Structural Characterization of a Cationic Zirconocene Dimethylaniline Complex and Related Catalytically Relevant Species

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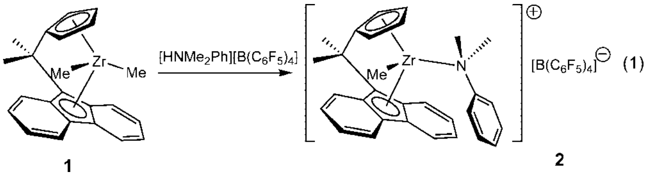
Summary: We report the first crystallographically characterized dimethylaniline complex of a group 4 metallocene. [(IPCF)-ZrMe(NMe_2Ph)][$B(C_6F_5)_4$] shows strongly coordinated NMe_2Ph which does not interchange in solution. DFT calculations suggest that the Zr−N bond is 23 kJ mol^{-1} stronger than the Zr−Me−Zr bond in [{(IPCF)ZrMe}$_2$(μ-Me)][$MeB(C_6F_5)_3$], the structure of which is also reported (IPCF = $Me_2C(C_5H_4)$(fluorenyl)).

One of the most widely used methods of generating cationic metallocene alkyl complexes is the protonolysis of metallocene dialkyls with ammonium salts.[1−3] The reaction of zirconocene dimethyls with dimethylanilinium tetraarylborate salts has found particularly widespread application, and in early pioneering work Turner was able to show that the use of [$HNMe_2Ph$][$B(C_6F_5)_4$] as a cation generating agent resulted in particularly active catalysts. This was thought to be due mainly to the low basicity of dimethylaniline ($pK_b = 8.85$; cf. $pK_b = 3.25$ for NEt_3)[4] and its correspondingly low ability to bind to the resulting cationic group 4 metal center.

During studies directed at determining the kinetics of metallocene catalyst activation with anilinium and triphenylcarbenium salts, we carried out reactions between (IPCF)$ZrMe_2$ (**1**) and [$HNMe_2Ph$][$B(C_6F_5)_4$] in toluene (M = Zr, Hf; IPCF = $Me_2C(C_5H_4)$(fluorenyl)) (eq 1).[5] Combining the two reagents gave a red-orange solution accompanied by the deposition of some red oil. Cooling this mixture overnight at −26 °C afforded red crystals of [(IPCF)ZrMe(NMe_2Ph)][$B(C_6F_5)_4$] (**2**) which were suitable for single-crystal X-ray diffraction (see below).



The aniline adduct proved surprisingly stable in solution at room temperature and above. The variable-temperature ^{1}H NMR spectra of **2** are in agreement with C_1 symmetry. An unexpected feature was the presence below +20 °C of two separate resonances for the two diastereotopic methyl groups of the coordinated dimethylaniline. These signals broaden above 0 °C, and a spectrum recorded at 40 °C showed coalescence to a singlet at δ 1.77. Dissociation and exchange of coordinated dimethylaniline is evidently not a facile process. The signal assigned to free dimethylaniline is found in the range δ 2.5−2.2 and is both temperature and concentration dependent. The assignment was confirmed by the addition of excess NMe_2Ph. However, subsequent experiments revealed that excess [$HNMe_2Ph$]$^+$[$B(C_6F_5)_4$]$^-$ also appears at the same chemical shift: i.e., it rapidly exchanges with and is indistinguishable from free DMA. For this reason, the signal has been labeled simply as DMA_{XS} (Figure 1). There was no observed exchange of this DMA_{XS} resonance and the Zr-coordinated DMA over the temperature range studied.

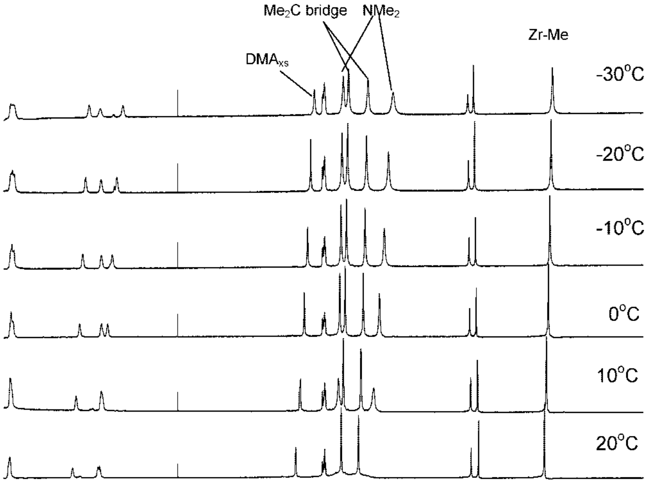


Figure 1. VT ^{1}H NMR spectra of [(IPCF)Zr(Me)NMe_2Ph]$^+$[B-$(C_6F_5)_4$]$^-$ (**2**) in toluene-d_8/1,2-difluorobenzene (1/1 v/v).

The structure of the cation in **2**·2(toluene) is shown in Figure 2. The phenyl group of the coordinated aniline fits into the groove of the fluorenyl moiety. The solid-state conformation is consistent with the solution NMR data.

To the best of our knowledge there is no previous example of a structurally characterized dimethylaniline complex of a group 4 metallocene and only one example of a zirconium nonmetallocene structure, Jordan's [(F_6-acen)Zr(CH_2CMe_3)-(NMe_2Ph)][$B(C_6F_5)_4$] (F_6-acen = *N,N′*-ethylenebis(trifluoroacetylacetoneiminato)).[6] This complex shows a comparable Zr−N$_{\text{aniline}}$ distance of 2.441(4) Å; in CD_2Cl_2 solution the −NMe_2 moiety appears as a singlet at δ 2.86, and there is rapid exchange with

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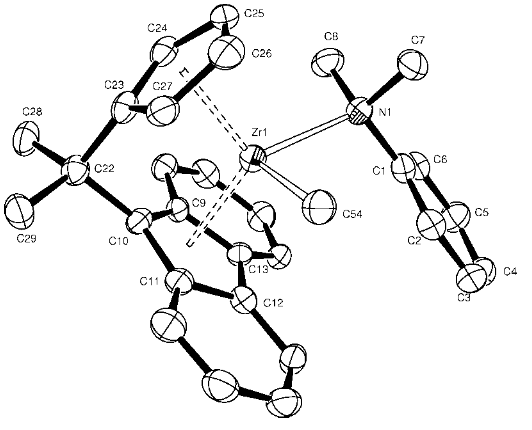
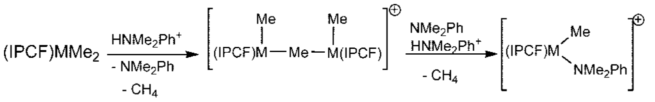


Figure 2. ORTEP representation of the $[(IPCF)ZrMe(NMe_2Ph)]^+$ cation, showing ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr−N(1) = 2.424(5), Zr−C(54) = 2.255(6), $Zr-Ct_{Cp}$ = 2.178, $Zr-Ct_{Flu}$ = 2.241; N(1)−Zr−C(54) = 96.75(19), $Ct_{Cp}-Zr-Ct_{Flu}$ = 118.13 (Ct = centroid of five-membered-ring ligand).

Scheme 1



free DMA. Cooling to −80 °C was necessary to show separate resonances for free and coordinated DMA; these signals coalesced at approximately −40 °C.

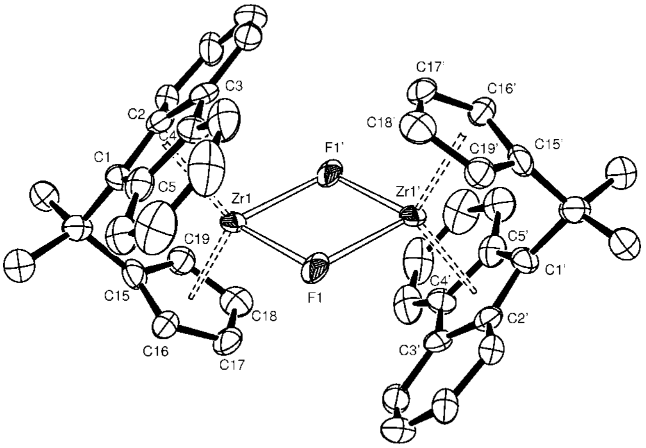


Figure 3. Structure of the $[\{(IPCF)Zr(\mu\text{-}F)\}_2]^{2+}$ dication in **5**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

A number of NMR spectroscopic studies have provided evidence for dimethylaniline coordination. Schaper et al. have studied the displacement of $MeB(C_6F_5)_3^-$ by DMA in benzene, giving an outer-sphere complex.[7] However, of the zirconocenes they studied, only in the case of the most open bis-Cp ligands could an equilibrium species with coordinated DMA be identified; there was no coordination to bis-indenyl or bis-benzindenyl species. A survey of the literature on spectroscopic studies of Zr−DMA species produced a mixture of accounts reporting either one or two NMe_2 signals, with considerable variation in their δ values. For example, in $[(EBI)Zr(Me)(NMe_2Ph)][B(4\text{-}C_6H_4F)_4]$ the resonances for the diastereotopic NMe_2 group were found upfield from free aniline (EBI = *rac*-C_2H_4(1-Ind)$_2$), at δ 1.83 and 1.34 (cf. δ 2.62 for free aniline, solvent C_6D_5Br at −20 °C).[8] Hollink et al. reported singlets at δ 3.20 and 3.03 in CD_2Cl_2 for $[Cp(^tBu_3P{=}N)Zr(Me)(NMe_2Ph)][B(C_6F_5)_4]$ but were unable to isolate the compound in an analytically pure form.[9] The spectroscopically observed DMA adducts $[Me_2Si(NBu^t)_2ZrR(NMe_2Ph)]^+$ show only single, very broad NMe_2 signals with highly solvent dependent chemical shifts (R = CH_2Ph, C_3H_6Ph, $CH_2CHMeCH_2Ph$).[10] Other relevant reports include the detection by Buchwald of weak DMA coordination in $[(EBTHI)M(H)NMe_2Ph)][Co(C_2B_9H_{11})_2]$ (M = Zr, Hf)[11] and that of Schrock et al., who reported polydentate zirconium and hafnium amido complexes where coordinated DMA (with equivalent methyl groups) did not exchange readily with free DMA on the NMR time scale.[12] The low ethylene polymerization activity of imino−oxazolinyl zirconium complexes is also thought to be due to DMA coordination.[13]

Extending the reaction of metallocene dimethyls with $[HNMe_2Ph][B(C_6F_5)_4]$ to the hafnocene $(IPCF)HfMe_2$ showed that the reaction is more complex and in fact proceeds in stages. In this case a mixture of $[(IPCF)HfMe(NMe_2Ph)]^+$ (**3**) and the binuclear cation $[\{(IPCF)HfMe\}_2(\mu\text{-}Me)]^+$ (**4**) was obtained. The binuclear species persisted over the temperature range from −30 to +20 °C and was only converted into the mononuclear cation after standing for several hours at room temperature (see the Supporting Information). Careful examination of the NMR spectra of $(IPCF)ZrMe_2/[HNMe_2Ph^+][B(C_6F_5)_4^-]$ mixtures at −40 °C showed that here too the methyl-bridged binuclear complex is produced in low concentration but is much less stable than the Hf analogue. It is clear therefore that the reaction of L_nMMe_2 with $HNMe_2Ph^+$ involves $[(L_nMMe)_2(\mu\text{-}Me)]^+$ as the primary product, which is cleaved by excess $HNMe_2Ph^+$ and DMA to give $[L_nMMe(NMe_2Ph)]^+$ (Scheme 1).

The reaction of **1** with $[Ph_3C][B(C_6F_5)_4]$ in place of $[HNMe_2Ph][B(C_6F_5)_4]$ gives the ion pair $[(IPCF)ZrMe^+\cdots B(C_6F_5)_4^-]$, which is, however, very unstable.[14] Storing the red-brown solution of this mixture in toluene/1,2-difluorobenzene at −26 °C for prolonged periods of time produced green needlelike crystals, along with a dark oily residue. The crystals were very poorly soluble and very sensitive to solvent removal; nevertheless, they were found to be suitable for X-ray analysis and were crystallographically identified as $[\{(IPCF)Zr(\mu\text{-}F)\}_2][B(C_6F_5)_4]_2\cdot 2$(toluene) (**5**·2(toluene)) (Figure 3). The identity of the bridging atom was determined by refinement of a number of possible candidates against the data set; the rest of the model was unchanged during this process. Only fluorine gave satisfactory displacement parameters after free refinement. Marks et al. have previously identified monofluoro-bridged complexes of the type $[\{(IPCF)ZrR\}_2(\mu\text{-}F)]^+$ (R = Me,[15] C_6F_5[16]) from similar reactions of **1** with various cation generating agents; both of these contain near-linear Zr−F−Zr bridges with Zr−F distances substantially shorter than those observed for **5** (ca.

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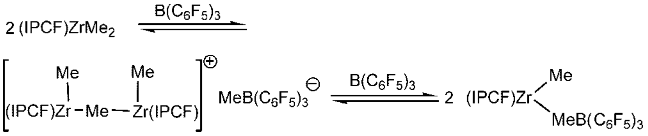
Table 1. Selected Bond Lengths (Å) and Angles (deg) of the Halide-Bridged Complexes $[\{(IPCF)Zr(\mu\text{-}X)\}_2]^{2+}[A^-]_2$

	X = F, A = $B(C_6F_5)_4$ (**5**)	X = Cl, A = $B(C_6F_5)_4$ (**6**)	X = Br, A = $Al(C_6F_5)_4{}^a$
Zr−X	2.454(4)	2.5898(11)	2.6772(13)
Zr−X′	2.481(5)	2.6046(11)	2.7155(13)
Zr−Ct_{Cp}	2.154	2.144	2.135
Zr−Ct_{Flu}	2.231	2.198	2.197
Zr···Zr′	2.528	3.844	3.896
Zr−X−Zr′	91.27(16)	95.47(4)	92.52(4)
X−Zr−X′	88.73(16)	84.53(4)	87.48(4)
Cp_{cent}−Zr−Flu_{cent}	118.18	119.40	120.23

[a] Reference 15.

Scheme 2



2.1−2.15 Å vs ≥2.45 Å for **5**). The formation of **5** provides evidence of yet another possible catalyst deactivation product in this system.

The chloro-bridged analogue $[\{(IPCF)Zr(\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2\cdot 2(toluene)$ (**6**·2(toluene)) was isolated from a reaction of **1** with $[HNMe_2Ph^+][B(C_6F_5)_4{}^-]$, which evidently contained a chloride impurity.[17] Pertinent structural parameters of **5** and **6** are collected in Table 1 for comparison, together with those of the known[15] bromo analogue.

Whereas the formation of cationic species with $HNMe_2Ph^+$ or $CPh_3{}^+$ salts is irreversible, the reaction of metallocene dimethyls with neutral Lewis acids LA is characterized by a set of equilibria, as studied by Brintzinger and co-workers for LA = $B(C_6F_5)_3$ (Scheme 2).[18]

The position of this equilibrium is strongly dependent on the size of LA: while for $B(C_6F_5)_3$ the mononuclear product $(IPCF)ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ is preferred,[19] bulkier anions such as $FPBB^-$, $MePBB^-$, and $[(C_6F_5)_3Al{-}F{-}Al(C_{12}F_9)_3]^-$ stabilize the binuclear cation $[\{(IPCF)ZrMe\}_2(\mu\text{-}Me)]^+$ (PBB = tris(perfluorobiphenylyl)borane).[15,16] We now found that cooling a mixture of **1** with $B(C_6F_5)_3$in a molar ratio of 2:1 at 4 °C gives crystalline $[\{(IPCF)ZrMe\}_2(\mu\text{-}Me)][MeB(C_6F_5)_3]$ (**7**) as orange plates (Figure 4). The structure of the cation is similar to previously reported examples but differs in the much more acute Zr−Me−Zr angle and the Me_{term}−Zr−Zr−Me_{term} torsion angle (Table 2). Isolation of **7** provides structural evidence for a hitherto missing member of the reaction equilibrium.

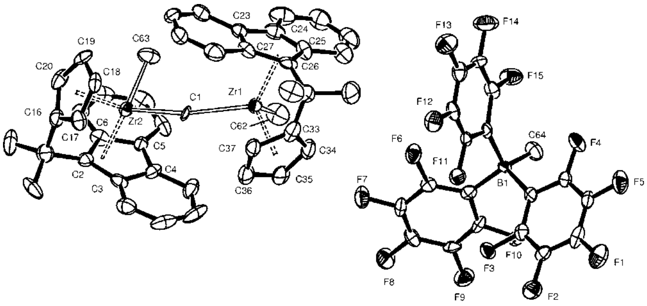


Figure 4. Structure of $[\{(IPCF)ZrMe\}_2(\mu\text{-}Me)][MeB(C_6F_5)_3]$ (**7**). Ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Ion Pairs $[\{(IPCF)ZrMe\}_2(\mu\text{-}Me)^+][A^-]$

	A = MeB $(C_6F_5)_3$ (**7**)	A = F $\{Al(C_6F_5)_3\}_2{}^a$	A = $(C_6F_5)_3AlF{-}Al$ $(C_{12}F_9)_3{}^a$
Zr−Me_{br}	2.429(10)	2.4179(3)	2.418(17)(av)
Zr−Me_{term}	2.257(8)	2.248(3)	2.253(18)
Zr−Me−Zr′	158.3(3)	180.0	161.1(6)
Zr···Zr′	4.857(10)	4.8358(4)	4.836(17)
Me_{term}−Zr−Zr′−Me'_{term}	61.24	180	62.79

[a] Reference 15.

In order to elucidate the strength of Zr−N and Zr−C bonding, we carried out a series of DFT calculations on the cations in **2** and **7** and, for comparison, on the pyridine analogue of **2**, $[(IPCF)ZrMe(py)]^+$. The bonding energy of the $[(IPCF)ZrMe]^+$ fragment and dimethylaniline in **2** was found to be −151 kJ mol^{-1}, significantly stronger than the Zr−C bond to the bridging methyl ligand in the homobinuclear complex **7** (−128 kJ mol^{-1}). Although these calculations did not include the effect of solvation, the energy difference of 23 kJ mol^{-1} is indicative of the surprisingly strong DMA binding in **2**.[20] Pyridine, on the other hand, is bound much some 47 kJ mol^{-1} more strongly than DMA, as befits a base that is a powerful catalyst poison.

Experimental Section

General Procedures. All manipulations were performed under dry nitrogen gas using standard Schlenk techniques. Solvents were purified by distillation under nitrogen from sodium−potassium alloy (light petroleum, bp 40−60 °C), sodium (low-sulfur toluene), or sodium−benzophenone (THF). $[HNMe_2Ph][B(C_6F_5)_4]$ was synthesized from $NMe_2Ph\cdot HCl$ and $Li[B(C_6F_5)_4]$ in dichloromethane and recrystallized from a dichloromethane/light petroleum solvent mixture. $Li[B(C_6F_5)_4]$ was made from $B(C_6F_5)_3$ and LiC_6F_5 in light petroleum[21] and was free from other borate impurities within NMR detection limits (^{19}F, ^{11}B) without further purification. The compounds $(IPCF)MMe_2$ (M = Zr (**1**), Hf) were synthesized following literature procedures.[22] Deuterated toluene was dried by stirring over Na/K alloy followed by trap-to-trap distillation; $1,2\text{-}F_2C_6H_4$ was degassed and dried over activated 4 Å molecular sieves. NMR (^1H, ^{13}C, ^{19}F, ^{11}B) spectra were recorded on a Bruker Avance DPX-300 spectrometer. Chemical shifts were referenced to residual solvent peaks.

Variable-temperature NMR spectra of ion pairs were recorded at temperature intervals of 10 °C. Acquisition relaxation delay (d1) was 12 s and time domain size 65 536 data points. A total of 32−64 scans were accumulated (^1H). Sample concentration was typically in the range 15−20 mM. For VT ^1H NMR experiments, samples were allowed to equilibrate at each temperature for 5−10 min. Stock solutions of DMA in toluene-d_8 were 0.1 M.

$[(IPCF)ZrMe(NMe_2Ph)][B(C_6F_5)_4]$ (2). $(IPCF)ZrMe_2$ (16.1 mg, 41 μmol) and $[HNMe_2Ph][B(C_6F_5)_4]$ (31.5 mg, 39 μmol) were dissolved in toluene (10 mL). This gave a red-orange solution, and a dark red oily residue settled on the bottom of the Schlenk tube. When

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(20) Strong DMA coordination was also observed in the reaction of $[HNMe_2Ph][B(C_6F_5)_4]$ with $(SBI)ZrMe_2$: $[(SBI)ZrMe(NMe_2Ph)]^+$ shows two signals for diastereotopic *N*-methyl groups around δ 2.1 and 1.5 (−30 to +20 °C) which coalesce and exchange with free DMA on heating to 50 °C (δ 1.95) (SBI = *rac*-$Me_2Si(Ind)_2$).

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the temperature was lowered overnight to −26 °C, red crystals formed on the sides of the vessel and, after a further couple of days, the solution was observed to have lightened in color, turning a very pale red, and more crystals had formed, identified crystallographically as **2**·2(toluene). Because of the small crop of crystalline material, an elemental analysis was not obtained. VT ^{1}H NMR studies of a solution generated from (IPCF)ZrMe$_2$ (9.0 mg, 23 μmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (18.2 mg, 23 μmol) in toluene-*d*$_8$/1,2-difluorobenzene (1/1 v/v) were conducted over the temperature range −30 to +20 °C. ^{1}H NMR (300.1 MHz, 0 °C, toluene-*d*$_8$/C$_6$H$_4$F$_2$; 1/1): δ 7.4−6.1 (Flu, overlapped with toluene, C$_6$H$_4$F$_2$, Me$_2$NPh and remaining C$_5$H$_4$ 1H), 5.23 (m, 1H, C$_5$H$_4$), 4.95 (m, 1H, C$_5$H$_4$), 4.87 (m, 1H, C$_5$H$_4$), 2.35 (s, 2H; free NMe$_2$), 1.90 (s, 3H, NMe), 1.83 (s, 3H, CMe), 1.60 (s, 3H, CMe), 1.34 (s, 3H, NMe), −0.78 (s, 3H, ZrMe).

In separate experiments, addition of DMA (5 μmol, 0.05 mL of stock solution) to a mixture of (IPCF)ZrMe$_2$ (4.9 mg, 13 μmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (9.8 mg, 12 μmol) in toluene-*d*$_8$/1,2-difluorobenzene (1/1 v/v) caused the signal at δ 2.35 to increase in intensity, accompanied by a downfield shift to δ 2.50 (at 0 °C). Warming to 40 °C resulted in coalescence of the NMe$_2$ signals of coordinated DMA at δ 1.77.

Freezing a mixture of solid [(IPCF)ZrMe$_2$ (7.0 mg, 18 μmol) and solid [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (14.8 mg, 18 μmol)] prior to solvent addition permitted the simultaneous formation of both **2** and **7** to be observed over the range −30 to 0 °C. The latter was indicated by the following ^{1}H NMR singlet resonances (300.1 MHz, 0 °C): δ −1.19 (ZrMe), −1.25 (ZrMe), −3.22 (μ-Me), and −3.39 (μ-Me), ratio of 2:4:2:1 for the two diastereomers of the [{(IPCF)ZrMe}$_2$(μ-Me)]$^+$ cation. However, by the time the sample reached 20 °C, none of this homodinuclear cation remained.

Reaction of (IPCF)HfMe$_2$ with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. The orange-red solution obtained from the reaction of (IPCF)HfMe$_2$ (8.2 mg, 20 μmol) with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (8.2 mg, 20 μmol) in toluene-*d*$_8$/1,2-difluorobenzene (1/1 v/v) was studied by ^{1}H NMR spectroscopy over the temperature range −30 to +20 °C. Resonances indicative of both [(IPCF)HfMe(NMe$_2$Ph)]$^+$ (**3**) and [{(IPCF)HfMe}$_2$(μ-Me)]$^+$ (**4**) were observed which persisted over the entire temperature range. An ambient-temperature ^{1}H NMR spectrum recorded after 24 h revealed predominantly signals belonging to **3**, with just a trace of **4** remaining. Cation **3**: ^{1}H NMR (300.1 MHz, 26 °C, toluene-*d*$_8$/C$_6$H$_4$F$_2$ 1/1) δ 7.7−6.0 (Flu, overlapped with toluene, difluorobenzene, DMA and remaining C$_5$H$_4$ 1H), 5.52 (m, 1H, C$_5$H$_4$), 5.11 (m, 1H, C$_5$H$_4$), 4.87 (m, 1H, C$_5$H$_4$), 2.48 (s, 6H, free NMe$_2$), 1.94 (s, 3H, CMe$_2$), 1.83 (b, 3H, NMe$_2$), 1.68 (s, 3H, CMe$_2$), 1.49 (b, 3H, NMe$_2$), −0.83 (s, 3H, HfMe). Cation **4**: ^{1}H NMR (300.1 MHz, 20 °C, toluene-*d*$_8$//C$_6$H$_4$F$_2$ 1/1) HfMe signals, all singlets, ratio of 2/2/1/1, −1.41 (HfMe), −1.45 (HfMe), −3.31 (μ-Me), −3.41 (μ-Me).

[{(IPCF)Zr(μ-F)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (5). (IPCF)ZrMe$_2$ (7.3 mg, 19 μmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (17.2 mg, 19 μmol) were dissolved in toluene (5 mL). The red-brown solution was stored at 4 °C. After several weeks, green needlelike crystals had formed, along with a dark oily residue, and the solution had turned more pale. The crystals, green blocks, were identified by single-crystal X-ray diffraction as **5**·2(toluene).

[{(IPCF)Zr(μ_2-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (6). In a 5 mm NMR tube equipped with a Teflon seal, (IPCF)ZrMe$_2$ (3.5 mg, 9 μmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. (7.2 mg, 9 μmol) were dissolved in toluene-*d*$_8$/C$_6$H$_4$F$_2$ (1 mL, 4/1 v/v), giving a purple solution. The sample was left at room temperature for several hours. During this time green crystals of **6**·2(toluene) were formed which were suitable for X-ray diffraction.

[{(IPCF)ZrMe}$_2$(μ-Me)][MeB(C$_6$F$_5$)$_3$] (7). (IPCF)ZrMe$_2$ (32.5 mg, 83 μmol) and B(C$_6$F$_5$)$_3$ (5.8 mL, 41 μmol, from a 71.3 mM stock solution in toluene) were combined to give an orange-red solution, which was stored at 4 °C. This yielded dark orange, featherlike crystals. The solid was identified by X-ray diffraction. Anal. Calcd for C$_{64}$H$_{48}$BF$_{15}$Zr$_2$: C, 59.35; H, 3.74. Found: C, 58.85; H, 4.31. ^{1}H NMR (300.1 MHz, 25 °C, toluene-*d*$_8$/1,2-difluorobenzene; ca. 4/1): δ 7.8−6.0 (Flu, overlapped with toluene, DFB, DMA, and remaining C$_5$H$_4$ 2H signals), 5.6−4.8 (C$_5$H$_4$ multiplets, total of 6H), 1.80−1.69 (4s, total of 12H, CMe), 1.25 (v br, s, 3H, MeB), −1.22 (s, 4H, ZrMe), −1.29 (s, 2H, ZrMe), −3.27 (s, 1H, μ-Me) and −3.39 (s, 2H, μ-Me).

Computational Details. The Gaussian-98 package was used for all calculations.[23] Calculations were carried out "in the gas phase" with the gradient-corrected functional B3LYP and the Lanl2dz basis set for all atoms. To establish comparison with the experiment, the interaction energy was calculated as a function of the Zr−N bond distance. The calculated equilibrium distance was shown to correspond very closely to the crystallographically determined value.

X-ray Crystallography. In all cases, crystals were suspended in perfluorinated polyether oil, mounted on a glass fiber, and transferred directly to the cold N$_2$ stream of the diffractometer. Data for compound **2** were collected on a Bruker-Nonius KappaCCD diffractometer equipped with a Bruker-Nonius FR591 molybdenum rotating anode (λ(Mo Kα) = 0.710 69 Å) and confocal mirrors; data collection and processing were controlled by the DENZO and SCALEPACK programs.[24] Diffraction data for compound **5** were collected on a Bruker SMART APEX2 CCD diffractometer at Daresbury SRS station 16.2smx operating at the wavelength λ = 0.797 70 Å; data collection and processing were carried out using the APEX2 and SAINT packages.[25] For compounds **6** and **7**, data collection took place on an Oxford Diffraction Xcalibur-3 system equipped with a molybdenum target and Enhance optics; collection and processing used the CrysAlis-CCD and -RED packages.[26]

In all cases, structure solution was carried out by the direct methods routines in the SIR-92 program[27] and refined by full-matrix least-squares methods on F^2 in SHELXL[28] within the WinGX program suite.[29] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. For crystal and refinement data see the Supporting Information (Table S1).

In compound **7**, the location of hydrogen atoms on the bridging carbon C(1) could not be determined from the diffraction data. The geometry at this carbon is also unlike that of the standard models for hydrogen placement. These hydrogen atoms were therefore omitted from the model, although they have been included in the calculation of the molecular formula.

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Supporting Information Available: Figures, tables, and CIF files giving NMR spectra of **2** and of hafnocene complexes and X-ray data for compounds **2**, **5**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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