. We have recently reported[10a] the formation of the cationic species $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]^+$ in quantitative yield and its reactions with donor ligands and chlorocarbon solvents[10b] to give the μ-chloro cationic compound $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]^+$.

Here we report the results of the methylation of $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, the isolation of the new cationic compound $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CN^tBu)(\mu\text{-}CH_3)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$, and its reactivity with water and isocyanides to give novel dinuclear cationic derivatives. The analytical and NMR spectroscopic characterization of these complexes is described and discussed.

Results and Discussion

Neutral Complexes. Methylation of toluene solutions of $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$[9c] with a stoichiometric amount of MgClMe at 80−90 °C for 18 h afforded the dinuclear dimethyl complex $[\{Zr(\eta^5\text{-}C_5H_5)(CH_3)\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, **1**, which was isolated as a microcrystalline red solid in 72% yield (Scheme 1). It is moisture sensitive but shows thermal stability in the solid, which allows it to be stored under inert atmosphere for weeks. It is soluble in aromatic hydrocarbons, dichloromethane, and chloroform, but insoluble in alkanes. The IR spectrum of **1** shows the characteristic absorption bands at 1644 [1612(sh)] cm^{-1} due to ν(C=N).

When the starting dichloro compound was reacted in toluene with 1 or 2 equiv of MgClMe at room temperature, an orange yellow oil was obtained, whose ^{1}H NMR spectrum in C_6D_6 indicated the presence of a mixture containing the dimethyl derivative **1** and the two isomers of the monomethyl derivative $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(CH_3)(Cl)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, **2a** and **2b** (Scheme 1). The NMR proton integral intensity shows that the reaction with 1 equiv of MgClMe gave a mixture of **1** (23%), **2a** (40%), and **2b** (37%), whereas the reaction with 2 equiv of MgClMe gave a mixture of of **1** (45%), **2a** (50%), and **2b** (5%). These experimental results highlighted notable differences in the reactivity of the two Zr−Cl bonds present in the starting dichloro compound.

The structure determination for compounds **1** and **2** by X-ray diffraction methods was not possible, because crystals suitable for a structural study were not obtained. However, the structural behavior of these complexes must be analogous to that reported for the starting chloro complex[9c] and for its related dimethyl derivative containing the 2,6-dimethylphenyl isocyanide $[\{Zr(\eta^5\text{-}C_5H_5)(CH_3)\}_2\{\mu\text{-}CN(2,6\text{-}Me_2C_6H_3)\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$,[9h] for which the X-ray diffraction studies indicate that the chlorine and the methyl groups are located in an *anti*-position and the angular isocyanide ligand adopts an asymmetrical η^1−η^2-bridging disposition with η^2-*side-on* complexation to one of the zirconium atoms, with the corresponding Zr−C bond distance longer than that to the other zirconium center. In the arrangement of ligands in the σ-ligand plane of the zirconium atom with the η^2-coordinated isocyanide ligand, the "N-inside" fashion is observed. This disposition indicates a dinuclear species containing two chiral zirconium atoms,

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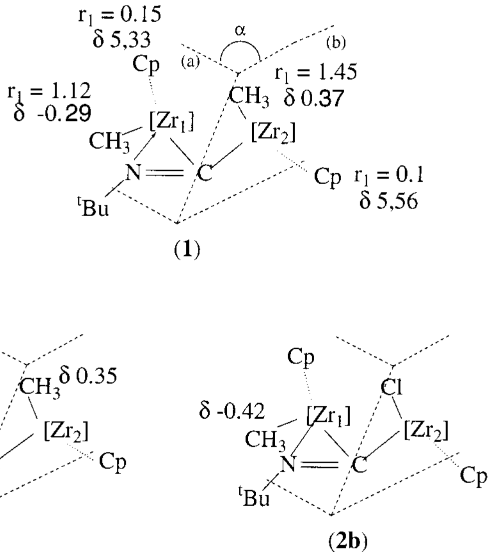
each showing a different coordination environment where the two metal atoms are inequivalent.

The ^{1}H NMR spectrum of complex **1**, in C_6D_6, shows two ABCD spin systems for the fulvalene ligand, two signals for the cyclopentadienyl ring, and one singlet for the *tert*-butyl group protons at δ 1.08. The methyl group protons appear as two singlets at δ +0.37 and −0.29. Likewise, its ^{13}C NMR spectrum indicates the presence of all of the expected resonances. The signals for the *tert*-butyl carbon atoms are observed at δ 65.7 and 30.2. The noteworthy signal assigned to the bridging isocyanide sp^2 carbon atom $[Zr]-C(N^tBu)-[Zr]$ appears at δ 296.0, similar to the signal found for the related dinuclear zirconium species containing bridging isocyanide ligands,[9c,11] but with 50 ppm deshielding with respect to the resonances found for terminal iminoacyl ligands in mononuclear zirconium derivatives.[12] In the monomethyl complexes **2a** and **2b** only one singlet for the methyl protons is observed at δ +0.35 and −0.42, respectively. The similarity in the chemical shifts of the methyl groups in **1** and **2a** at δ +0.37 and +0.35 and in **1** and **2b** at −0.29 and −0.42 suggests that the methyl groups in each pair must occupy very similar chemical environments; that is, they must be bonded to the same type of zirconium atom. These observations allow the structures of **2a** and **2b** to be distinguished.

The resonances for the methyl carbons in the ^{13}C NMR spectrum of **1** appear at δ 9.9 and 16.2. Selective decoupling $^{13}C\{^1H\}$ NMR experiments show that the signals at δ −0.29 in the ^{1}H and δ 9.9 in the ^{13}C NMR spectra correspond to the same methyl group. The large difference in the chemical shifts for the methyl proton and carbon resonances ($\Delta\delta = 0.66$ ppm (^{1}H) and 6.3 ppm (^{13}C)) can only be explained by assuming considerable differences of the electronic densities (total electronic charges) on the zirconium atoms in compound **1**. The η^2-side-on coordination of the isocyanide bridge to one of the zirconium atoms involves donation of the free electron pair of the nitrogen atom to the metal center, to give the transition metal a formally 18-electron valence shell. The increase of electronic density at this zirconium center must cause shielding of the NMR signals for all of the directly bonded ligands. This proposal is consistent with the proton spin−lattice relaxation rates ($r_1 = 1/T_1$), measured at 243 K (T_1 min) in toluene-d_8 solution, where the r_1 values mainly depend on the number of neighboring protons and the internuclear distances (R^{-3}).[13] Assuming short distances between the Zr_1-Cp and the Zr_2-Me groups, we can now assign the resonances in the dimethyl complex **1**, shown in Figure 1, and consequently establish the structures of the monomethyl complexes **2a** and **2b**.

These experimental results allow us to conclude that the ease of methylation of the $[Zr_2]-Cl$ bond in the chloro compound $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ and in compounds **2** is greater than the $[Zr_1]-$Cl bond, probably due to the presence of the vacant $2a_1$ orbital in the Zr_2 atom. Complete conversion of the mixture of the monomethyl species **2a** and **2b** into the dimethyl derivative **1** requires 2 equiv of MgClMe and warming of the reaction mixture to 80 °C.



(**1**)

(**2a**) (**2b**)

Figure 1. r_1 **means the proton spin−lattice relaxation rates (1/T_1) measured at 243 K for the corresponding protons. Planes (a) and (b) symbolize the bent metallocene wedges for both Zr_1 and Zr_2 atoms. α denotes the angle between both planes.**

With the aim of making a comparative study we also synthesized the isocyanide-bridged zirconium complex $[\{Zr(\eta^5\text{-}1,3\text{-}^tBu_2C_5H_3)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, **3**, by reaction of the known zirconium(III) compound $[\{Zr(\eta^5\text{-}1,3\text{-}^tBu_2C_5H_3)(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$[14] with 1 equiv of CN^tBu in toluene (Scheme 1). Compound **3** was isolated as an orange-yellow microcrystalline solid in high yield and was analytically and spectroscopically characterized (see Experimental Section). It is a thermally stable and moisture-sensitive solid which is soluble in aromatic hydrocarbons, dichloromethane, and chloroform but insoluble in alkanes. Characteristic absorption at 1642 [1616(sh)] cm^{-1} due to ν(C=N) is observed in the IR spectrum of **3**, similar to that found for compound **1** and other analogous complexes.[9c,h] The ^{1}H and ^{13}C NMR spectra of complex **3** in C_6D_6 show two different metal fragments. However all attempts made to methylate complex **3** with MgClMe under varying conditions always gave an unresolvable mixture of unidentified compounds.

Cationic Complexes. The reaction of the dimethyl complex $[\{Zr(\eta^5\text{-}C_5H_5)(CH_3)\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, **1**, with 1 equiv of the Lewis acid $B(C_6F_5)_3$ in dichloromethane at −78 °C led to the immediate formation of the new zirconium cationic compound $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$, **4**, isolated as a yellow crystalline solid in 80% yield (Scheme 2) and characterized by elemental analysis and NMR and IR spectroscopy. It is oxygen- and moisture-sensitive but can be stored under an inert atmosphere for weeks, as it shows thermal stability in the solid. It is soluble in dichloromethane and chloroform and insoluble in toluene and hydrocarbons. Complex **4** remains unaltered for weeks in chlorinated solvents in contrast with the reactivity observed for the

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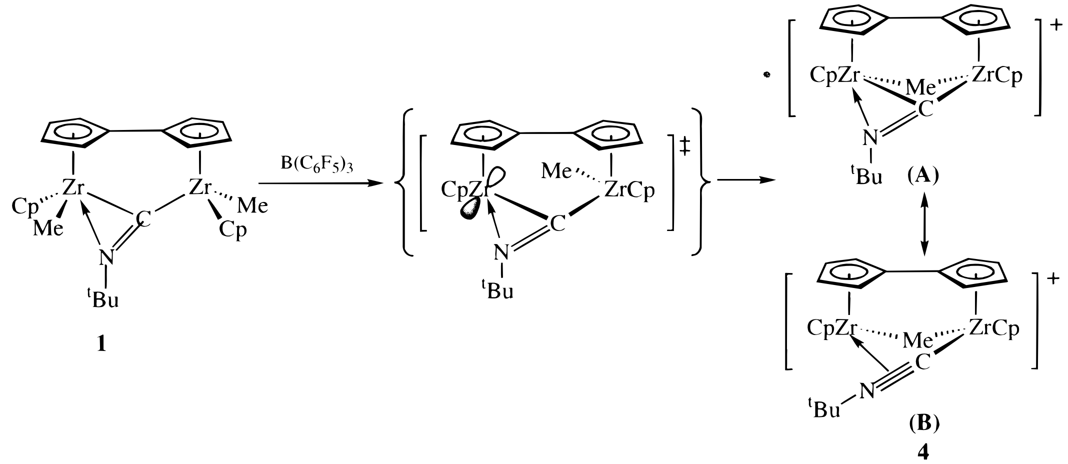
Scheme 2



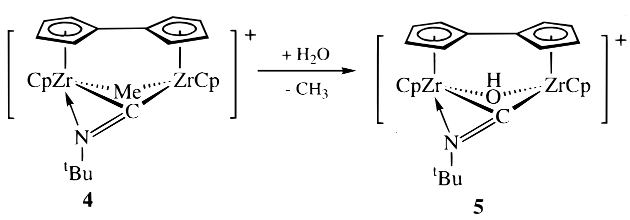
μ-methylene dinuclear cationic complex $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}CH_3)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$, which reacts in dichoromethane or choroform[10b] to give μ-chloro species $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$.

The IR spectrum of the cationic complex **4** shows the $\nu(C{=}N)$ absorption band at 1700 [1674(sh)] cm^{-1}, significantly shifted to higher wavenumbers with respect to the neutral complexes **1**−**3**, as observed for other analogous cationic compounds[2a,11] and in agreement with observed crystallographic data. The carbon−nitrogen bond distance found for the bridging isocyanide ligand in the cationic compound $[\{Zr(\eta^5\text{-}C_5H_5)(Cl)\}_2(\mu\text{-}C{\equiv}CMe)(\mu\text{-}CNCMe_2CH_2{}^tBu)](BPh_4)$ is 1.218 Å,[11] shorter than that found for the neutral compounds $[\{Zr(\eta^5\text{-}C_5H_5)(Cl)\}_2\{\mu\text{-}CN(2,6\text{-}Me_2C_6H_3\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, 1.273 Å,[9h] and $[\{Zr(\eta^5\text{-}C_5H_5)(Cl)\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, 1.249 Å.[9c]

The ^1H NMR (CD_2Cl_2) spectrum of **4** at 293 K shows two ABCD spin systems for the fulvalene and two singlets for the cyclopentadienyl ring protons. The methyl group bonded to boron appears as a broad signal at δ 0.42. The $^{13}C\{^1H\}$ NMR spectrum exhibits 10 resonances for the fulvalene group and two resonances for the cyclopentadienyl ligands due to the differing ligand arrangement at each zirconium atom in the molecule. The bridging methyl group is identified by one singlet at δ −2.00 in the ^1H NMR and δ 8.45 ($^1J_{C-H}$ = 112.5 Hz) in the $^{13}C\{^1H\}$ NMR spectra, respectively, the typical range for the resonances of bridging methyl groups.[15] The signals for the *tert*-butyl carbon atoms are observed at δ 66.3 and 30.4, and a resonance at δ 269.8 is also observed for the bridging isocyanide carbon $[Zr]{-}C(N^tBu){-}[Zr]$.

A comparison of the ^{13}C chemical shifts between the neutral complex **1** and the cationic derivative **4** indicates no substantial differences in the fulvalene, cyclopentadienyl, methyl, and t*ert*-butyl resonances. However, a significant difference is observed for the bridge carbon of the isocyanide ligand, which is 26.2 ppm more shielding in **4** with respect to the corresponding resonance found for starting neutral species **1**, instead of the usual deshielding expected for cationic species. Similar ^{13}C NMR behavior has been observed previously for the organic acylium cations and was explained by a substantial change from sp^2 to sp carbon hybridization. Therefore, the bonding in the isocyanide moiety in **4** may be described by the two resonance structures **A** and **B** shown in Scheme 2, with a significant contribution from **B**.

Scheme 3



Hydrolysis of a dichloromethane solution of compound **4** with 1 equiv of H_2O/D_2O takes place with elimination of methane to give the μ-hydroxo cationic derivative $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}OH/D)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$, **5** (Scheme 3), isolated as a brown-yellow solid. Hydrolysis with an excess of water gives a mixture of products insoluble in all common solvents that could not be characterized. There are some recent precedents for μ-hydroxo dinuclear zirconium cationic systems.[16]

The IR spectrum of **5** exhibits characteristic $\nu(OH)$ and $\nu(C{=}N)$ absorption bands at 3647 and 1670 cm^{-1}, respectively,[17] and its $^1H/^2H$ NMR spectra in CD_2Cl_2 show singlets at δ 2.04 assigned to the bridging hydroxo group.

Compound **4** reacts with excess isocyanides RNC (R = ᵗBu, 2,6-$Me_2C_6H_3$) in dichloromethane at −78 °C to give the cationic adducts $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(CH_3)(CNR)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (R = ᵗBu, **6**; R = 2,6-$Me_2C_6H_3$, **7**), which were isolated as yellow crystalline solids (Scheme 4).

Treatment with any molar ratio of isocyanide at room temperature allows the unaltered starting materials to be recovered, indicating that coordination of the isocyanide to the metal center before the insertion reaction is entropically driven; consequently coordination is more favorable at low temperature. Nevertheless, after for-

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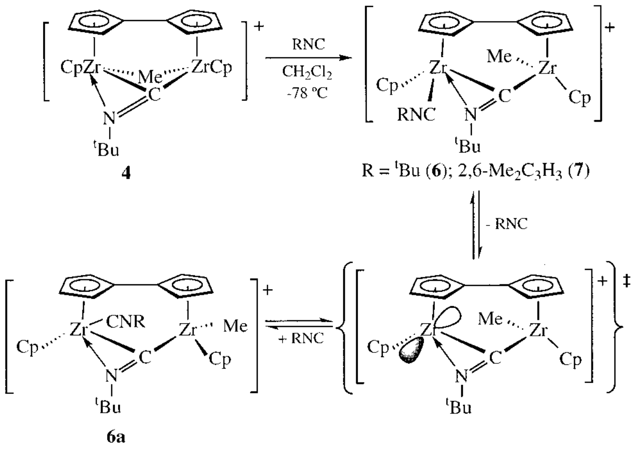
mation at low temperature, compounds **6** and **7** do not dissociate the isocyanide ligand when they are stored at room temperature, as solids, or in solution under an inert atmosphere. Therefore the isocyanides coordinated to complex **4** do not participate in further insertion processes. Complexes **6** and **7** are moisture sensitive and show thermal stability in the solid. They are soluble in dichloromethane and chloroform, but insoluble in toluene and hydrocarbons. The IR spectra of complexes **6** and **7** show the ν(C≡N) absorption band respectively at 2187, shifted to a higher wavenumber compared with that observed for free CN^{t}Bu (2143 cm^{-1}), and at 2154 cm^{-1}, unmodified with respect to free CN(2,6-$Me_2C_6H_3$) (2155 cm^{-1}), as expected for coordination to a d^0 zirconium(IV) metal center.[6f,g,10c] Characteristic ν(C=N) IR absorptions at 1660 and 1656 cm^{-1} are also observed. The IR and analytical data for **6** and **7** are consistent with the presence of one coordinated isocyanide ligand to one of the electrophilic zirconium atoms and a bridging isocyanide group.

In the ^{1}H NMR spectra of **6** and **7** in CD_2Cl_2 at 25 °C the signal for the (μ-CH_3) group in the initial cationic complex **4** (δ −2.0) has disappeared and new resonances appear at δ −0.25 (**6**) and δ −0.18 (**7**) corresponding to the terminal methyl groups, which are observed in the ^{13}C NMR spectra at δ 20.8 and 21.4, respectively. Bearing in mind the assignment discussion of the resonances for methyl groups in the dimethyl complex **1** and the chemical shifts in the ^{13}C NMR spectra, we could conclude that the methyl group in **6** and **7** bonds to the Zr_2 atom (as shown in Figure 1), and therefore, the isocyanide ligands must be coordinated to the Zr_1 atom to formally complete an 18-electron valence shell at this metal center.

The resonances for the *tert*-butyl group protons of the bridge isocyanide ligand are observed at δ 1.30 (**6**) and δ 1.33 (**7**), whereas that for the coordinated *tert*-butyl isocyanide in **6** appears at δ 1.70. Compound **7** shows one singlet corresponding to two equivalent methyl groups of the coordinated aryl isocyanide ligand. The resonance due to the coordinated isocyanide carbon was not detected in the spectra of either complex.[6f,g,18] The carbon resonances of the bridge Zr−*C*(N^{t}Bu)−Zr moiety in complexes **6** and **7** are not substantially shielding with respect to complex **4** (see Experimental Section). These NMR data indicate the presence of two differently coordinated zirconium atoms, in accordance with the observation of two ABCD spin systems in the proton, 10 resonances in the carbon spectra for the fulvalene ligand, and two signals for the cyclopentadienyl rings.

Attempts to obtain single crystals of **6** and **7** suitable for X-ray crystallography were unsuccessful. Their structures can be considered as dinuclear systems with two zirconium atoms bridged by fulvalene and asymmetrical "CN^{t}Bu" ligands, with one neutral zirconium center bonded to terminal methyl and cyclopentadienyl ligands in a tetrahedral arrangement and a cationic zirconium center stabilized by coordination with the terminal isocyanide ligand. The molecule contains two chiral metal centers, although the spectroscopic data indicate that only one of the possible diastereoisomers is formed.

Scheme 4



Complex **6** is rearranged, at room temperature, in CD_2Cl_2 for 72 h to give a mixture of two compounds in 1:1 ratio (**6** and **6a**), which remained unchanged for weeks. The ^{1}H NMR spectrum shows a set of signals corresponding to **6** and a new set of resonances assigned to **6a**, with the same multiplicity but with slightly different chemical shifts (see Experimental Section). In the ^{13}C NMR spectrum the resonances for the terminal methyl group are observed at δ 20.8 (**6**) and 21.7 (**6a**), corresponding to the methyl groups bonding to the Zr_2 atom (Figure 1), as evidenced by the spectroscopic data obtained for **1**.

Recently we described the reactions of the μ-methylene dinuclear cationic zirconium [{Zr(η^5-C_5H_5)}$_2$(μ-CH_2)(μ-CH_3)(μ-η^5-C_5H_4-η^5-C_5H_4)][MeB(C_6F_5)$_3$] complex with phosphines and THF to give the related mixture of cationic diastereomeric adducts [{Zr(η^5-C_5H_5)}$_2$(μ-CH_2)(CH_3)(L)(μ-η^5-C_5H_4-η^5-C_5H_4)][MeB(C_6F_5)$_3$] (L = PMe_3, PMe_2Ph, PPh_3, THF) observing an exchange process between PPh_3 and THF free and coordinated, respectively.[10b] We could propose that the dissociation of the isocyanide in complex **6** leads to the formation of the transition state for the S_N1 reactions, in which the free isocyanide coordinates to the zirconium center at the two possible sides with the same probability to give isomer **6** in which the nitrogen atom is occupying the *inside* position in the σ-ligand plane at the bent metallocene wedge and the isomer **6a** with the nitrogen atom ocuppying the *outside* position in this σ-ligand plane (Scheme 4). Isomers **6** and **6a** are formed in 1:1 ratio. The *inside* coordination of iminoacyl and related ligands is generally preferred,[19] similar to the preference for the *inside* η^2-acyl conformer found for titanium and zirconium compounds by energy profile studies.[20] However, X-ray crystallography shows that in the cationic [$ZrCp_2$(η^2-N,C-picolyl)(PMe_3)]$^+$ compound the nitrogen atom prefers to be coordinated *outside*.[21] Some examples are also known in which the *inside* and the *outside* isomers are about equivalent in energy and, by ^{1}H NMR

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spectroscopy, the presence in solution of a mixture of both isomers has been deduced.[19,21,22]

Concluding Remarks

The use of the fulvalene ligand as a bridging system between two zirconocene fragments is a valuable strategy to design new cationic dinuclear zirconium derivatives and to study their reactivity. This report shows that neutral dinuclear zirconium(IV) complexes containing one fulvalene and one *tert*-butyl isocyanide bridge can be generated by oxidative addition of isocyanide to the easily accessible zirconium(III) $[(ZrCp')_2(\mu\text{-Cl})(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ ($Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$) derivatives. Addition of $B(C_6F_5)_3$ to the methyl derivative $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]\text{-}[BMe(C_6F_5)_3]$ results in the clean formation of the cationic $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ complex, from which new dinuclear zirconium cationic adducts $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(CH_3)(CNR)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ ($R = {}^tBu$, 2,6-$Me_2C_6H_3$) can be very easily prepared by addition of isocyanides, whereas the μ-hydroxo cationic $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}OH)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)]$ compound is obtained by hydrolysis.

Experimental Section

General Considerations. All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox model HE-63 or VAC HE-543-6. Solvents were purified by distillation under argon from an appropriate drying agent (sodium for toluene, sodium–potassium alloy for hexane, sodium benzophenone for diethyl ether, and P_2O_5 for dichloromethane and chloroform). MgClMe·1.5THF, *tert*-butyl isocyanide, and 2,6-dimethylphenyl isocyanide (Aldrich) were commercially obtained and used without further purification. $[\{Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4{-}C_5H_4)]$,[9a] $[\{Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4{-}C_5H_4)]$,[14] $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$,[9c] and $B(C_6F_5)_3$[23] were prepared by published procedures. C, H, and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer using KBr pellets. NMR spectra were recorded on a Varian Unity 500 Plus spectrometer, and chemical shifts are referenced to carbon resonances (^{13}C) and the residual protons (^1H) in the solvent.

Synthesis of $[\{Zr(\eta^5\text{-}C_5H_5)(CH_3)\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, 1. A 0.62 g (3.36 mmol) sample of MgClMe·1.5THF was added to a solution of $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (1.0 g, 1.68 mmol) in toluene (25 mL) at room temperature. The reaction mixture was warmed to 80–90 °C and stirred for 18 h. The color of the reaction mixture slowly changed from yellow to black-red. After cooling to room temperature and filtration, the solvent was removed and a red solid was obtained, which was washed with diethyl ether and hexane. Recrystallization from toluene/hexane gave 0.67 g (72%) of **1** as a red microcrystalline solid. IR (KBr): ν (cm^{-1}) = 1644 [1612(sh)] (C=N). ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 5.55, 5.40 (s, 2 × 5H, C_5H_5); 5.92, 5.91, 5.39, 5.27, 5.09, 4.55, 4.51, 4.33 (two ABCD spin systems, $C_{10}H_8$); 1.08 (s, 9H, ^{t}*Bu*NC); 0.37 (s, 3H), −0.29 (s, 3H) (Zr−CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ 108.9, 108.0 (C_5H_5); 119.4, 115.4, 111.5, 110.9, 101.3, 100.8, 99.3, 98.9, 97.9, 93.6 ($C_{10}H_8$); 65.7, 30.2 (^{t}*Bu*NC); 16.2, 9.9 (Zr−CH_3); 296.0 (^{t}BuN*C*). Anal. Calcd for $C_{27}H_{35}NZr_2$: C 58.54, H 6.00, N 2.53. Found: C 58.67, H 5.86, N 2.42.

Synthesis of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(CH_3)(Cl)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, 2a, 2b. A 0.31 g (1.68 mmol) sample of MgClMe·1.5THF was added to a solution of $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (1.0 g, 1.68 mmol) in toluene (25 mL) at room temperature, and the reaction mixture was stirred for 18 h. A yellow solution resulted. After filtration, the solvent was removed and a yellow oil was obtained. Spectroscopic data showed the presence of **1** (23%) + **2a** (40%) + **2b** (37%). ^1H NMR (500 MHz, C_6D_6, 25 °C): **2a**: δ 5.71, 6.64 (s, 2 × 5H, C_5H_5); 6.5−4.5 (two ABCD spin systems, $C_{10}H_8$); 1.00 (s, 9H, ^{t}*Bu*NC); 0.35 (s, 3H, CH_3). **2b**: δ 5.65, 6.51 (s, 2 × 5H, C_5H_5); 6.5−4.5 (two ABCD spin systems, $C_{10}H_8$); 1.35 (s, 9H, ^{t}*Bu*NC); −0.42 (s, 3H, CH_3).

Following the same procedure (room temperature) using 0.62 g (3.36 mmol) of MgClMe·1.5THF and 1.0 g (1.68 mmol) of $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ the formation of a mixture of **1** (45%) + **2a** (50%) + **2b** (5%) was spectroscopically detected.

Synthesis of $[\{Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)Cl\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4\text{-}C_5H_4)]$, 3. *tert*-Butyl isocyanide (0.14 mL, 1.22 mmol) was added via syringe to a solution of $[\{Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\mu\text{-}Cl)\}_2\text{-}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (0.90 g, 1.22 mmol) in toluene (50 mL) at room temperature. The reaction mixture was stirred for 12 h and the color of the solution changed from purple to yellow. The solvent was removed, and a yellow solid was obtained. Recrystallization from diethyl ether/hexane gave 0.86 g (87%) of a yellow microcrystalline solid characterized as **3**. IR (KBr): ν (cm^{-1}) = 1642 [1616(sh)] (C=N). ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 6.60, 6.10, 5.95, 5.85, 5.71, 5.50 (two ABC spin systems, C_5H_3); 6.65, 6.35, 6.30, 5.92, 5.91, 5.25, 5.05, 4.84 (two ABCD spin systems, $C_{10}H_8$); ~1.45 (27 H), 1.44 (s, 9H), 1.31 (s, 9H) (^{t}*Bu*NC). $^{13}C\{^1H\}$ NMR (125 MHz C_6D_6, 25 °C): δ 151.9−95.8 (10 resonances of C_5H_3 and 10 resonances of $C_{10}H_8$); 35.4, 34.2, 33.7, 33.6, 32.3, 32.2, 31.6, 31.2 (^{t}Bu); 65.7, 30.8 (^{t}*Bu*NC).; 293.0 (^{t}BuN*C*). Anal. Calcd for $C_{41}H_{59}NCl_2Zr_2$: C 60.11, H 7.21, N 1.71. Found: C 60.44, H 7.16, N 1.86.

Synthesis of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe\ (C_6F_5)_3]$, 4. A 0.40 g (0.99 mmol) sample of $B(C_6F_5)_3$ were added to a solution of $[\{Zr(\eta^5\text{-}C_5H_5)(CH_3)\}_2(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, **1** (0.55 g, 0.99 mmol), in dichloromethane (10 mL) at −78 °C. The color of the reaction mixture immediately changed from red to brown-yellow. The solution was stirred for 30 min and warmed to room temperature. The solvent was removed, and a yellow solid was obtained, which was washed with hexane to give **4** (0.67 g, 72%) as a dichloromethane monosolvate, as indicated by ^1H NMR integration. IR (KBr): ν (cm^{-1}) = 1700 [1674(sh)] (C=N). ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 5.96, 5.86 (s, 2 × 5H, C_5H_5); 6.38, 5.94, 5.81, 5.44, 5.37, 5.07, 5.08, 4.65 (two ABCD spin systems, $C_{10}H_8$); 1.46 (s, 9H, ^{t}*Bu*NC); −2.00 (s, 3H, Zr_2-μ-CH_3); 0.42 (br, *Me*B). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 25 °C): δ 107.8, 105.6 (C_5H_5); 109.4, 108.5, 107.8, 106.4, 104.5, 103.6, 102.9, 101.0, 100.9, 97.8 ($C_{10}H_8$); 66.4, 30.4 (^{t}*Bu*NC); 8.45 (Zr−CH_3); 269.8 (^{t}BuN*C*); ≈10.0 (br, *Me*B). Anal. Calcd for $C_{45}H_{33}NBF_{15}\text{-}Zr_2\cdot 1CH_2Cl_2$: C 48.01, H 3.07, N 1.22. Found: C 48.22, H 3.07, N 1.21.

Synthesis of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}OH)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe\ (C_6F_5)_3]$, 5. A 7 mL sample of deoxygenated and distilled water was added via syringe to a solution of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CN^tBu)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$, **4** (0.45 g, 0.42 mmol), in dichloromethane (5 mL) at room temperature. The solution was stirred for 30 min with formation of a white precipitate. After filtration, the solvent was removed and a brown-yellow solid was obtained, which was washed with hexane to give **5** (0.14 g, 31%) as a dichloromethane partial solvate, as indicated by ^1H NMR integration. IR (KBr): ν (cm^{-1}) = 3647 (OH); 1670 (C=N). ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 6.06, 6.05 (s, 2 × 5H, C_5H_5); 6.80, 6.40, 5.61, 5.42, 5.30, 5.20, 5.11, 4.90 (two ABCD spin

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systems, $C_{10}H_8$); 2.04 (s, 1H, μ-OH); 1.54 (s, 9H, ^{t}*Bu*NC); 0.49 (br, *Me*B). ${}^{13}C\{{}^1H\}$ NMR (125 MHz, CD_2Cl_2, 25 °C): δ 110.3, 107.6 (C_5H_5); 114.1, 111.9, 108.9, 107.2, 105.5, 101.6, 101.5, 99.6 ($C_{10}H_8$); 30.8 (^{t}*Bu*NC); ~10.0 (br, *Me*B). Anal. Calcd for $C_{44}H_{31}NBOF_{15}Zr_2\cdot 1/2CH_2Cl_2$: C 48.16, H 2.97, N 1.26. Found: C 48.35, H 2.98, N 1.06.

Synthesis of [{Zr(η^5-C_5H_5)}$_2$(CH_3)(CN^tBu)(μ-CN^tBu)(μ-η^5-C_5H_4-η^5-C_5H_4)] [BMe(C_6F_5)$_3$], 6. A 0.031 mL (0.28 mmol) sample of CN^tBu was added via syringe to a solution of [{Zr(η^5-C_5H_5)}$_2$(μ-CH_3)(μ-CN^tBu)(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$], **4** (0.30 g, 0.28 mmol), in dichloromethane (10 mL) at −78 °C. The solution was stirred for 30 min and warmed to room temperature. The solvent was removed, and a yellow solid was obtained, which was washed with hexane to give **6 (**0.15 g, 48%) as a dichloromethane partial solvate, as indicated by ${}^1H$ NMR integration. IR (KBr): ν (cm^{-1}) = 2187 (C≡N); 1660 (C=N); ${}^1H$ NMR (500 MHz, CD_2Cl_2, 25 °C): δ 6.09, 5.52 (s, 2 × 5H, C_5H_5); 6.32, 6.12, 6.02, 5.93, 5.47, 5.41, 4.60, 4.22 (two ABCD spin systems, $C_{10}H_8$); 1.70 (s, 9H), 1.30 (s, 9H) (^{t}*Bu*NC); −0.25 (s, 3H, Zr−CH_3); 0.49 (br, *Me*B). ${}^{13}C\{{}^1H\}$ NMR (125 MHz, CD_2Cl_2, 25 °C): δ 109.4, 105.4 (C_5H_5); 117.4, 112.4, 111.6, 110.7, 104.4, 101.9, 101.5, 100.9, 97.9, 97.8 ($C_{10}H_8$); 62.5, 30.0, 29.9, 29.5 (^{t}*Bu*NC); 20.8 (Zr−CH_3); 265.6 (^{t}BuN*C*); ~10.0 (br, *Me*B). Anal. Calcd for $C_{50}H_{42}N_2BF_{15}Zr_2\cdot 1/2CH_2Cl_2$: C 50.92, H 3.52, N 2.35. Found: C 50.97, H 3.67, N 2.25.

6a: ${}^1H$ NMR (500 MHz, CD_2Cl_2, 25 °C): δ 6.27, 5.70 (s, 2 × 5H, C_5H_5); 6.56, 6.13, 6.03, 5.59, 5.54, 4.64, 4.31 (two ABCD spin systems, $C_{10}H_8$); 1.71 (s, 9H), 1.30 (s, 9H) (^{t}*Bu*NC); −0.08 (s, 3H, Zr−CH_3); 0.49 (br, *Me*B). ${}^{13}C\{{}^1H\}$ NMR (125 MHz, CD_2Cl_2, 25 °C): δ 111.6, 107.2 (C_5H_5); 118.3, 110.3, 108.2, 105.6, 104.9, 103.5, 103.3, 103.0, 99.1, 97.5 ($C_{10}H_8$); 63.3, 30.1, 29.4, 29.9 (^{t}*Bu*NC); 21.7 (Zr−CH_3); (^{t}BuN*C*) signal not observed; ~10.0 (br, *Me*B).

Synthesis of [{Zr(η^5-C_5H_5)}$_2$(CH_3){CN(2,6-$Me_2C_6H_3$}(μ-CN^tBu)(μ-η^5-C_5H_4-η^5-C_5H_4)] [BMe(C_6F_5)$_3$], 7. A 0.030 g (0.23 mmol) sample of CN(2,6-$Me_2C_6H_3$) was added via syringe to a solution of [{Zr(η^5-C_5H_5)}$_2$(μ-CH_3)(μ-CN^tBu)(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$], **4** (0.25 g, 0.23 mmol), in dichloromethane (10 mL) at −78 °C. The solution was stirred for 30 min and warmed to room temperature. The solvent was removed, and a yellow solid was obtained, which was washed with hexane to give **7 (**0.18 g, 64%) as a dichloromethane partial solvate, as indicated by ${}^1H$ NMR integration. IR (KBr): ν (cm^{-1}) = 2154 (C≡N); 1656 (C=N). ${}^1H$ NMR (500 MHz, CD_2Cl_2, 25 °C): δ 7.4−7.3 [m, 3H, CN(2,6-Me_2C_6*H_3*)]; 6.09, 5.63 (s, 2 × 5H, C_5H_5); 6.41, 6.39, 6.09, 6.04, 5.54, 5.49, 4.70, 4.37 (two ABCD spin systems, $C_{10}H_8$); 2.60 [s, 6H, CN(2,6-*Me_2*C_6H_3)]; 1.33 (s, 9H, ^{t}*Bu*NC); −0.18 (s, 3H, Zr−CH_3); 0.49 (br, *Me*B). ${}^{13}C\{{}^1H\}$ NMR (125 MHz, CD_2Cl_2, 25 °C): δ 136.1, 131.9, 129.6 [CN(2,6-Me_2*C_6*H_3)]; 109.5, 105.5 (C_5H_5); 117.8, 112.6, 111.8, 110.6, 107.3, 104.6, 101.8, 101.1, 98.1, 97.7 ($C_{10}H_8$); 29.6, 29.5 (^{t}*Bu*NC); 21.4 (Zr−CH_3); 19.5 [CN(2,6-*Me_2*C_6H_3)]; 263.9 (^{t}BuN*C*); ~10.0 (br, *Me*B). Anal. Calcd for $C_{54}H_{42}N_2BF_{15}Zr_2\cdot 1/2CH_2Cl_2$: C 52.78, H 3.47, N 2.26. Found: C 52.82, H 3.49, N 2.17.

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