tolyl)$_3$)$_2$: (1) For the acidic species, HCl and $CH_3C(O)Cl$, direct attack on the oxygen occurs with no evidence for an intermediate. (2) For MeI and EtI, oxidative-addition leads to an observable six-coordinate intermediate, which then reductively eliminates the alcohol providing the first example of carbon–hydroxide coupling on a metal center. In terms of bond formation reactions by reductive elimination, the hydroxide is more similar to a hydride and the methoxide is more similar to the methyl than the hydroxide and methoxide are to each other. (3) Reaction of H_2 with *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ results in elimination of H_2O and formation of $H_3Ir(CO)(P(p\text{-tolyl})_3)_2$ in a reaction that is partially reversible.

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Lewis-Base-Free Cationic Zirconocene Complexes Containing an Alkenyl Ligand

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Electrophilic cations $[Cp'_2ZrMe(NMe_2Ph)_n][B(4\text{-}C_6H_4F)_4]$ (**1**) ($n = 1$, $Cp'_2 = (C_5H_5)_2$ (**a**), $\{(Me_3Si)C_5H_4\}_2$ (**b**), $\{(Me_3C)C_5H_4\}_2$ (**c**), *rac*-C_2H_4(indenyl)$_2$ (**d**); $n = 0$, $Cp' = C_5Me_5$ (**e**)), generated in situ by protonolysis, react with internal alkynes to give Lewis-base-free alkenyl complexes $[Cp'_2ZrC(R^1){=}C(R^2)Me][B(4\text{-}C_6H_4F)_4]$ ($R^1 = SiMe_3$, $R^2 = Me$, **2a–d**; $R^1 = R^2 = Ph$, **3a–e**). ^1H, ^{13}C, and ^{29}Si NMR spectroscopy suggests that agostic coordination of a Si–Me group to the zirconium center occurs for complexes **2** in solution. The structure of **2d**·CH_2Cl_2 has been determined by X-ray crystallography. Crystal data: $C_{52}H_{49}BCl_2F_4SiZr$, $M = 950.99$, monoclinic, $P2_1/n$, $a = 15.402$ (3) Å, $b = 17.606$ (3) Å, $c = 16.960$ (3) Å, $Z = 4$, and $R = 0.050$ for 5392 "observed" reflections. The alkenyl ligand in **2d** interacts with electron-poor zirconium via agostic coordination of a Si–C and a C–H bond of the α-$SiMe_3$ group (Zr–Si = 2.935 (2) Å; Zr–C = 2.578 (5) Å; Zr–H = 2.26 (7) Å). ^{19}F NMR spectroscopy shows that the anion is noncoordinating in complexes **2**, **3c**, and **3e**; labile fluorine coordination to zirconium in complexes **1**, **3a**, **3b**, and **3d** results in upfield-shifted ^{19}F NMR resonances for the anion.

Introduction

The high reactivity of group 4 metallocene/alkylaluminoxane catalysts for alkene polymerization[1] is attributed to the presence of an electrophilic cationic active species, $[Cp'_2MR]^+$, in combination with a poorly coordinating anion.[2] Although insertion reactions of unsaturated molecules with model Lewis base complexes, $[Cp'_2MR(L)][BPh_4]$ (M = Ti, Zr), have been extensively investigated,[3] more electrophilic base-free complexes, closely related to the proposed catalyst active spcies, have been less well studied.[4,5] Because of the coordinating ability and facile degradation of $[BPh_4]^-$,[4,6,7] alternative anions such as fluorinated $[BPh_4]^-$ or carboranes are required for the stabilization of reactive base-free complexes.[6,8] Incorporation of fluorine in the 4-positions of $[BPh_4]^-$ was expected to suppress π-coordination of a benzene ring[7] and result in reactive cationic complexes. We report here the reaction of highly electrophilic methylzirconocene cations with bulky disubstituted alkynes and the unusual structure of a highly electron-deficient alkenyl product.

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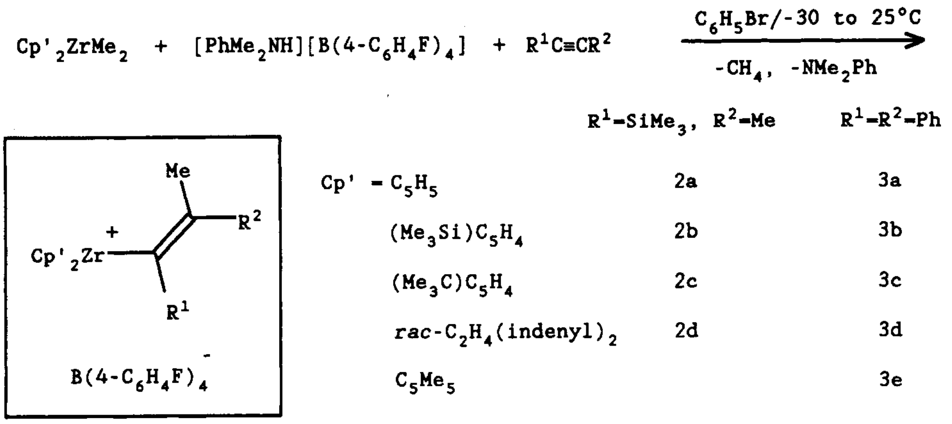
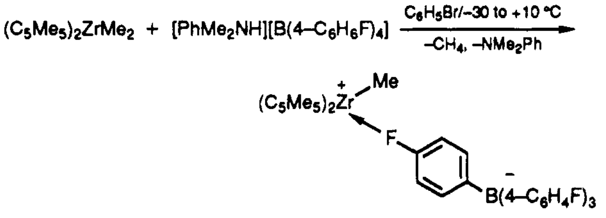
0276-7333/91/2310-3910$02.50/0

Scheme I



Results and Discussion

The reaction of $(C_5Me_5)_2ZrMe_2$ with $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ in bromobenzene (eq 1) deposits, on hexane addition, a yellow microcrystalline solid of composition (elemental analysis, NMR) $(C_5Me_5)_2ZrMe\{B(4\text{-}C_6H_4F)_4\}\cdot 0.2C_6H_5Br$ (**1e**). Remarkable coordination of one phenyl group of the anion to zirconium via a fluorine atom is shown by the presence of two ^{19}F NMR resonances ($C_2D_2Cl_4$, -30 °C) in a 3:1 ratio (δ -121.1 and -135.5 ppm, respectively).[8] Similar upfield fluorine shifts on coordination to a transition-metal cation have been observed for $[BF_4]^-$ or $[EF_6]^-$ (E = P, Sb).[9] Interaction of one phenyl group with zirconium is confirmed by the observation of ^1H and ^{13}C NMR resonances at -30 °C for two kinds of phenyl rings in a 1:3 ratio. The low steric demands of the Zr–F–R bridge apparently makes $[R\text{–}F]^-$ a good ligand for such a sterically crowded cation.



(1)

1e

Protonolysis of less crowded dimethylzirconocenes in C_6D_5Br gives labile *N,N*-dimethylaniline adducts, $[Cp'_2ZrMe(NMe_2Ph)_n][B(4\text{-}C_6H_4F)_4]$ ($n \leq 1$; $Cp'_2 = (C_5H_5)_2$, $\{(Me_3Si)C_5H_4\}_2$, $\{(Me_3C)C_5H_4\}_2$, *rac*-$C_2H_4(\text{indenyl})_2$; **1a–d**). Resonances due to the methyl groups and phenyl ortho hydrogens of coordinated NMe_2Ph are found upfield of the corresponding resonances for the observed free aniline in the ^1H NMR spectra; ligand chirality in **1d** leads to diastereotopic N*Me*$_2$Ph resonances at δ 1.83 and 1.34 ppm, compared to δ 2.62 for free aniline. Unlike **1b** and **1d**, solutions of **1c** containing the bulky $(Me_3C)C_5H_4$ ligand also show resonances due to another species, possibly an aniline-free adduct analogous to **1e**. The slight upfield shift and broadening of the single ^{19}F NMR resonance for **1b–d** compared to the free anion provides evidence for weak anion–cation interaction. Although **1a** shows low solubility in C_6D_5Br, ^1H and ^{19}F NMR studies in $C_2D_2Cl_4$ solution at -30 °C show that the anion is noncoordinating and that the aniline-coordinated adduct is the major cationic species present. Attempted precipitation of **1d** with hexane affords a complex mixture containing <1.0 equiv of NMe_2Ph.

The cationic complexes **1** decompose at varying rates (minutes to hours at 25 °C) in C_6D_5Br to give $Cp'_2ZrMe(4\text{-}C_6H_4F)$, $B(4\text{-}C_6H_4F)_3$, and NMe_2Ph (**1a,b,d**) and other unidentified products (**1c,e**). Although the complex stability appears to be concentration dependent, the stability increases with Cp' bulk: **1a** < **1b–d** < **1e**. There is no evidence from ^{19}F NMR spectroscopy for fluorine abstraction from the anion to give, for example, $Cp'_2ZrMe(F)$.[10] Despite the only moderate stability of complexes **1** in solution, they may be trapped by reaction with disubstituted alkynes.

Reaction of the in situ generated cations with $Me_3SiC{\equiv}CMe$ or $PhC{\equiv}CPh$ gives alkenyl complexes **2a–d** and **3a–e**, respectively, as shown in Scheme I. Addition of hexane results in the precipitation of the products (yields 60–90%), which, except for complexes **3a,d,e**, may be obtained in analytically pure form by recrystallization from CH_2Cl_2/hexane solution. Attempted reaction of complex **1a** with highly crowded $Me_3SiC{\equiv}CSiMe_3$ leads, in contrast, only to decomposition products. Complexes **2** and **3** under nitrogen are indefinitely stable in the solid state at -40 °C, but crystalline samples kept at 25 °C decompose over a period of days. Whereas solutions of complexes **2** in CD_2Cl_2 are stable for several hours at 25 °C, the lower stability of complexes **3** necessitates use of the less reactive $C_2D_2Cl_4$ for NMR studies. Because of the complex nature of the solid-state and solution decomposition reactions, they have not been further examined.

In order to compare the reactivity of **1** with alkynes to that of a Lewis base adduct, $[(C_5H_5)_2ZrMe(THF)][B(4\text{-}C_6H_4F)_4]$[3] was prepared as a pale yellow solid by protonolysis of $(C_5H_5)_2ZrMe_2$ in the presence of THF and characterized by ^1H and ^{13}C NMR spectroscopy. Whereas complexes **2** and **3** are formed within 1 min at or below 25 °C, the reaction between $[(C_5H_5)_2ZrMe(THF)][B(4\text{-}C_6H_4F)_4]$ (ca. 0.07 M) and 1.2 equiv of $Me_3SiC{\equiv}CMe$ or $PhC{\equiv}CPh$ in C_6D_5Br is only 12% and 5% complete, respectively, after 2 h at 25 °C. Extended reaction times lead, for $Me_3SiC{\equiv}CMe$, to extensive product decomposition and, for both alkynes, to only partial conversion ($PhC{\equiv}CPh$: 36% after 6 days) to $[(C_5H_5)_2Zr\{CR^1{=}CHR^2\}(THF)][B(4\text{-}C_6H_4F)_4]$ (**2a**·THF, **3a**·THF).

Lewis base adducts of the alkenyl complexes may be more cleanly prepared in situ by addition of THF or MeCN to solutions of complexes **2** (in CD_2Cl_2) or **3** (in C_6D_5Br), respectively. However, only analytically pure crystalline **2a**·MeCN (2 isomers, 4:1 ratio) and precipitate **3a**·THF have been isolated and further characterized by both ^1H and ^{13}C NMR spectroscopy. The observation of

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^1H NMR resonances for both free and coordinated MeCN on addition of excess MeCN to complexes **2** or **3** shows that MeCN exchange, if it occurs, is slow on the NMR time scale. In contrast, with the exception of the THF adducts of **2a** and **3a,b,d**, which show coordination-shifted THF resonances, all other THF adducts show only free THF resonances, although the cation resonances are clearly shifted compared to the base-free adducts.

With the exception of complexes **2d** and **3d**, which contain the inherently chiral *rac*-C_2H_4(indenyl)$_2$Zr fragment, all the complexes **2** and **3** show NMR resonances for *equivalent* cyclopentadienyl ligands, indicating that the alkenyl ligand lies in the equatorial plane of symmetry. Structural and NMR studies show that complexes **2** contain the bulky $SiMe_3$ substituent in the sterically less favorable α-position. Such regiospecificity probably arises because the alkyne methyl substituent most effectively stabilizes the postulated δ+ charge at the β-carbon in the transition state and the $SiMe_3$ group stabilizes the δ- charge at the α-carbon, provided steric effects are not dominant.[3c,11,12] Alternatively, an attractive interaction of a Si–Me bond of the coordinated alkyne with $[Cp'_2ZrMe]^+$ *before* insertion may be responsible for the product regiochemistry. Only in the case of the reaction of crowded **1e** with $Me_3SiC{\equiv}CMe$ is a complex *mixture* of α- and β-$SiMe_3$-substituted isomers (and other products) obtained.

The free anion resonance observed in the ^{19}F NMR spectrum (CD_2Cl_2, -90 °C, δ -121.3 ppm) for each of complexes **2** confirms that separated cations and anions are present. The cations show restricted rotation of the $SiMe_3$ group about the C_α–Si bond. The ^1H and ^{13}C NMR spectra of complexes **2** in CD_2Cl_2 each show a single Si*Me*$_3$ resonance at 25 °C, which broadens (**2a**) and splits into a more complex pattern (**2b–d**) at lower temperatures. Thus, the ^{13}C NMR spectrum of complex **2c** at -90 °C contains two Si*Me* resonances at δ 1.2 and -1.2 ppm, in a 1:2 ratio, with $^1J_{CH}$ values of 110 and 119 Hz, respectively. Chiral complex **2d**, at -60 °C, shows three equal Si*Me* resonances at δ 2.7, -0.5, and -5.2 ppm with $^1J_{CH}$ values of 116, 124, and 122 Hz, respectively. The lower coupling constant for the downfield resonance in each case is indicative of an agostic interaction[13] of a methyl C–H bond with zirconium; rapid methyl rotation averages out the different $^1J_{CH}$ values in the unique methyl group. No low-energy C–H vibration bands in the region 2700–2350 cm^{-1}, characteristic of some forms of agostic C–H–M bonding, may be observed in the IR spectra of complexes **2a–d** (or **3a,c,e**) in Nujol mull.

Band shape analysis of the variable-temperature ^1H NMR spectrum of **2d** showed that $\Delta G^\ddagger$ for $SiMe_3$ rotation is 10.7 (±0.2) kcal mol^{-1} at -15 °C (coallescence temperature). Steric crowding plays an important role in the restricted $SiMe_3$ rotation. The energy barrier for the fluxional process decreases as the steric bulk of the cyclopentadienyl ligand decreases in the series (approximate $\Delta G^\ddagger$, kcal mol^{-1}, -90 °C): **2c** (8.9) > **2b** (8.1) > **2a** (7.1).

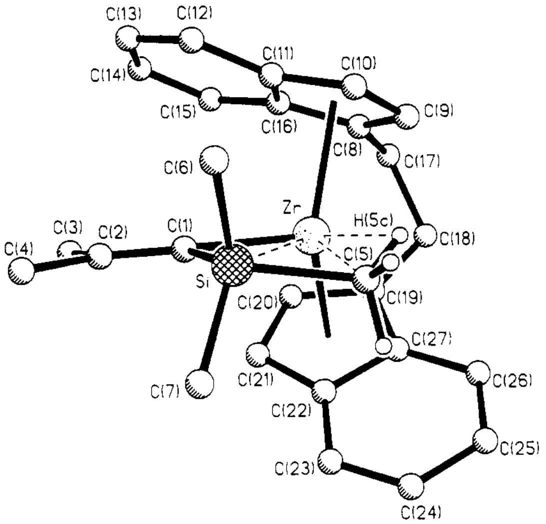

Figure 1. Molecular geometry of the cation in **2d**. Hydrogen atoms, except for those of the coordinated methyl group, have been omitted for clarity.

Table I. Crystallographic Data for Complex 2d

formula: $C_{52}H_{49}BCl_2F_4SiZr$
fw: 950.99
cryst syst: monoclinic
space group: $P2_1/n$ (No. 14)
cryst dimens: 0.35 × 0.40 × 0.50 mm
Nicolet P3m: 2θ range 4.0–50.0°
no. of rflns: 8557
no. of indep rflns: 7962
no. of rflns ($I > 2\sigma(I)$): 5392
$R = 5.0\%$; $R_w = 5.8\%$ (5392 rflns)
$w^{-1} = \sigma_c^2(F_o) + 0.0005F_o^2$

$a = 15.402$ (3) Å
$b = 17.606$ (3) Å
$c = 16.960$ (3) Å
$\beta = 101.87$ (2)°
$V = 4500$ (2) Å^3
$Z = 4$
$D_x = 1.40$ g cm^{-3}
$T = -73$ °C
$\lambda = 0.71069$ Å (Mo Kα)
$\mu = 4.4$ cm^{-1} (graphite monochromator)
$S = 1.54$

The importance of agostic interactions in restricting $SiMe_3$ rotation is seen, however, in the observation that Lewis base adducts of complexes **2** undergo more facile $SiMe_3$ rotation than the base-free complexes. Thus, whereas the ^1H NMR spectrum (CD_2Cl_2, -90 °C) of **2c** shows two sharp Si*Me* resonances (2:1 ratio), **2c**·MeCN exhibits a single sharp ("averaged") Si*Me* resonance. Similarly, whereas **2d** shows three sharp resonances at -90 °C, the two isomers of **2d**·MeCN (85:15 ratio) show three *broad* SiMe resonances and a single sharp Si*Me* resonance, respectively. It is tempting to assign the major isomer of **2d** as the endo isomer,[3b] with the $SiMe_3$ adjacent to a bulky indenyl group such that the slower $SiMe_3$ rotation results from steric interaction of the groups. The minor isomer might be assigned as the exo complex,[3b] in which the more freely rotating $SiMe_3$ group is adjacent to the coordinated acetonitrile ligand. However, we have no conclusive evidence for the structures of the two isomers of **2d**·MeCN.

Important evidence for agostic interaction of a *Si–C* bond with zirconium is provided by ^{29}Si NMR spectroscopy. The *Si*Me$_3$ resonances (CD_2Cl_2, 0 °C) of **2a** and **2c** at δ -54.7 and -59.6 ppm, respectively, are located 43.1 and 46.9 ppm upfield, respectively, of the resonances for the Lewis base adducts, **2a**·MeCN and **2c**·MeCN, in which agostic coordination is presumably weaker. Such a novel upfield shift of the ^{29}Si NMR resonance on coordination of a β-Si–C bond is reminiscent of upfield ^1H and ^{13}C NMR resonances for the β-CH_n fragment of alkyl groups involved in agostic β-C–H–M bonding in related d^0 cations;[14] it should be noted, however, that the ^{13}C NMR resonance

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Table II. Bond Lengths (Å) for the Cation of 2d

Zr···Si	2.935 (2)	Zr–C(1)	2.180 (5)
Zr···C(5)	2.578 (5)	Zr···H(5C)	2.263 (67)
Zr–C(8)	2.482 (5)	Zr–C(9)	2.452 (5)
Zr–C(10)	2.504 (5)	Zr–C(11)	2.606 (5)
Zr–C(16)	2.558 (5)	Zr–C(19)	2.457 (5)
Zr–C(20)	2.453 (4)	Zr–C(21)	2.511 (5)
Zr–C(22)	2.568 (5)	Zr–C(27)	2.527 (5)
Si–C(1)	1.895 (5)	Sr–C(5)	1.953 (6)
Si–C(6)	1.866 (5)	Si–C(7)	1.869 (6)
C(1)–C(2)	1.334 (6)	C(2)–C(3)	1.501 (6)
C(2)–C(4)	1.517 (7)	C(5)–H(5A)	0.945 (67)
C(5)–H(5B)	1.002 (76)	C(5)–H(5C)	0.964 (80)
C(8)–C(9)	1.406 (6)	C(8)–C(16)	1.430 (7)
C(8)–C(17)	1.512 (7)	C(9)–C(10)	1.405 (7)
C(10)–C(11)	1.423 (7)	C(11)–C(12)	1.418 (7)
C(11)–C(16)	1.436 (7)	C(12)–C(13)	1.356 (8)
C(13)–C(14)	1.426 (9)	C(14)–C(15)	1.353 (8)
C(15)–C(16)	1.429 (7)	C(17)–C(18)	1.532 (8)
C(18)–C(19)	1.503 (7)	C(19)–C(20)	1.419 (6)
C(19)–C(27)	1.417 (7)	C(20)–C(21)	1.412 (7)
C(21)–C(22)	1.431 (7)	C(22)–C(23)	1.418 (7)
C(22)–C(27)	1.453 (7)	C(23)–C(24)	1.354 (7)
C(24)–C(25)	1.413 (8)	C(25)–C(26)	1.366 (8)
C(26)–C(27)	1.423 (6)		

Table III. Selected Bond Angles (deg) for the Cation of 2d

Si–Zr–C(1)	40.2 (1)	Si–Zr–C(5)	40.8 (1)
C(1)–Zr–C(5)	80.6 (2)	Si–Zr–H(5C)	58.3 (19)
C(1)–Zr–H(5C)	98.3 (19)	C(5)–Zr–H(5C)	21.7 (20)
Zr–Si–C(1)	48.0 (1)	Zr–Si–C(5)	59.7 (1)
C(1)–Si–C(5)	107.0 (2)	C(1)–Si–C(6)	115.0 (2)
C(5)–Si–C(6)	106.1 (2)	C(1)–Si–C(7)	114.1 (2)
C(5)–Si–C(7)	101.4 (2)	C(6)–Si–C(7)	111.7 (3)
Zr–C(1)–Si	91.8 (2)	Zr–C(1)–C(2)	146.1 (4)
Si–C(1)–C(2)	121.8 (4)	C(1)–C(2)–C(3)	122.5 (4)
C(1)–C(2)–C(4)	125.4 (4)	C(3)–C(2)–C(4)	112.1 (4)
Zr–C(5)–Si	79.4 (2)	Zr–C(5)–H(5A)	150.3 (53)
Si–C(5)–H(5A)	98.9 (44)	Zr–C(5)–H(5B)	103.0 (39)
Si–C(5)–H(5B)	111.3 (42)	Zr–C(5)–H(5C)	60.4 (39)
Si–C(5)–H(5C)	122.2 (43)	Zr–H(5C)–C(5)	97.9 (46)
C(9)–C(8)–C(16)	107.1 (4)	C(9)–C(8)–C(17)	126.2 (4)
C(16)–C(8)–C(17)	126.7 (4)	C(8)–C(9)–C(10)	109.5 (4)
C(9)–C(10)–C(11)	108.2 (4)	C(10)–C(11)–C(12)	133.0 (5)
C(10)–C(11)–C(16)	106.9 (4)	C(12)–C(11)–C(16)	120.1 (4)
C(11)–C(12)–C(13)	117.9 (5)	C(12)–C(13)–C(14)	122.6 (5)
C(13)–C(14)–C(15)	121.0 (5)	C(14)–C(15)–C(16)	118.7 (5)
C(8)–C(16)–C(11)	108.2 (4)	C(8)–C(16)–C(15)	132.4 (4)
C(11)–C(16)–C(15)	119.6 (5)	C(8)–C(17)–C(18)	110.3 (4)
C(17)–C(18)–C(19)	110.2 (4)	C(18)–C(19)–C(20)	126.4 (4)
C(18)–C(19)–C(27)	126.7 (4)	C(20)–C(19)–C(27)	106.9 (4)
C(19)–C(20)–C(21)	110.1 (4)	C(20)–C(21)–C(22)	107.5 (4)
C(21)–C(22)–C(23)	133.5 (5)	C(21)–C(22)–C(27)	106.9 (4)
C(23)–C(22)–C(27)	119.6 (4)	C(22)–C(23)–C(24)	119.0 (5)
C(23)–C(24)–C(25)	121.7 (5)	C(24)–C(25)–C(26)	118.3 (5)
C(19)–C(27)–C(22)	108.6 (4)	C(19)–C(27)–C(26)	132.1 (5)
C(22)–C(27)–C(26)	119.4 (4)		

Table IV. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 2d

	x	y	z	U(eq)[a]
Zr	2329 (1)	7516 (1)	9306 (1)	18 (1)
Si	3800 (1)	6464 (1)	9276 (1)	24 (1)
C(1)	2580 (3)	6429 (3)	8778 (3)	21 (1)
C(2)	2246 (3)	5877 (3)	8267 (3)	22 (2)
C(3)	1303 (3)	5880 (3)	7808 (3)	30 (2)
C(4)	2755 (4)	5191 (3)	8065 (3)	34 (2)
C(5)	4034 (3)	7478 (3)	9739 (3)	27 (1)
H(5A)	4552 (51)	7369 (41)	10129 (44)	80
H(5B)	5231 (46)	7835 (42)	9350 (44)	80
H(5C)	3688 (49)	7694 (40)	10097 (44)	80
C(6)	4147 (3)	5782 (3)	10124 (3)	35 (2)
C(7)	4565 (3)	6437 (3)	8552 (3)	40 (2)
C(8)	1210 (3)	7828 (3)	10121 (3)	22 (2)
C(9)	2052 (3)	7871 (3)	10631 (3)	24 (2)
C(10)	2424 (3)	7140 (3)	10745 (3)	28 (2)
C(11)	1795 (3)	6612 (3)	10327 (3)	29 (2)
C(12)	1781 (4)	5808 (3)	10277 (3)	36 (2)
C(13)	1051 (5)	5472 (3)	9829 (4)	48 (2)
C(14)	311 (4)	5895 (3)	9407 (4)	44 (2)
C(15)	301 (3)	6663 (3)	9441 (3)	33 (2)
C(16)	1044 (3)	7045 (3)	9921 (3)	23 (2)
C(17)	599 (3)	8489 (3)	9834 (3)	30 (2)
C(18)	1071 (3)	9074 (3)	9401 (3)	28 (2)
C(19)	1525 (3)	8683 (3)	8808 (3)	23 (2)
C(20)	1168 (3)	8092 (3)	8270 (3)	23 (1)
C(21)	1808 (3)	7837 (3)	7843 (3)	26 (2)
C(22)	2585 (3)	8292 (3)	8092 (3)	23 (2)
C(23)	3416 (3)	8325 (3)	7856 (3)	30 (2)
C(24)	4021 (4)	8847 (3)	8204 (3)	36 (2)
C(25)	3849 (3)	9351 (3)	8802 (3)	32 (2)
C(26)	3061 (3)	9349 (3)	9053 (3)	26 (2)
C(27)	2399 (3)	8819 (3)	8696 (3)	20 (1)
F(1)	4592 (2)	4667 (2)	7709 (2)	45 (1)
F(2)	9827 (2)	7271 (2)	6745 (2)	41 (1)
F(3)	7264 (2)	3318 (2)	3312 (2)	42 (1)
F(4)	10252 (2)	2376 (2)	8816 (2)	57 (1)
B	7931 (4)	4399 (3)	6629 (3)	21 (2)
C(28)	6993 (3)	4481 (3)	6946 (3)	21 (1)
C(29)	6441 (3)	5128 (3)	6779 (3)	28 (2)
C(30)	5644 (3)	5199 (3)	7033 (3)	30 (2)
C(31)	5382 (3)	4606 (3)	7459 (3)	31 (2)
C(32)	5861 (3)	3961 (3)	7622 (3)	28 (2)
C(33)	6671 (3)	3907 (3)	7370 (3)	25 (2)
C(34)	8420 (3)	5231 (3)	6633 (3)	22 (1)
C(35)	8975 (3)	5411 (3)	6100 (3)	23 (2)
C(36)	9451 (3)	6085 (3)	6132 (3)	28 (2)
C(37)	9365 (3)	6601 (3)	6708 (3)	30 (2)
C(38)	8828 (3)	6479 (3)	7254 (3)	30 (2)
C(39)	8376 (3)	5788 (3)	7212 (3)	26 (2)
C(40)	7730 (3)	4054 (3)	5702 (3)	20 (1)
C(41)	8397 (3)	3735 (3)	5360 (3)	24 (2)
C(42)	8261 (3)	3490 (3)	4566 (3)	28 (2)
C(43)	7418 (3)	3560 (3)	4103 (3)	27 (2)
C(44)	6723 (3)	3855 (3)	4388 (3)	27 (2)
C(45)	6892 (3)	4094 (3)	5189 (3)	23 (2)
C(46)	8593 (3)	3826 (3)	7238 (3)	23 (2)
C(47)	9219 (3)	4092 (3)	7903 (3)	28 (2)
C(48)	9773 (3)	3614 (3)	8438 (3)	35 (2)
C(49)	9697 (4)	2849 (4)	8302 (3)	40 (2)
C(50)	9105 (4)	2541 (3)	7675 (3)	41 (2)
C(51)	8559 (3)	3039 (3)	7148 (3)	32 (2)
Cl(1)	7338 (2)	1308 (1)	5946 (1)	102 (1)
Cl(2)	7751 (3)	1459 (2)	4385 (2)	168 (2)
C(52)	7243 (6)	1853 (5)	5106 (5)	78 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

ascribed to the agostic methyl in complexes **2** is generally observed *downfield* of the resonance(s) of the noncoordinated methyl groups.

X-ray crystal structure analysis for ethylenebis(indenyl) complex **2d** as its dichloromethane solvate shows that the complex exists as isolated cations and anions. The structure of the cation in **2d** is illustrated in Figure 1, crystal data are given in Table I, bond distances and angles are given in Tables II and III, respectively, and atomic coordinates are given in Table IV. The study confirms that a SiMe group interacts strongly with the metal center, but via coordination of both a Si–C and a C–H bond, such that the metal attains a formal 18-electron count. The Zr···C(5) separation of 2.578 (5) Å compares to a normal Zr–C(sp^3) single-bond length of ca. 2.33 Å,[15] whereas the Zr···Si separation of 2.935 (2) Å is only slightly greater than the Zr–Si single-bond distance of 2.813 (2) Å in $(C_5H_5)_2Zr(SiPh_3)Cl$.[16] Coordination of the Si–CH_3 bond results in clear Si–C bond lengthening by ca. 0.1 Å. The remaining major structural features of the alkenyl ligand

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(Zr–C(1) and C(1)–C(2) bond distances and Zr–C(1)–C(2) and Zr–C(1)–Si bond angles) are relatively similar to those of the related Lewis base adduct $[(C_5H_5)_2Zr\{C(Me){=}C(Me)(n\text{-}Pr)\}(THF)][BPh_4]$.[3b]

The structure of **2d** is of particular importance, since the hydrogens of the coordinated methyl group were independently located, unlike the poorly refined related structure of $[(C_5H_5)_2TiC(SiMe_3){=}C(Ph)Me][AlCl_4]$.[2c] In contrast to other species showing agostic Si–Me–M bonding, in which *two* methyl hydrogens generally point towards the metal,[17] in **2d** one of the hydrogens, H(5c), is uniquely close to zirconium (Zr···H distances: 2.26 (7) Å, H(5c); 2.97 (7) Å, H(5b); 3.43 (7) Å, H(5a)). Ab initio MO calculations[18] on the model complex $[Ti\{C(SiH_2CH_3){=}CH_2\}Cl_2]^+$ suggested, in contrast, that the methyl group should adopt a *staggered* conformation to maximize more important β-Si–C–M bonding and minimize repulsion between the hydrogens and titanium. Considering that coordinated methyl rotation about the $Si–CH_3$ bond is fast (solution NMR) and therefore the different agostic C–H–M bonding modes are relatively similar in energy, and that the metal and ligands in the model system and **2** are very different, further speculation about the origin of the differences in C–H–M bonding is unwarranted. It is likely, however, that electron donation from the C(5)–H(5c) bond to the metal plays a subsidiary role to donation from the Si–C(5) bond.

Unlike complexes **2a–d**, weak anion coordination to the cations, via a Zr–F–C interaction involving one phenyl group, is confirmed by ^{19}F NMR spectroscopy for PhC≡CPh insertion products **3a,b,d**. Solutions of complex **3a** in $C_2D_2Cl_4$/toluene-d_8 show two major fluorine resonances at –55 °C (3:1 ratio of peaks at δ –121.9 and –175.8 ppm), which broaden as the temperature is raised, coalesce at ca. 0 °C, and give a single broad resonance at δ –134.9 ppm at 50 °C. More crowded **3b,d** ($C_2D_2Cl_4$, –30 °C) show relatively sharp "averaged" resonances at δ –126.2 and –126.9 ppm, respectively, due to rapid exchange of the two fluorine environments. More sterically crowded compounds **3c** (Cp′ = $(Me_3C)C_5H_4$) and **3e** (Cp′ = C_5Me_5), and Lewis base adduct **3a**·THF, contain "free" counteranion (δ –121.8 ppm).

Among complexes **3**, only crowded **3e** shows evidence of restricted rotation of the α-phenyl ring. The unusual upfield location of the α-phenyl *o*- and *m*-hydrogen resonances (C_6D_5Br, –30 °C; δ 6.41 and 6.67 ppm, respectively) and of the *broad o*-carbon resonance ($C_2D_2Cl_4$, –30 °C; δ 114.7 ppm) may be due to a weak in-plane $C_o–H_o–Zr$ agostic interaction, in combination with the ring current effect of the β-phenyl ring on the fluxional *in-plane* α-phenyl group. Electron donation from the filled π-orbital of the ipso-carbon to zirconium, related to bonding in η^2-benzyl complexes,[19] may be more significant in the less crowded complexes **3a–d**.

Conclusions

The labile anion $[B(4\text{-}C_6H_4F)_4]^-$ has allowed the in situ synthesis of highly electrophillic methylzirconocene cations, which, with bulky alkynes, are significantly more reactive than Lewis base adducts. The electron deficiency of the alkenyl products is reflected in weak anion coordination for the less crowded compounds and in unusual coordination of Si–C and C–H σ-bonds to zirconium in complexes **2**. A related secondary interaction of the β-C–H bond of the growing polymer chain with the metal[14] may play an important role in the stereoselectivity of alkene polymerization by metallocene catalysts.

Experimental Section

All experiments were performed under nitrogen in a Braun MB 200-G drybox or under argon with standard Schlenk techniques. Bromobenzene (Aldrich, "Gold Label") was dried by distillation from calcium. Other solvents were dried by refluxing over and distilling from standard reagents. NMR solvents and 1-(trimethylsilyl)prop-1-yne were dried over 4-Å molecular sieves before use. *rac*-C_2H_4(indenyl)$_2ZrCl_2$, containing less than 5% of the meso isomer, was prepared by following the improved procedure of Collins.[20] $\{(Me_3Si)C_5H_4\}_2ZrCl_2$,[21] $\{(Me_3C)C_5H_4\}_2ZrCl_2$,[22] and $(C_5Me_5)_2ZrCl_2$[23] were obtained by literature methods. The dichloride complexes were converted to dimethylzirconocene complexes by reaction with LiMe in ether, followed by recrystallization from toluene/hexane solution. $Na[B(C_6H_5F)_4]$ was obtained by literature methods[24] and converted to $[PhMe_2NH][B(C_6H_4F)_4]$ by a metathesis reaction with $[PhMe_2NH]Cl$ in cold distilled water. All other reagents were purchased from commercial sources and used without further purification.

^1H NMR (200.00 MHz) spectra were recorded on a Varian XL-200 instrument, and ^{13}C NMR (75.43 MHz), ^{19}F NMR (283.23 MHz), and ^{29}Si NMR (59.60 MHz) spectra were recorded on a Varian VXR-300 instrument. NMR data are listed in parts per million downfield from TMS for proton, carbon, and silicon and relative to $CFCl_3$ for fluorine. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, Germany.

Reaction of $(C_5H_5)_2ZrMe_2$ with $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$. Addition of a solution of $(C_5H_5)_2ZrMe_2$ (6 mg, 0.024 mmol) in C_6D_5Br (0.7 mL) to solid $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (12 mg, 0.023 mmol) in a reaction bottle at –30 °C resulted in the deposition of a yellow solid (believed to be $[(C_5H_5)_2ZrMe(NMe_2Ph)][B(4\text{-}C_6H_4F)_4]$); on warming to 25 °C (<5 min) a yellow solution containing $B(4\text{-}C_6H_4F)_3$, NMe_2Ph, and $(C_5H_5)_2ZrMe(4\text{-}C_6H_4F)$ was obtained. ^1H NMR of neutral complex (25 °C): δ 7.2–7.0 (m, 4, C_6H_4F), 5.89 (s, 10, C_5H_5), 0.17 (s, 3, Zr-*Me*). When the above reaction was repeated in $C_2D_2Cl_4$ in an NMR tube at –30 °C, $[(C_5H_5)_2ZrMe(NMe_2Ph)][B(4\text{-}C_6H_4F)_4]$ (**1a**) was observed spectroscopically as the major product (ca. 70%) in addition to unidentified decomposition products. ^1H NMR (–30 °C): δ, 7.25 (br, 8, *o*-C_6H_4F), 7.14 (dd, coord NMe_2Ph *m*-H), 6.77 (dd, 8, *m*-C_6H_4F), 6.70 (d, 2, coord NMe_2Ph *o*-H), 5.93 (s, 10, C_5H_5), 2.62 (s, 6, coord NMe_2Ph), 0.76 (s, 3, Zr-*Me*); *p*-H of NMe_2Ph obscured. ^{19}F NMR (–30 °C): δ –121.6 ($\Delta\nu_{1/2}$ = 28 Hz).

Reaction of $[\{(Me_3Si)C_5H_4\}_2ZrMe_2]$ with $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$. Addition of a solution of $\{(Me_3Si)C_5H_4\}_2ZrMe_2$ (20 mg, 0.051 mmol) in C_6D_5Br (0.7 mL) to solid $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (26 mg, 0.051 mmol) in a reaction bottle at –30 °C, followed by warming to ca. 10 °C, gave a yellow solution containing $[\{(Me_3Si)C_5H_4\}_2ZrMe(NMe_2Ph)][B(4\text{-}C_6H_4F)_4]$ (**1b**) as the major product, together with decomposition products. ^1H NMR (–30 °C): δ 7.72 (br, 8, *o*-C_6H_4F), 7.03 (m, 8, *m*-C_6H_4F), 6.39 (d, 2, coord NMe_2Ph *o*-H), 6.03, 5.78, 5.75, 5.62 (s, 2, $(Me_3Si)C_5H_4$), 1.89 (s, 6, coord NMe_2Ph), 0.65 (s, 3, Zr-*Me*), 0.08 (s, 18, $(Me_3Si)C_5H_4$); other resonances obscured. ^{19}F NMR (–30 °C): δ –122.6 ($\Delta\nu_{1/2}$ = 44 Hz). The broadening and upfield shift of the anion ^{19}F NMR resonance compared to that for the "free" anion (δ –122.2, $\Delta\nu_{1/2}$ = 24 Hz) is indicative of a weak anion–cation interaction. The mixture of complexes decomposed at 25 °C ($t_{1/2}$ ca. 10 min) to a mixture of $B(4\text{-}C_6H_4F)_3$, NMe_2Ph, and $[\{Me_3Si)C_5H_4\}_2ZrMe(4\text{-}C_6H_4F)$. ^1H NMR (25 °C): δ 6.30, 6.15, 6.13, 5.96 (s, 2,

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$(Me_3Si)C_5H_4$), 0.19 (s, 3, Zr–*Me*), 0.09 (s, 18, $(Me_3Si)C_5H_4$); other resonances obscured.

Reaction of $[\{(Me_3C)C_5H_4\}_2ZrMe_2]$ with $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$. Addition of a solution of $\{(Me_3C)C_5H_4\}_2ZrMe_2$ (14 mg, 0.039 mmol) in C_6D_5Br to solid $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (20 mg, 0.041 mmol) at −30 °C, followed by warming to 25 °C, gave a yellow solution containing $[\{(Me_3C)C_5H_4\}_2ZrMe(NMe_2Ph)][B(4\text{-}C_6H_4F)_4]$ (**1c**) as the major product. ^{1}H NMR (−30 °C): δ 7.72 (br, 8, *o*-C_6H_4F), 6.99 (dd, 8, *m*-C_6H_4F), 6.43 (d, 2, NMe_2Ph *o*-H), 5.77, 5.69, 5.51, 5.36 (m, 2, $(Me_3C)C_5H_4$), 1.91 (br, 6, NMe_2Ph), 0.90 (s, 18, $(Me_3C)C_5H_4$), 0.74 (s, 3, Zr–*Me*); other resonances obscured. ^{1}H NMR (25 °C): δ 7.64 (br, 8, *o*-C_6H_4F), 6.90 (dd, 8, *m*-C_6H_4F), 6.60 (d, 2, NMe_2Ph *o*-H), 6.09, 5.81 (vbr, 4, $(Me_3C)C_5H_4$), 2.63 (br, 6, NMe_2Ph), 0.90 (s, 18, $(Me_3C)C_5H_4$), 0.74 (s, 3, Zr–*Me*). ^{19}F NMR (−30 °C): δ −122.9 ($\Delta\nu_{1/2}$ = 85 Hz). ^{19}F NMR (25 °C): δ −124.3 ($\Delta\nu_{1/2}$ = 105 Hz). The broadening and upfield shift of the anion ^{19}F NMR resonance compared to that for the "free" anion (see above) suggest that the above complex is in temperature-dependent equilibrium with "$\{(Me_3C)C_5H_4\}_2ZrMe(B(4\text{-}C_6H_4F)_4)$" [−30 °C; $(Me_3C)C_5H_4$: δ 0.83 ppm; other resonances broad/obscured] and free NMe_2Ph. The downfield shift of the *average* NMe_2Ph resonance (−30 °C, δ 2.44 ppm; 25 °C, δ 2.63 ppm) as the temperature is raised suggests that the equilibrium is shifted in the direction of the aniline-free species at higher temperatures. The mixture of complexes decomposed at 25 °C ($t_{1/2}$ ca. 60 min) to unidentified products.

Reaction of *rac*-$C_2H_4(indenyl)_2ZrMe_2$ with $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$. A solution of *rac*-$C_2H_4(indenyl)_2ZrMe_2$ (15 mg, 0.040 mmol) in C_6D_5Br (0.7 mL) at −30 °C was added to solid $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (20 mg, 0.041 mmol) in a reaction bottle at −30 °C. The stirred reaction mixture was warmed to 25 °C over 5 minutes and rapidly filtered to give an intense yellow solution. The ^{1}H NMR resonances of [*rac*-$C_2H_4(indenyl)_2ZrMe(NMe_2Ph)][B(4\text{-}C_6H_4F)_4]$ (**1d**) were assigned by using a 2-D COSY NMR experiment. ^{1}H NMR (C_6D_5Br, −20 °C): δ 7.70 (br, 8, *o*-C_6H_4F), 7.52 (d, 1, ind C_6), 6.95 (m, 9, *m*-C_6H_4F and NMe_2Ph *m*-H), 5.97 (m, 1, NMe_2Ph *p*-H), 5.91, 5.79 (d, 1, ind C_5), 5.75 (m, 2, NMe_2Ph *o*-H), 5.71, 4.39 (d, 1, ind C_5), 3.5–3.0 (m, 4, $-CH_2CH_2-$), 1.83, 1.34 (s, 3, NMe_2Ph), −0.50 (Zr–*Me*); other resonances obscured. ^{1}H NMR (C_6D_5Br, 25 °C): 1.91 (vbr, 6, NMe_2Ph). ^{19}F NMR (C_6D_5Br, −30 °C): δ −122.4 ($\Delta\nu_{1/2}$ = 35 Hz). The slight broadening and upfield shift of the anion ^{19}F NMR resonance compared to that for the "free" anion (see above) is indicative of a weak anion–cation interaction. The solutions of **1d** in C_6D_5Br decomposed at 25 °C ($t_{1/2}$ ca. 30 min) to give $B(4\text{-}C_6H_4F)_3$, NMe_2Ph, and *rac*-$C_2H_4(indenyl)_2ZrMe(4\text{-}C_6H_4F)$. ^{1}H NMR (25 °C): δ 6.66 (dd, 2, C_6H_4F), 6.53 (d, 1, ind C_5), 6.43 (dd, 2, C_6H_4F), 6.31, 5.91, 5.84 (d, 1, ind C_5), 3.3–1.9 (m, 4, $-CH_2CH_2-$), −0.75 (Zr–*Me*); other resonances obscured.

Preparation of $(C_5Me_5)_2ZrMe\{B(4\text{-}C_6H_4F)_4\}$ (1e). Bromobenzene (10 mL) at −30 °C was added to a mixture of $(C_5Me_5)_2ZrMe_2$ (300 mg, 0.77 mmol) and $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (370 mg, 0.72 mmol) in a reaction bottle at −30 °C. The stirred mixture was warmed to 10 °C over 10 min and then rapidly filtered to remove a small amount of unreacted starting material. Addition of hexane (12 mL) at 0 °C gave a yellow microcrystalline solid, which was separated and washed twice with hexane (20 mL). After being dried at 25 °C in the glovebox (1 h), 580 mg of product was obtained. NMR spectroscopy and elemental analysis showed the presence of ca. 0.2 equiv of C_6H_5Br. ^{1}H NMR (C_6D_5Br, 25 °C): δ 7.63 (br, 8, *o*-C_6H_4F), 6.84 (br, 8, *m*-C_6H_4F), 1.52 (s, 30, C_5Me_5), 0.44 (s, 3, Zr–*Me*). ^{1}H NMR ($C_2D_2Cl_4$, −30 °C): δ 7.30 (br, 2, *o*-C_6H_4F), 7.15 (br, 6, *o*-$B(C_6H_4F)_3$), 6.82 (br, 6, *m*-$B(C_6H_4F)_3$), 6.35 (vbr, 2, *m*-C_6H_4F), 1.89 (s, 30, C_5Me_5), 0.66 (s, 3, Zr–*Me*). ^{1}H NMR ($C_2D_2Cl_4$, 25 °C): δ 7.21 (br, 8, *o*-C_6H_4F), 6.76 (br, 8, *m*-C_6H_4F), 1.93 (s, 30, C_5Me_5), 0.70 (s, 3, Zr–*Me*). ^{13}C NMR ($C_2D_2Cl_4$, −30 °C): 163.1 (br, *p*–C_6H_4F), 160.3 (d, $^1J_{CF}$ = 240 Hz, *p*-$B(C_6H_4F)_3$), 158.9 (br, *ipso*-$B(C_6H_4F)_3$), 138.2 (*o*-C_6H_4F), 137.2 (*o*-$B(C_6H_4F)_3$), 125.4 (C_5Me_5), 112.8 (*m*-$B(C_6H_4F)_3$), 110.6 (*m*-C_6H_4F), 51.7 (Zr–*Me*), 11.9 (C_5Me_5); *ipso*-C_6H_4F resonance obscured. ^{19}F NMR ($C_2D_2Cl_4$ −30 °C): δ −121.1 ($\Delta\nu_{1/2}$ = 35 Hz, 3 F), −135.5 ($\Delta\nu_{1/2}$ = 70 Hz, 1 F). Anal. Calcd for $C_{46.2}H_{50}BBr_{0.2}F_4Zr$: C, 69.50; H, 6.27; F, 9.59. Found (repeat analysis in parentheses): C, 69.57 (69.45); H, 6.31 (6.22); F, 9.29 (9.10). A 0.005 M solution of **1e** in C_6D_5Br decomposed to the extent of ca. 50% within 2 h at 25 °C.

Preparation of $[(C_5H_5)_2ZrMe(THF)][B(4\text{-}C_6H_4F)_4]$. A solution of THF (73 μL, 0.90 mmol) in bromobenzene (8 mL) at −30 °C was added to a mixture of $(C_5H_5)_2ZrMe_2$ (150 mg, 0.60 mmol) and $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (320 mg, 0.62 mmol) in a reaction bottle at −30 °C. The stirred mixture was allowed to warm to 25 °C over 5 min and filtered, and hexane (10 mL) was then added to deposit a pale yellow oil. The oil was washed with hexane (2 × 10 mL) while it was vigorously stirred to give a solid, which was dried in vacuo to give 360 mg of product (86% yield). The product was shown by NMR spectroscopy to be ca. 95% pure. Attempted crystallization of the complex from various solvent combinations failed as, in each case, an oil was obtained. Solutions of the complex in C_6D_5Br or CD_2Cl_2 show <10% decomposition after 24 h at 25 °C. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.22 (m, 8, *o*-C_6H_4F), 6.77 (dd, 8, *m*-C_6H_4F), 6.40 (s, 10, C_5H_5), 3.72, 1.98 (m, 4, THF), 0.82 (s, 3, Zr–*Me*). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 159.6 (d, $^1J_{CF}$ = 238 Hz, *p*-C_6H_4F), 158.0 (q, $^1J_{CB}$ = 50 Hz, *ipso*-C_6H_4F), 136.3 (*o*-C_6H_4F), 114.5 (C_5H_5), 111.6 (d, $^2J_{CF}$ = 18 Hz, *m*-C_6H_4F), 76.8 (THF), 43.9 (Zr–*Me*), 25.0 (THF).

Preparation of $[(C_5H_5)_2ZrC(SiMe_3){=}CMe_2][B(4\text{-}C_6H_4F)_4]$ (2a). A solution of 1-(trimethylsilyl)prop-1-yne (150 μL, 1.00 mmol) in bromobenzene (8 mL) at −30 °C was added to a mixture of $(C_5H_5)_2ZrMe_2$ (210 mg, 0.84 mmol) and $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (420 mg, 0.82 mmol) in a reaction bottle at −30 °C. The stirred mixture was warmed to 25 °C and filtered, and hexane (15 mL) was then added to give an orange oil, which solidified on washing with hexane (10 mL). Reprecipitation from dichloromethane solution (5 mL) with hexane (15 mL), followed by washing with hexane (2 × 10 mL) and drying in vacuo, gave 460 mg (75%) of pure product. Crystalline analytically pure material was obtained by slow cooling of a dichloromethane/hexane solution to −40 °C. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.22 (m, 8, *o*-C_6H_4F), 6.76 (dd, 8, *m*-C_6H_4F), 6.33 (s, 10, C_5H_5), 1.93, 1.65 (s, 3, $C(SiMe_3){=}CMe_2$), 0.19 (s, 9, $C(SiMe_3){=}CMe_2$). ^{1}H NMR (CD_2Cl_2, −90 °C): δ 7.12 (m, 8, *o*-C_6H_4F), 6.76 (dd, 8, *m*-C_6H_4F), 6.27 (s, 10, C_5H_5), 1.82, 1.55 (s, 3, $C(SiMe_3){=}CMe_2$), 0.11 (br, 9, $C(SiMe_3){=}CMe_2$). ^{13}C NMR (CD_2Cl_2, −60 °C): δ 213.6 ($C(SiMe_3){=}CMe_2$), 161.7 ($C(SiMe_3){=}CMe_2$), 158.6 (d, $^1J_{CF}$ = 240 Hz, *p*-C_6H_4F), 157.0 (q, $^1J_{CB}$ = 50 Hz, *ipso*-C_6H_4F), 135.4 (*o*-C_6H_4F), 112.7 (C_5H_5), 111.4 (d, $^2J_{CF}$ = 16 Hz, *m*-C_6H_4F), 31.1, 27.0 ($C(SiMe_3){=}CMe_2$), 0.4 (sharp, $^1J_{CH}$ = 120 Hz, $C(SiMe_3){=}CMe_2$). ^{19}F NMR (CD_2Cl_2, −90 °C): δ −121.3 (m, $\Delta\nu_{1/2}$ = 20 Hz). ^{19}F NMR spectra of complexes **2b–d** show an identical sharp multiplet. ^{29}Si NMR (CD_2Cl_2, 0 °C): δ −54.7 ppm. Anal. Calcd for $C_{41}H_{41}BF_4SiZr$: C, 66.56; H, 5.59; F, 9.80; Si, 3.80. Found: C, 66.56; H, 5.66; F, 10.27; Si, 3.71. Reaction of THF (excess) with a solution of **2a** in CD_2Cl_2 gave a THF adduct, obtained as a yellow precipitate on addition of hexane. ^{1}H NMR (anion: see **2a**): δ 6.35 (s, 10, C_5H_5), 3.76, 1.92 (m, 4, THF), 1.85, 1.45 (s, 3, $C(SiMe_3){=}CMe_2$), 0.21 (s, 9, $C(SiMe_3){=}CMe_2$).

Preparation of $[(C_5H_5)_2Zr\{C(SiMe_3){=}CMe_2\}(NCMe)][B(4\text{-}C_6H_4F)_4]$ (2a·MeCN). Addition of acetonitrile (200 μL, 3.80 mmol) to a solution of complex **2a** (250 mg, 0.34 mmol) in dichloromethane (4 mL) resulted in an instantaneous color change from red to yellow. Addition of hexane (5 mL) resulted in the precipitation of a yellow solid, which was washed with hexane (2 × 10 mL) and dried in vacuo. A 230-mg (85%) amount of the yellow title complex (two isomers, 4:1 ratio) was obtained. An analytically pure sample was obtained by recrystallization from dichloromethane/hexane solution. ^{1}H NMR (CD_2Cl_2, 25 °C) (anion: see **2a**): major isomer, δ 6.28 (s, 10, C_5H_5), 2.15 (br, 3, NC*Me*), 1.72, 1.03 (s, 3, $C(SiMe_3){=}CMe_2$), 0.23 (s, 9, $C(SiMe_3){=}CMe_2$); minor isomer, δ 0.09 (br, 9, $C(SiMe_3){=}CMe_2$); other resonances obscured. ^{13}C NMR (CD_2Cl_2, 10 °C) (anion: see **2a**): major isomer, δ 187.3 ($C(SiMe_3){=}CMe_2$), 138.2 ($C(SiMe_3){=}CMe_2$), 133.9 (N*C*Me), 112.5 (C_5H_5), 30.5, 9.9 ($C(SiMe_3){=}CMe_2$), 2.6 (NC*Me*), 2.0 ($C(SiMe_3){=}CMe_2$); minor isomer, δ 113.5 (C_5H_5), 29.7 ($C(SiMe_3){=}CMe_2$), 2.9 ($C(SiMe_3){=}CMe_2$); other resonances obscured. ^{29}Si NMR of in situ prepared sample (CD_2Cl_2, 0 °C): δ −11.6 ppm. Anal. Calcd for $C_{43}H_{44}BF_4NSiZr$: C, 66.13; H, 5.68; N, 1.79; F, 9.73. Found: C, 65.58; H, 5.87; N, 1.70; F, 9.67.

Preparation of $[\{(Me_3Si)C_5H_4\}_2ZrC(SiMe_3){=}CMe_2][B(4\text{-}C_6H_4F)_4]$ (2b). Reaction of a solution of 1-(trimethylsilyl)prop-1-yne (50 μL, 0.34 mmol) in bromobenzene (3 mL) with a mixture of $\{(Me_3Si)C_5H_4\}_2ZrMe_2$ (109 mg, 0.28 mmol) and $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (138 mg, 0.27 mmol), in a procedure similar to that leading to **2a** above, gave 150 mg (73%) of product as an orange solid. Slow cooling of a CH$_2$Cl$_2$/hexane solution provided a crystalline sample, which was shown by NMR spectroscopy and elemental analysis to contain 0.5 equiv of CH$_2$Cl$_2$ of crystallization. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) (anion: see **2a**): δ 6.87, 6.75 (obscured), 6.33, 6.24 (s, 2, (Me$_3$Si)C$_5$*H*$_4$), 1.95, 1.68 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 0.29 (s, 18, (*Me*$_3$Si)C$_5$H$_4$), 0.23 (s, 9, C(Si*Me*$_3$)=CMe$_2$). ^{1}H NMR (CD$_2$Cl$_2$, −90 °C): δ 6.82, 6.75 (obscured), 6.27, 6.15 (s, 2, (Me$_3$Si)C$_5$*H*$_4$), 1.84, 1.57 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 0.36 (br, 6, C(Si*Me*$_3$)=CMe$_2$), 0.20 (s, 18, (*Me*$_3$Si)C$_5$H$_4$), −0.33 (br, 3, C(Si*Me*$_3$)=CMe$_2$). ^{13}C NMR (CD$_2$Cl$_2$, −90 °C) (anion: see **2a**): δ 213.9 (*C*(SiMe$_3$)=CMe$_2$), 161.8 (C(SiMe$_3$)=*C*Me$_2$), 124.9, 122.3, 117.8, 117.4, 113.7 ((Me$_3$Si)*C*$_5$H$_4$), 31.1, 27.1 (C(SiMe$_3$)=C*Me*$_2$), 2.6 (1 C, C(Si*Me*$_3$)=CMe$_2$), 1.0 (2 C, C(Si*Me*$_3$)=CMe$_2$), −1.2 ((*Me*$_3$Si)C$_5$H$_4$). Anal. Calcd for $\mathrm{C_{47.5}H_{58}BClF_4Si_3Zr}$: C, 61.56; H, 6.31. Found: C, 61.65; H, 6.23. Addition of THF (1.0 equiv or excess) to a solution of **2b** in CD$_2$Cl gave an orange fluxional THF adduct. ^{1}H NMR (25 °C) (anion: see **2a**): δ 6.32, 6.21 (m, 2, (Me$_3$Si)C$_5$*H*$_4$), 1.92, 1.61 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 0.28 (s, 18, (*Me*$_3$Si)C$_5$H$_4$), 0.22 (s, 9, C(Si*Me*$_3$)=CMe$_2$); only "free" THF resonances observed, δ 3.68, 1.82 (m, 4).

Addition of acetonitrile (excess) to a solution of **2b** in CD$_2$Cl$_2$ gave a yellow acetonitrile adduct. ^{1}H NMR (25 °C) (anion: see **2a**): δ 6.93, 6.29 (m, 2, (Me$_3$Si)C$_5$*H*$_4$), 6.18 (m, 4, (Me$_3$Si)C$_5$*H*$_4$), 2.20 (s, 3, *Me*CN), 1.71, 0.97 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 0.24 (s, 9, C(Si*Me*$_3$)=CMe$_2$), 0.22 (s, 18, (*Me*$_3$Si)C$_5$H$_4$).

Preparation of [{(Me$_3$C)C$_5$H$_4$}$_2$ZrC(SiMe$_3$)=CMe$_2$][B(4-C$_6$H$_4$F)$_4$] (2c). Reaction of a solution of 1-(trimethylsilyl)prop-1-yne (150 μL, 1.0 mmol) in bromobenzene (8 mL) with a mixture of {(Me$_3$C)C$_5$H$_4$}$_2$ZrMe$_2$ (300 mg, 0.83 mmol) and [PhMe$_2$NH][B(4-C$_6$H$_4$F)$_4$] (420 mg, 0.82 mmol) was carried out by using a procedure similar to that leading to **2a** above. A microcrystalline solid was obtained directly on addition of hexane to the filtered reaction mixture, and the solid was recrystallized from dichloromethane/hexane solution to give 650 mg (88%) of orange crystals, after drying in vacuo. NMR spectroscopy and elemental analysis showed the crystals to contain 0.5 equiv of CH$_2$Cl$_2$ of crystallization. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) (anion: see **2a**): δ 6.75 (obscured), 6.46, 6.09, 5.98 (m, 2, (Me$_3$C)C$_5$*H*$_4$), 1.96, 1.68 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 1.25 (s, 18, (*Me*$_3$C)C$_5$H$_4$), 0.31 (s, 9, C(Si*Me*$_3$)=CMe$_2$). ^{1}H NMR (CD$_2$Cl$_2$, −90 °C): δ 6.74 (obscured), 6.38, 5.97, 5.91 (m, 2, (Me$_3$C)C$_5$*H*$_4$), 1.85, 1.56 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 1.12 (s, 18, (*Me*$_3$C)C$_5$H$_4$), 0.33 (s, 6, C(Si*Me*$_3$)=CMe$_2$), 0.07 (s, 3, C(Si*Me*$_3$)=CMe$_2$). ^{13}C NMR (CD$_2$Cl$_2$, −90 °C) (anion: see **2a**): δ 208.1 (*C*(SiMe$_3$)=CMe$_2$), 160.7 (C(SiMe$_3$)=*C*Me$_2$), 146.4, 118.6, 111.0, 108.4, 103.5 ((Me$_3$C)*C*$_5$H$_4$), 32.4 ((Me$_3$*C*)C$_5$H$_4$), 30.1 ((*Me*$_3$C)C$_5$H$_4$), 29.8, 27.7 (C(SiMe$_3$)=C*Me*$_2$), 1.2 (1 C, $^1J_{\mathrm{CH}}$ = 110 Hz, C(Si*Me*$_3$)=CMe$_2$), −1.2 (2 C, $^1J_{\mathrm{CH}}$ = 119 Hz, C(Si*Me*$_3$)=CMe$_2$). ^{29}Si NMR (CD$_2$Cl$_2$, 0 °C): δ −59.6 ppm. Anal. Calcd for $\mathrm{C_{49.5}H_{58}BClF_4SiZr}$: C, 66.46; H, 6.54; F, 8.50; Si, 3.14. Found (repeat analysis in parentheses): C, 66.86 (66.53); H, 6.52 (6.42); F, 8.56; Si, 2.98.

Addition of THF (excess) to a solution of **2c** in CD$_2$Cl$_2$ gave a yellow fluxional THF adduct. ^{1}H NMR (25 °C) (anion: see **2a**): δ 6.60, 6.55, 6.09, 5.92 (m, 2, (Me$_3$C)C$_5$*H*$_4$), 1.88, 1.53 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 1.23 (s, 18, (*Me*$_3$C)C$_5$H$_4$), 0.29 (s, 9, C(Si*Me*$_3$)=CMe$_2$); only "free" THF resonances observed.

Addition of acetonitrile (excess) to a solution of **2c** in CD$_2$Cl$_2$ gave a yellow acetonitrile adduct. ^{1}H NMR (25 °C) (anion: see **2a**): δ 6.65, 6.13, 6.03, 6.02 (m, 2, (Me$_3$C)C$_5$*H*$_4$), 2.16 (s, 3, NC*Me*), 1.69 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 1.22 (s, 18, (*Me*$_3$C)C$_5$H$_4$), 1.07 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 0.21 (s, 9, C(Si*Me*$_3$)=CMe$_2$). ^{1}H NMR (−90 °C) (anion: see **2a**): δ 6.61, 6.14, 5.80, 5.76 (m, 2, (Me$_3$C)C$_5$*H*$_4$), 2.16 (s, 3, NC*Me*), 1.57 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 1.12 (s, 18, (*Me*$_3$C)C$_5$H$_4$), 0.93 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 0.10 (s, 9, C(Si*Me*$_3$)=CMe$_2$). ^{29}Si NMR (CD$_2$Cl$_2$, 0 °C): δ −12.7 ppm.

Preparation of [*rac*-C$_2$H$_4$(indenyl)$_2$ZrC(SiMe$_3$)=CMe$_2$][B(4-C$_6$H$_4$F)$_4$] (2d). Reaction of 1-(trimethylsilyl)prop-1-yne (95 μL, 0.64 mmol) in bromobenzene (3 mL) at −30 °C with *rac*-C$_2$H$_4$(indenyl)$_2$ZrMe$_2$ (200 mg, 0.53 mmol) and [PhMe$_2$NH][B(4-C$_6$H$_4$F)$_4$] (260 mg, 0.51 mmol), in a procedure similar to that leading to **2c** above, gave 335 mg of pure product (66%) as an orange crystalline solid, after recrystallization and drying in vacuo. Large X-ray-quality crystals were obtained by slow cooling of a solution of **2d** in dichloromethane/hexane. The product was shown by NMR spectroscopy, elemental analysis, and a crystal structure determination to contain 1 equiv of CH$_2$Cl$_2$ of crystallization. ^{1}H NMR (CD$_2$Cl$_2$, 40 °C) (anion: see **2a**): δ 7.8–7.0 (m, 9, ind), 6.43, 6.30, 6.10 (d, 1, ind C$_5$), 4.1–3.6 (m, 4, –C*H*$_2$C*H*$_2$–), 1.75, 1.27 (s, 3, C(SiMe$_3$)=C*Me*$_2$), −0.19 (br, 9, C(Si*Me*$_3$)=CMe$_2$). ^{1}H NMR (CD$_2$Cl$_2$, −90 °C): δ 7.7–7.1 (m, 9, ind), 6.40, 6.30, 6.22 (d, 1, ind C$_5$), 4.0–3.4 (m, 4, –C*H*$_2$C*H*$_2$–), 1.64, 1.12 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 0.27, 0.02, −1.26 (s, 3, C(Si*Me*$_3$)=CMe$_2$). ^{13}C NMR (CD$_2$Cl$_2$, −90 °C) (anion: see **2a**): δ 208.1 (*C*(SiMe$_3$)=CMe$_2$), 160.7 (C(SiMe$_3$)=*C*Me$_2$), 128.4, 126.8, 125.7, 125.4, 125.3, 124.5, 124.4, 124.3, 123.8, 123.0, 122.8, 120.8, 120.7, 117.3, 114.0, 112.2, 106.3, 103.8 (ind), 30.8 (C(SiMe$_3$)=C*Me*$_2$), 28.6, 28.2 (–C*H*$_2$C*H*$_2$–), 26.2 (C(SiMe$_3$)=C*Me*$_2$), 2.7 ($^1J_{\mathrm{CH}}$ = 116 Hz, C(Si*Me*$_3$)=CMe$_2$), −0.5 ($^1J_{\mathrm{CH}}$ = 124 Hz, C(Si*Me*$_3$)=CMe$_2$), −5.2 ($^1J_{\mathrm{CH}}$ = 122 Hz, C(Si*Me*$_3$)=CMe$_2$). Anal. Calcd for $\mathrm{C_{52}H_{49}BCl_2F_4SiZr}$: C, 65.68; H, 5.19; F, 7.99; Si, 2.95. Found: C, 65.50; H, 5.23; F, 7.85; Si, 3.13.

Addition of THF to a solution of **2d** in CD$_2$Cl$_2$ gave a red fluxional THF adduct. ^{1}H NMR (25 °C) (anion: see **2a**): δ 7.7–7.2 (m, 9, ind), 6.87, 6.40, 6.30, 6.23 (m, 1, ind C$_5$), 4.0–3.5 (m, 4, –C*H*$_2$C*H*$_2$–), 1.72, 1.28 (s, 3, C(SiMe$_3$)=C*Me*$_2$), −0.14 (s, 9, C(Si*Me*$_3$)=CMe$_2$); only "free" THF resonances observed.

Addition of acetonitrile (excess) to a solution of **2d** in CD$_2$Cl$_2$ gave a yellow acetonitrile adduct. ^{1}H NMR (25 °C) (anion: see **2a**): δ 7.7–7.1 (m, 9, ind), 6.38 (m, 2, ind C$_5$), 6.20 (m, 1, ind C$_5$), 3.8–3.2 (m, 4, –C*H*$_2$C*H*$_2$–), 1.97 (NC*Me*), 1.63, 1.12 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 0.15 (s, 9, C(Si*Me*$_3$)=CMe$_2$). ^{1}H NMR (−90 °C) (anion: see **2a**): major isomer, δ 7.7–7.0 (m, 9, ind), 6.34, 6.20, 6.16 (m, 1, ind C$_5$), 3.7–3.1 (m, 4, –C*H*$_2$C*H*$_2$), 1.81 (s, 3, NC*Me*), 1.51, 1.00 (s, 3, C(SiMe$_3$)=C*Me*$_2$), 0.17, 0.14, −0.09 (s, 3, C(Si*Me*$_3$)=CMe$_2$); minor isomer, 6.43, 6.25 (m, 1, ind C$_5$), 1.97 (s, 3, NC*Me*), 1.55, 1.28 (s, 3, C(SiMe$_3$)=C*Me*$_2$), −0.09 (br, 9, C(Si*Me*$_3$)=CMe$_2$); other resonances obscured.

Preparation of [(C$_5$H$_5$)$_2$ZrC(Ph)=C(Ph)Me][B(4-C$_6$H$_4$F)$_4$] (3a). A solution of diphenylethyne (125 mg, 0.64 mmol) in bromobenzene (5 mL) at −30 °C was added to a mixture of (C$_5$H$_5$)$_2$ZrMe$_2$ (150 mg, 0.60 mmol) and [PhMe$_2$NH][B(4-C$_6$H$_4$F)$_4$] (298 mg, 0.58 mmol) in a reaction bottle at −30 °C. The stirred mixture was warmed to 10 °C and filtered, and hexane (15 mL) was then added to give a yellow oil, which was washed with hexane (10 mL). Dissolution of the oil in bromobenzene, followed by addition of hexane, again gave an oil, which solidified on extensive washing with hexane (3 × 10 mL). A 410-mg amount of yellow product (85%) was obtained after drying in vacuo. The product was contaminated with *traces* of unidentified complexes, and attempted crystallization from dichloromethane/hexane or bromobenzene/hexane solution led only to decomposition. ^{1}H NMR (C$_6$D$_5$Br, 25 °C): 7.63 (br, 8, *o*-C$_6$H$_4$F), 6.83 (dd, 8, *m*-C$_6$H$_4$F), 6.18 (s, 10, C$_5$*H*$_5$), 1.73 (s, 3, C(Ph)=C(Ph)*Me*); phenyl resonances obscured. ^{1}H NMR (C$_2$D$_2$Cl$_4$, −30 °C): δ 7.48 (br, 4, Ph), 7.33 (br, 2, Ph), 7.23 (br, 8, *o*-C$_6$H$_4$F), 7.12, 7.02 (br, 2, Ph), 6.71 (br, 8, *m*-C$_6$H$_4$F), 6.34 (s, 10, C$_5$*H*$_5$), 1.96 (s, 3, C(Ph)=C(Ph)*Me*). ^{13}C NMR (C$_2$D$_2$Cl$_4$, −30 °C): δ 182.7 (*C*(Ph)=C(Ph)Me), 160.8 (brd, *p*-C$_6$H$_4$F), 159.3 (br, *ipso*-C$_6$H$_4$F), 142.9, 142.2 (1 C, *ipso*-Ph), 137.2 (*o*-C$_6$H$_4$F), 134.8 (2 C, Ph), 131.1 (1 C, *p*-Ph), 130.7, 128.4 (2 C, Ph), 127.0 (2 C, Ph and 1 C, *p*-Ph), 122.6 (C(Ph)=*C*(Ph)Me), 112.5 (*m*-C$_6$H$_4$F and *C*$_5$H$_5$), 24.9 (C(Ph)=C(Ph)*Me*). ^{19}F NMR (C$_2$D$_2$Cl$_4$, −30 °C): δ −121.3 ($\Delta\nu_{1/2}$ = 370 Hz), −175 (vbr). ^{19}F NMR (C$_2$D$_2$Cl$_4$/C$_7$D$_8$, −55 °C): δ −121.9 ($\Delta\nu_{1/2}$ = 45 Hz, 3 F), −175.8 ($\Delta\nu_{1/2}$ = 75 Hz, 1 F); minor peaks, δ −121.4, −122.2. ^{19}F NMR (C$_2$D$_2$Cl$_4$/C$_7$D$_8$, 50 °C): δ −134.9 ($\Delta\nu_{1/2}$ = 290 Hz).

Addition of acetonitrile (excess) to a solution of **3a** in C$_6$D$_5$Br gave an instantaneous color change from orange to yellow and (after 10 min) resulted in the precipitation of a yellow solid. ^{1}H NMR (C$_6$D$_5$Br, 25 °C): 7.62 (br, 8, *o*-C$_6$H$_4$F), 6.92 (m, 8, *m*-C$_6$H$_4$F), 5.66 (s, 10, C$_5$*H*$_5$), 1.85 (s, 3, NC*Me*), 0.95 (s, 3, C(Ph)=C(Ph)*Me*); Ph resonances obscured.

Preparation of [(C$_5$H$_5$)$_2$Zr{C(Ph)=C(Ph)Me}(THF)][B(4-C$_6$H$_4$F)$_4$] (3a·THF). Addition of tetrahydrofuran (200 μL, 2.46 mmol) to a solution of complex **3a** (470 mg, 0.58 mmol) in bromobenzene (4 mL) resulted in an instantaneous color change from dark to pale yellow. Addition of hexane (5 mL) resulted in the precipitation of a yellow solid, which was washed with hexane (2 × 10 mL) and dried in vacuo. A 380-mg (75%) amount of yellow [(C$_5$H$_5$)$_2$Zr{C(Ph)=C(Ph)Me}(THF)][B(4-C$_6$H$_4$F)$_4$] was obtained. ^{1}H NMR (C$_6$D$_5$Br, 25 °C): δ 7.65 (br, 8, *o*-C$_6$H$_4$F), 6.94 (m, 8, *m*-C$_6$H$_4$F), 5.82 (s, 10, C$_5$H$_5$), 2.36 (br, 4, THF), 1.67 (s, 3, C-

(Ph)=C(Ph)*Me*), 0.97 (br, 4, THF); other Ph resonances obscured. ^{1}H NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ 7.28 (br, 8, *o*-$\mathrm{C_6H_4F}$), 7.01 (br, 4, Ph), 6.78 (m, 8, *m*-$\mathrm{C_6H_4F}$), 6.29 (s, 10, $\mathrm{C_5}H_5$), 2.89 (br, 4, THF), 1.92 (s, 3, C(Ph)=C(Ph)*Me*), 1.51 (br, 4, THF); other Ph resonances obscured. ^{13}C NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ 182.2 (*C*(Ph)=C(Ph)Me), 159.9 (d, $^1J_\mathrm{CF}$ = 239 Hz, *p*-$\mathrm{C_6H_4F}$), 158.3 (q, $^1J_\mathrm{BC}$ = 49 Hz, *ipso*-$\mathrm{C_6H_4F}$), 144.7 (2 C, *ipso*-Ph), 137.1 (*o*-$\mathrm{C_6H_4F}$), 133.7 (2 C, Ph), 130.4 (1 C, *p*-Ph), 130.1 (2 C, Ph; 1 C, *p*-Ph), 128.0, 127.5 (2 C, Ph), 126.4 (C(Ph)=*C*(Ph)Me), 112.3 (*m*-$\mathrm{C_6H_4F}$ and $C_5\mathrm{H_5}$), 78.6 (THF), 26.4 (THF), 25.4 (C(Ph)=C(Ph)*Me*). ^{19}F NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ −121.8 ($\Delta\nu_{1/2}$ = 27 Hz).

Preparation of $[\{\mathrm{(Me_3Si)C_5H_4}\}_2\mathrm{ZrC(Ph)=C(Ph)Me}][\mathrm{B(4\text{-}C_6H_4F)_4}]$ (3b). A solution of diphenylethyne (54 mg, 0.28 mmol) in bromobenzene (4 mL) was reacted with $\{\mathrm{(Me_3Si)C_5H_4}\}_2\mathrm{ZrMe_2}$ (100 mg, 0.25 mmol) and $[\mathrm{PhMe_2NH}][\mathrm{B(4\text{-}C_6H_4F)_4}]$ (127 mg, 0.25 mmol) in a procedure similar to that leading to **3a** above. The red oil obtained was redissolved in bromobenzene (4 mL) and hexane then added to again give an oil, which, however, crystallized on further stirring. After washing with hexane (2 × 10 mL) and drying in vacuo, 150 mg (62%) of pure red crystalline product was obtained. Recrystallization from cold dichloromethane/hexane solution gave an analytically pure sample. ^{1}H NMR ($\mathrm{C_6D_5Br}$, 25 °C): δ 7.62 (br, 8, *o*-$\mathrm{C_6H_4F}$), 6.84 (dd, 8, *m*-$\mathrm{C_6H_4F}$), 6.29, 6.18 (m, 2, $\mathrm{(Me_3Si)C_5}H_4$), 6.11 (m, 4, $\mathrm{(Me_3Si)C_5}H_4$), 1.72 (s, 3, C(Ph)=C(Ph)*Me*), 0.07 (s, 18, $(Me_3\mathrm{Si})\mathrm{C_5H_4}$); Ph resonances obscured. ^{1}H NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ 7.40 (m, 2, Ph), 7.23 (br, 14, *o*-$\mathrm{C_6H_4F}$ and Ph), 7.03 (m, 2, Ph), 6.71 (dd, 8, *m*-$\mathrm{C_6H_4F}$), 6.63, 6.49 (m, 2, $\mathrm{(Me_3Si)C_5}H_4$), 6.40 (m, 4, $\mathrm{(Me_3Si)C_5}H_4$), 1.86 (s, 3, C(Ph)=C(Ph)*Me*), 0.22 (s, 18, $(Me_3\mathrm{Si})\mathrm{C_5H_4}$). ^{13}C NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ 183.3 (*C*(Ph)=C(Ph)Me), 160.8 (d, $^1J_\mathrm{CF}$ = 237 Hz, *p*-$\mathrm{C_6H_4F}$), 158.5 (q, $^1J_\mathrm{BC}$ = 50 Hz, *ipso*-$\mathrm{C_6H_4F}$), 144.6, 142.0 (1 C, *ipso*-Ph), 137.1 (*o*-$\mathrm{C_6H_4F}$), 134.5 (2 C, Ph), 133.0 (C(Ph)=*C*(Ph)Me), 131.6 (1 C, *p*-Ph), 128.4 (2 C, Ph), 127.9 (2 C, Ph), 127.7 (1 C, *p*-Ph; 2 C, $\mathrm{(Me_3Si)}C_5\mathrm{H_4}$), 125.4 (2 C, $\mathrm{(Me_3Si)}C_5\mathrm{H_4}$), 123.3 (2 C, α-Ph: *o*-C), 119.4, 118.3, 115.8, (2 C, $\mathrm{(Me_3Si)}C_5\mathrm{H_4}$), 112.3 (d, $^2J_\mathrm{CF}$ = 14 Hz, *m*-$\mathrm{C_6H_4F}$), 25.1 (C(Ph)=C(Ph)*Me*), −0.2 ($(Me_3\mathrm{Si})\mathrm{C_5H_4}$). ^{19}F NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ −126.2 ($\Delta\nu_{1/2}$ = 100 Hz. Anal. Calcd for $\mathrm{C_{55}H_{55}BF_4Si_2Zr}$: C, 69.52; H, 5.83; F, 8.00; Si, 5.91. Found: C, 69.56; H, 5.96; F, 7.66; Si, 6.16.

Addition of THF (excess) to a solution of **3b** in $\mathrm{C_6D_5Br}$ gave a yellow THF adduct. ^{1}H NMR (25 °C): δ 7.63 (br, 8, *o*-$\mathrm{C_6H_4F}$), 6.95 (dd, 8, *m*-$\mathrm{C_6H_4F}$), 6.42, 6.24 (m, 2, $\mathrm{(Me_3Si)C_5}H_4$), 6.04 (m, 4, $\mathrm{(Me_3Si)C_5}H_4$), 2.49 (br, 4, THF), 1.78 (s, 3, C(Ph)=C(Ph)*Me*), 1.05 (br, 4, THF), 0.22 (s, 18, $(Me_3\mathrm{Si})\mathrm{C_5H_4}$); Ph resonances obscured.

Addition of acetonitrile (excess) to a solution of **3b** in $\mathrm{C_6D_5Br}$ gave a yellow acetonitrile adduct. ^{1}H NMR (25 °C): δ 7.66 (br, 8, *o*-$\mathrm{C_6H_4F}$), 6.95 (dd, 8, *m*-$\mathrm{C_6H_4F}$), 6.60 (m, 1, Ph), 6.39, 5.95 (m, 2, $\mathrm{(Me_3Si)C_5}H_4$), 5.84 (m, 4, $\mathrm{(Me_3Si)C_5}H_4$), 1.94 (s, 3, NC*Me*), 0.95 (s, 3, C(Ph)=C(Ph)*Me*), 0.02 (s, 18, $(Me_3\mathrm{Si})\mathrm{C_5H_4}$); Ph resonances obscured.

Preparation of $[\{\mathrm{(Me_3C)C_5H_4}\}_2\mathrm{ZrC(Ph)=C(Ph)Me}][\mathrm{B(4\text{-}C_6H_4F)_4}]$ (3c). A solution of diphenylethyne (120 mg, 0.60 mmol) in bromobenzene (8 mL) was reacted with a mixture of $\{\mathrm{(Me_3C)C_5H_4}\}_2\mathrm{ZrMe_2}$ (200 mg, 0.55 mmol) and $[\mathrm{PhMe_2NH}][\mathrm{B(4\text{-}C_6H_4F)_4}]$ (280 mg, 0.55 mmol) in a procedure similar to that leading to **3a** above. The red oil obtained was redissolved in cold dichloromethane (3 mL), and cold hexane (10 mL) was added to give an oil, which crystallized on further stirring. The solid was washed twice with hexane (10 mL) and then dried in vacuo to give 350 mg (66%) of pure red product. NMR spectroscopy and elemental analysis showed the crystals to contain 0.5 equiv of $\mathrm{CH_2Cl_2}$ of crystallization. ^{1}H NMR ($\mathrm{C_6D_5Br}$, 25 °C): δ 7.66 (br, 8, *o*-$\mathrm{C_6H_4F}$), 6.95 (dd, 8, *m*-$\mathrm{C_6H_4F}$), 6.37, 5.95, 5.71, 5.36 (m, 2, $\mathrm{(Me_3C)C_5}H_4$), 1.61 (s, 3, C(Ph)=C(Ph)*Me*), 0.64 (s, 30, $(Me_3\mathrm{C})\mathrm{C_5H_4}$); phenyl resonances obscured. ^{1}H NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ 7.48 (m, 3, Ph), 7.36 (m, 2, Ph), 7.25 (br, 11, *o*-$\mathrm{C_6H_4F}$ and Ph), 7.07 (m, 2, Ph), 6.80 (m, 10, *m*-$\mathrm{C_6H_4F}$ and $\mathrm{(Me_3C)C_5}H_4$), 6.44, 6.06, 5.84 (m, 2, $\mathrm{(Me_3C)C_5}H_4$), 1.82 (s, 3, C(Ph)=C(Ph)*Me*), 0.93 (s, 30, $(Me_3\mathrm{C})\mathrm{C_5H_4}$). ^{13}C NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ 182.6 (*C*(Ph)=C(Ph)Me), 159.9 (d, $^1J_\mathrm{CF}$ = 238 Hz, *p*-$\mathrm{C_6H_4F}$), 158.4 (q, $^1J_\mathrm{BC}$ = 49 Hz, *ipso*-$\mathrm{C_6H_4F}$), 146.7 (2 C, $\mathrm{(Me_3C)}C_5\mathrm{H_4}$), 144.9, 141.0 (1 C, *ipso*-Ph), 137.0 (*o*-$\mathrm{C_6H_4F}$), 136.7 (2 C, Ph), 135.7 (C(Ph)=*C*(Ph)Me), 131.5 (1 C, *p*-Ph), 128.5 (2 C, Ph), 128.0 (2 C, Ph; 1 C, *p*-Ph), 119.6 (2 C, $\mathrm{(Me_3C)}C_5\mathrm{H_4}$), 119.1 (2 C, α-Ph *o*-C), 114.0 (2 C, $\mathrm{(Me_3C)}C_5\mathrm{H_4}$), 112.5 ($^2J_\mathrm{BC}$ = 16 Hz, *m*-$\mathrm{C_6H_4F}$), 108.9, 106.3 (2 C, $\mathrm{(Me_3C)}C_5\mathrm{H_4}$), 33.4 ($\mathrm{(Me_3}C\mathrm{)C_5H_4}$), 29.5 ($(Me_3\mathrm{C})\mathrm{C_5H_4}$), 24.8 (C(Ph)=C(Ph)*Me*). ^{19}F NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ −121.8 ($\Delta\nu_{1/2}$ = 21 Hz). Anal. Calcd for $\mathrm{C_{57.5}H_{56}BClF_4Zr}$: C, 71.90; H, 5.88. Found: C, 71.51; H, 6.06.

Addition of THF (excess) to a solution of **3c** in $\mathrm{C_6D_5Br}$ gave a yellow fluxional THF adduct. ^{1}H NMR (25 °C): δ 7.64 (br, 8, *o*-$\mathrm{C_6H_4F}$), 6.93 (dd, 8, *m*-$\mathrm{C_6H_4F}$), 6.28 (m, 2, $\mathrm{(Me_3C)C_5}H_4$), 5.86 (m, 4, $\mathrm{(Me_3C)C_5}H_4$), 5.76 (m, 2, $\mathrm{(Me_3C)C_5}H_4$), 1.77 (s, 3, C(Ph)=C(Ph)*Me*), 1.16 (s, 30, $(Me_3\mathrm{C})\mathrm{C_5H_4}$); phenyl resonances obscured and only "free" THF resonances observed.

Addition of acetonitrile to a solution of **3c** in $\mathrm{C_6D_5Br}$ gave a yellow acetonitrile adduct. ^{1}H NMR (25 °C): δ 7.67 (m, 8, *o*-$\mathrm{C_6H_4F}$), 6.94 (br, 8, *o*-$\mathrm{C_6H_4F}$), 6.54 (m, 2, Ph), 6.41 (m, 2, $\mathrm{(Me_3C)C_5}H_4$), 5.58, (m, 4, $\mathrm{(Me_3C)C_5}H_4$), 5.38 (m, 2, $\mathrm{(Me_3C)C_5}H_4$), 1.94 (s, 3, NC*Me*), 0.85 (s, 18, $(Me_3\mathrm{C})\mathrm{C_5H_4}$), 0.78 (s, 3, C(Ph)=C(Ph)*Me*); phenyl resonances obscured.

Preparation of [*rac*-$\mathrm{C_2H_4(indenyl)_2ZrC(Ph)=C(Ph)Me}][\mathrm{B(4\text{-}C_6H_4F)_4}]$ (3d). A solution of diphenylethyne (78 mg, 0.40 mmol) in bromobenzene (5 mL) was reacted with a mixture of *rac*-$\mathrm{C_2H_4(indenyl)_2ZrMe_2}$ (143 mg, 0.38 mmol) and $[\mathrm{PhMe_2NH}][\mathrm{B(4\text{-}C_6H_4F)_4}]$ (190 mg, 0.37 mmol) in a procedure similar to that leading to **3a** above. The red oil obtained was redissolved in bromobenzene (5 mL) and hexane (15 mL) added to again give an oil, which solidified on washing with hexane (3 × 10 mL). After drying in vacuo, 290 mg (82%) of dark red solid product was obtained. The product was contaminated with traces of unidentified complexes, and attempted crystallization from dichloromethane/hexane or bromobenzene/hexane solution led only to decomposition. ^{1}H NMR ($\mathrm{C_6D_5Br}$, 25 °C): δ 7.63 (br, 8, *o*-$\mathrm{C_6H_4F}$), 6.80 (dd, 8, *m*-$\mathrm{C_6H_4F}$), 5.77, 5.53, 5.32 (m, 1, ind $\mathrm{C_5}$), 3.5–3.0 (m, 4, $-\mathrm{C}H_2\mathrm{C}H_2-$), 1.42 (s, 3, C(Ph)=C(Ph)*Me*). ^{1}H NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ 7.6–6.7 (m, 18, ind $\mathrm{C_6}$ and Ph), 7.23 (br, 8, *o*-$\mathrm{C_6H_4F}$), 6.71 (m, 8, *m*-$\mathrm{C_6H_4F}$), 6.29, 6.14, 5.62, 5.47 (br, 1, ind $\mathrm{C_5}$), 4.0–3.5 (m, 4, $\mathrm{C}H_2\mathrm{C}H_2$), 1.59 (s, 3, C(Ph)=C(Ph)*Me*). ^{13}C NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ 190.7 (*C*(Ph)=C(Ph)Me), 160.7 (d, $^1J_\mathrm{CF}$ = 237 Hz, *p*-$\mathrm{C_6H_4F}$), 158.8 (q, $^1J_\mathrm{BC}$ = 50 Hz, *ipso*-$\mathrm{C_6H_4F}$), 144.8, 144.0 (1 C, *ipso*-Ph), 137.0 (*o*-$\mathrm{C_6H_4F}$), 134.9, 133.4, 132.4, 129.0, 128.2, 127.8, 127.6, 127.1, 126.5, 126.0, 125.7, 125.2, 123.7, 122.9, 121.6, 121.1 (ind, Ph, C(Ph)=*C*(Ph)Me), 114.5, 113.1 (ind $\mathrm{C_5}$), 112.5 (d, $^2J_\mathrm{CF}$ = 15 Hz, *m*-$\mathrm{C_6H_4F}$), 107.8, 105.3 (ind $\mathrm{C_5}$), 29.8, 28.5 ($-\mathrm{C}H_2\mathrm{C}H_2-$), 27.1 (C(Ph)=C(Ph)*Me*). ^{19}F NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ −126.9 ($\Delta\nu_{1/2}$ = 60 Hz).

Addition of THF (excess) to a solution of **3d** in $\mathrm{C_6D_5Br}$ gave a yellow THF adduct. ^{1}H NMR (25 °C): δ 7.63 (br, 8, *o*-$\mathrm{C_6H_4F}$), 6.93 (dd, 8, *m*-$\mathrm{C_6H_4F}$), 6.28, 5.78, 5.60 (m, 1, ind $\mathrm{C_5}$), 2.2 (vbr, THF), 1.69 (s, 3, C(Ph)=C(Ph)*Me*); other resonances obscured.

Addition of acetonitrile (excess) to a solution of **3d** in $\mathrm{C_6D_5Br}$ gave a yellow acetonitrile adduct. ^{1}H NMR (25 °C): δ 7.66 (br, 8, *o*-$\mathrm{C_6H_4F}$), 6.95 (dd, 8, *m*-$\mathrm{C_6H_4F}$), 6.49 (m, 1, ind $\mathrm{C_5}$), 6.20 (m, 1, Ph), 5.85, 5.63, 5.53 (m, 1, ind $\mathrm{C_5}$), 1.57 (NC*Me*), 0.83 (s, 3, C(Ph)=C(Ph)*Me*); other resonances obscured.

Preparation of $[\mathrm{(C_5Me_5)_2ZrC(Ph)=C(Ph)Me}][\mathrm{B(4\text{-}C_6H_4F)_4}]$ (3e). A solution of diphenylethyne (78 mg, 0.40 mmol) in bromobenzene (5 mL) was reacted with a mixture of $\mathrm{(C_5Me_5)_2ZrMe_2}$ (150 mg, 0.38 mmol) and $[\mathrm{PhMe_2NH}][\mathrm{B(4\text{-}C_6H_4F)_4}]$ (190 mg, 0.37 mmol) in a procedure similar to that leading to **2a** above. The obtained red oil was redissolved in bromobenzene (5 mL) and hexane added to again give an oil, which solidified on extensive washing with hexane (3 × 10 mL). A 260-mg amount of red product (85%) was obtained after drying in vacuo. The product contained traces of unidentified impurities, and attempted crystallization from dichloromethane/hexane or bromobenzene/hexane solution led only to decomposition. ^{1}H NMR ($\mathrm{C_6D_5Br}$, −30 °C): δ 7.71 (m, 8, *o*-$\mathrm{C_6H_4F}$), 7.15 (br, 2, Ph), 7.06 (m, Ph), 6.98 (br, 8, *m*-$\mathrm{C_6H_4F}$), 6.85 (*t*, 1, *p*-Ph), 6.67 (t, 2, *m*-Ph), 6.41 (d, 2, *o*-Ph), 1.45 (s, 30, $\mathrm{C_5}Me_5$), 1.35 (s, 3, C(Ph)=C(Ph)*Me*). ^{1}H NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ 7.24 (m, 8, *o*-$\mathrm{C_6H_4F}$), 6.79 (br, 8, *m*-$\mathrm{C_6H_4F}$), 1.89 (s, 30, $\mathrm{C_5}Me_5$), 1.66 (s, 3, C(Ph)=C(Ph)*Me*); phenyl resonances obscured. ^{13}C NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ 194.4 (*C*(Ph)=C(Ph)Me), 159.9 (d, $^1J_\mathrm{CF}$ = 238 Hz, *p*-$\mathrm{C_6H_4F}$), 158.5 (q, $^1J_\mathrm{BC}$ = 50 Hz, *ipso*-$\mathrm{C_6H_4F}$), 148.5 (C(Ph)=*C*(Ph)Me), 142.3, 139.8 (1 C, *ipso*-Ph), 137.0 (*o*-$\mathrm{C_6H_4F}$), 136.3 (2 C, Ph), 132.8 (1 C, *p*-Ph), 128.8, 128.3 (2 C, Ph), 128.1 (1 C, *p*-Ph), 127.8 ($C_5\mathrm{Me_5}$), 114.7 (br, 2 C, α-Ph *o*-C), 112.5 (d, $^2J_\mathrm{CF}$ = 15 Hz, *m*-$\mathrm{C_6H_4F}$), 27.5 (C(Ph)=C(Ph)*Me*), 11.9 ($\mathrm{C_5}Me_5$). ^{19}F NMR ($\mathrm{C_2D_2Cl_4}$, −30 °C): δ −121.8 ($\Delta\nu_{1/2}$ = 45 Hz).

Addition of THF (excess) to a solution of **3e** in C_6D_5Br did not result in any changes in the ^1H NMR spectrum. However, addition of acetonitrile (excess) resulted in the formation of a yellow acetonitrile adduct. ^1H NMR (25 °C): δ 7.67 (m, 8, o-C_6H_4F), 6.95 (br, 8, o-C_6H_4F), 2.09 (s, 3, NC*Me*), 1.61 (s, 30, C_5Me_5), 1.43 (s, 3, C(Ph)=C(Ph)*Me*); phenyl resonances obscured.

Reaction of $[(C_5H_5)_2ZrMe(THF)][B(4\text{-}C_6H_4F)_4]$ with Alkynes. The reaction of the title complex (15 mg, 0.043 mmol) with $Me_3SiC{\equiv}CMe$ (3.8 μL, 0.051 mmol) or $PhC{\equiv}CPh$ (4.6 mg, 0.051 mmol) in C_6D_5Br (0.6 mL) was monitored by ^1H NMR spectroscopy. The following conversion information was obtained for the reaction with $PhC{\equiv}CPh$, which was not accompanied by a solution color change: 2 h, 5%, 4 h, 9%, 20 h, 17%; 44 h, 25%, 144 h, 36%; very little decomposition was observed. The reaction with $Me_3SiC{\equiv}CMe$ was accompanied by a solution color change to intense yellow and the following conversions to product: 2 h, 12%; 4 h, 17%; 20 h, 21%; 44 h, 15%; 144 h, 10%; resonances due to a large number of side products were observed for the longer reaction times.

Crystal Structure Determination of [*rac*-C_2H_4(indenyl)$_2$ZrC(SiMe$_3$)=CMe$_2$][B(4-C_6H_4F)$_4$]·CH_2Cl_2 (2d). A single crystal of **2d** (approximate dimensions 0.35 × 0.40 × 0.50 mm) was mounted in a thin-walled glass capillary under N_2 and held in place with silicone grease. All diffraction measurements were at low temperature (200 K) on a Nicolet P3m diffractometer fitted with an LT-1 crystal-cooling device, using graphite-monochromated Mo Kα X-radiation. Unit cell dimensions were determined from 32 centered reflections in the range $11.0 < 2\theta < 30.3°$. A total of 9086 diffracted intensities, including check reflections, were measured in a unique quadrant of reciprocal space for $4.0 < \theta < 50.0°$ by Wyckoff ω scans. Three check reflections (329, 581, 10,6,2) remeasured after every 50 ordinary data showed no decay and variation of ±3% over the period of data collection; an appropriate correction was therefore applied. Of the 8557 intensity data (other than checks) collected, 7962 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences; of these, 5392 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied in the basis of 302 azimuthal scan data; maximum and minimum transmission coefficients were 0.840 and 0.780, respectively. Lorentz and polarization corrections were applied.

The structure was solved by direct and Fourier methods. All non-hydrogen atoms were assigned anisotropic displacement parameters, and all hydrogen atoms, fixed isotropic displacement parameters. All non-hydrogen atoms and the hydrogen atoms H(5A), H(5B), and H(5C) (which were located in difference Fourier syntheses) were refined without positional constraints. All other hydrogen atoms were constrained to idealized geometries (C–H = 0.96 Å; H–C–H = 109.5°). Full-matrix least-squares refinement of this model (559 parameters) converged to final residual indices $R = 0.050$, $R_w = 0.058$, and $S = 1.54$. Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variation in F_o due to counting statistics and $g = 0.0005$ was chosen to minimize the variation in S as a function of $|F_o|$. Final difference electron density maps showed no features outside the range +0.8 to −0.8 e Å^{-3}, the largest of these being close to the chlorine atoms of the dichloromethane of solvation. All calculations were carried out on a Nicolet R3m/V structure determination system using programs of the SHELXTL-PLUS package.[25] Complex neutral-atom scattering factors were taken from ref 26.

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Supplementary Material Available: For **2d**, complete lists of bond angles for the cation, anisotropic displacement parameters, and hydrogen atomic parameters (3 pages); a listing of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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(25) Sheldrick, G. M. SHELXTL-PLUS Rev 2.4. Göttingen, FRG, 1988.

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