CC and CN Coupling of Nitriles Mediated by $B(C_6F_5)_3$ and Cp_2ZrPh_2

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Syntheses and structural characterizations of various zirconocenes have been explored from the reaction of the Cp_2ZrPh_2 precursor and nitriles (RCN) in the absence or in the presence of $B(C_6F_5)_3$. In the absence of $B(C_6F_5)_3$, the thermolysis of Cp_2ZrPh_2 with RCN affords azametallacyclic dimer complexes $[Cp_2Zr\{C_6H_4(RCN)\}]_2$ (**1**, R = CH_3; **2**, *p*-F_3C-C_6H_4). Reaction of complex **2** with 1 equiv of $B(C_6F_5)_3$ in toluene gives the monomeric borane adduct $[Cp_2Zr\{\eta^2\text{-C,N-}C_6H_4C(F_3CC_6H_4)N\cdot B(C_6F_5)_3\}]$ (**3**). When Cp_2ZrPh_2 is treated in toluene at 80 °C with CH_3CN in the presence of $B(C_6F_5)_3$, a complex formulated as $[Cp_2Zr\{\eta^2\text{-C,N-}C_6H_4C(CH_3)NH\}\{NCCHC(CH_3)NH\cdot B(C_6F_5)_3\}]$ (**4**) is formed, which results from an unprecedented C,C coupling between two acetonitrile molecules and insertion of a CN group of one acetonitrile molecule into the benzyne. By contrast, the reaction of Cp_2ZrPh_2 with *p*-F_3C-C_6H_4CN in the presence of $B(C_6F_5)_3$ produces $[Cp_2Zr\{\eta^3\text{-C,N,N}'\text{-}C_6H_4C(F_3CC_6H_4)N\text{-}C(F_3CC_6H_4)N\cdot B(C_6F_5)_3\}]$ (**5**), due to the insertion of a CN bond of the nitrile into the benzyne moiety and a C,N coupling between the benzylic carbon atom of a second Lewis acid adduct *p*-F_3C-$C_6H_4CN\cdot B(C_6F_5)_3$ and the nitrogen atom of the first inserted nitrile.

Introduction

Nitriles show a very rich coordination chemistry, some aspects of which have been reviewed.[1] In previous reports, we demonstrated that the presence of a Lewis acid in a tris(pentafluorophenyl)borane adduct of nitriles modifies the reactivity of the CN bond toward group 4 and 5 metallocenes, and a number of η^2-C,N metallazirine complexes of vanadium and titanium of general formula $[Cp_2M(\eta^2\text{-C,N-RNC})\cdot B(C_6F_5)_3]$ have been prepared.[2] More recently, exploration on the reactivity of related borane adducts of TCNX [X = E (tetracyanoethylene), Q (7,7,8,8-tetracyano-*p*-quinodimethane)] with Cp_2V has shown a different type of bonding in which the $[TCNX]^{2-}$ ligand is σ bonded to vanadium(III) or vanadium(IV) centers through a nitrile nitrogen atom, such as in complexes $[(Cp_2V)_2\{(F_5C_6)_3B\cdot(\mu_4\text{-TCNX})\cdot B(C_6F_5)_3\}]$ and $[(Cp_2V)\{(F_5C_6)_3B\cdot(\mu_4\text{-TCNX})\cdot B(C_6F_5)_3\}]_2$.[3] On the other hand, the reactivity of nitriles with group 4 metal complexes has been the subject of numerous studies in which a CN insertion reaction and C−H activation have been observed.[4]

In pioneer studies on the thermolytic reaction of Cp_2ZrPh_2, Erker established the formation of a nascent benzyne complex.[5] The chemistry and reactivity of this molecule was explored toward many functional groups.[6] In particular, nitriles were shown to afford azametallacycles.[4a] The high reactivity of the nitrile bond in Lewis acid adducts of nitriles should change the pattern of this reaction and may lead to interesting developments in organic synthesis. Herein, we report our results on the thermolysis of Cp_2ZrPh_2 in the presence of "activated" nitriles $RCN\cdot B(C_6F_5)_3$ (R = CH_3,[7a] *p*-F_3C-C_6H_4[7b]).

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of argon, collected by distillation, and stored in a drybox over activated 4 Å molecular sieves. Deuterated solvents were degassed and dried over activated 4 Å molecular sieves. NMR spectra were recorded on Bruker AC 200, AM 250, AMX 400, Avance 400, and Avance 500 spectrometers and referenced internally to residual protio-solvent (^{1}H) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{19}F NMR spectra were recorded on a Bruker AC 200

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Table 1. Crystallographic Data, Data Collection, and Refinement Parameters for Compounds 1−5

	1	**2**	**3**·(1.5 toluene)	**4**	**5**
chemical formula	$C_{36}H_{34}N_2Zr_2$	$C_{48}H_{36}F_6N_2Zr_2$	$C_{52.5}H_{29.5}BF_{18}NZr$	$C_{80}H_{46}B_2F_{30}N_6Zr_2$	$C_{50}H_{22}BF_{21}N_2Zr$
fw	677.09	937.23	1118.30	1865.29	1151.73
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a, Å	8.4275(4)	27.057(5)	11.8872(12)	30.7452(17)	12.5777(12)
b, Å	17.1273(8)	9.938(2)	14.1704(14)	14.0485(7)	13.860(3)
c, Å	9.8083(5)	16.465(3)	14.2280(16)	18.9224(9)	17.955(2)
α, deg	90		89.479(13)	90	98.313(13)
β, deg	100.015(4)	103.10(3)	74.665(13)	102.140(4)	104.660(9)
γ, deg	90		75.927(12)	90	116.40(2)
V, Å^3	1394.16(12)	4312.14(14)	2238.0(4)	7990.2(7)	2590.3(6)
Z	2	8	2	4	2
D_{calc}, g cm^{-3}	1.613	1.444	1.659	1.551	1.477
μ(Mo Kα), mm^{-1}	0.777	0.544	0.362	0.379	0.323
F(000)	688	1888	1117	3712	1140
θ range, deg	3.41−26.31	2.19−26.16	2.28−26.13	3.19−23.21	3.18−24.35
no. of measd reflns	9958	20 697	22 408	21 423	16 728
no. of unique reflns/R_{int}	2851/0.0222	4224/0.0749	8235/0.0471	5701/0.0413	8501/0.0598
no. of params/restraints	182/0	290/30	669/0	546/2	665/72
final R indices all data	R1 = 0.0249	R1 = 0.0469	R1 = 0.0483	R1 = 0.0465	R1 = 0.0851
	wR2 = 0.0539	wR2 0.1108	wR2 = 0.1046	wR2 = 0.0876	wR2 = 0.1772
final R indices [$I > \sigma 2(I)$]	R1 = 0.0213	R1 = 0.0388	R1 = 0.0387	R1 = 0.0332	R1 = 0.0635
	wR2 = 0.0528	wR2 = 0.1066	wR2 = 0.0999	wR2 = 0.0822	wR2 = 0.1627
goodness of fit	1.076	1.057	1.053	1.011	0.975
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.435 and −0.431	0.518 and −0.925	1.045 and −0.581	0.350 and −0.349	1.152 and −0.794

(188.298 MHz) or Avance 400 spectrometer (376.441 MHz) (reference $CFCl_3$). ^{11}B NMR (128.37 MHz; reference BF_3·Et_2O) spectra were recorded on a Bruker AMX 400 spectrometer. Chemical shifts are quoted in δ (ppm). Multiplicities and peak types are abbreviated: singlet, s; doublet, d; triplet, t; broad, br; Cq, quaternary carbon. Infrared spectra were prepared as KBr pellets under argon in a glovebox and were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). Elemental analyses (C, H, N) were performed at the Laboratoire de Chimie de Coordination (Toulouse, France). [Cp_2ZrPh_2] and $B(C_6F_5)_3$ were prepared according to literature procedures.[8,9]

Crystal Structure Determination. Crystal data collection and processing parameters are given in Table 1. Crystals of **1** (yellow needles), **2** (yellow parallelepipeds), **3** (colorless blocks), **4** (light yellow platelets), and **5** (yellow parallelepipeds) were obtained. The selected crystals, sensitive to air and moisture, were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 180 K in a stream of cold N_2. For all the structures data were collected at low temperature (T = 180 K) on a Stoe imaging plate diffraction system (IPDS), equipped with an Oxford Cryosystems cryostream cooler device or an Oxford Diffraction Kappa CCD Excalibur diffractometer equipped with a cryojet from Oxford Instruments and using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections, and crystal decay was monitored during data collection by measuring 200 reflections by image; no significant fluctuation of intensities was observed. Structures have been solved by means of direct methods using the program SIR92[10a] and subsequent difference Fourier maps. Models were refined by least-squares procedures on F^2 by using SHELXL-97[10b] integrated in the package WINGX version 1.64,[10c] and empirical absorption corrections were applied on data.[10d] For compound **5**, it was not possible to properly resolve diffuse electron-density residuals (crystallization solvent molecules: one and a half toluene molecules). Treatment with the SQUEEZE program from PLATON[10d] resulted in a smooth refinement. Since a few low-order reflections are missing from the data set, the electron count is underestimated. Consequently, the values given for ρ_{calc}, F(000), and the molecular weight are valid only for the ordered part of the structure. Details of the structure solution and refinements are given in the Supporting Information (CIF file). A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for all structures has been deposited at the Cambridge Crystallographic Data Centre.

Synthesis of [$Cp_2Zr\{C_6H_4(RCN)\}]_2$ (1, R = CH_3; 2, *p*-F_3C-C_6H_4). To a toluene solution (10 mL) of [Cp_2ZrPh_2] (74 mg, 0.2 mmol) was added 2 equiv of nitrile RCN [R = CH_3 (80 μL), *p*-F_3C-C_6H_4 (36 mg)]. The resulting solution was heated for 15 h at 80 °C without stirring and left at room temperature. Yellow crystals are formed, filtered from the solution, and washed with toluene and small portions of pentane. Yield of **1**: 53 mg (58%). Anal. Calcd for $C_{36}H_{34}N_2Zr_2$ (677.12): C 63.86, H 5.06, N 4.14. Found: C 63.37, H 5.23, N 4.19. Yield of **2**: 80 mg (85%). Anal. Calcd for $C_{48}H_{36}F_6N_2Zr_2$ (937.26): C 61.51, H 3.87, N 2.99. Found: C 61.55, H 4.18, N 3.11. The poor solubility of **1** and **2** in common solvents precluded their NMR analysis. (Note: the same reaction but with 4 equiv of RCN led to the same compounds.)

Synthesis of [$Cp_2Zr\{\eta^2$-C,N-$C_6H_4C(F_3CC_6H_4)N$·$B(C_6F_5)_3\}$] (3). A mixture of solid **2** (94 mg, 0.1 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol) in toluene (3 mL) was heated for 7 h at 80 °C. The yellow solution was left at room temperature one week to produce yellow crystals of **3**. Unoptimized yield: 53 mg (58%). Anal. Calcd for $C_{42}H_{18}BF_{18}NZr$·(1.5 toluene) (1118.81): C 56.25, H 2.55, N 1.30. Found: C 56.36, H 2.70, N 1.25. ^{1}H NMR (298 K, CD_2Cl_2, 500.33 MHz): 7.30−7.15 (m, 8H, C_6H_4, obscured by the aromatic signals of 1.5 toluene of crystallization), 6.88 (m, 1H, C_6H_4), 6.35 (d, 1H, C_6H_4), 6.24 (s, 10H, Cp), 2.36 (s, 1.5 $C_6H_5CH_3$). ^{1}H NMR (193 K, CD_2Cl_2, 400 MHz): 7.38 (d, 1H, C_6H_4), 7.27 (d, 1H, C_6H_4), 7.25−7.13 (m, C_6H_4, overlapped by the aromatic signals of 1.5 toluene of crystallization), 6.82 (t, 1H, C_6H_4), 6.51 (d, 1H, C_6H_4), 6.35 (d, 1H, C_6H_4), 6.28 (d, $^1J_{HF}$ 3.6 Hz, 5H, Cp), 6.21 (s, 5H, Cp), 2.33 (s, 4.5H, $C_6H_5CH_3$ of crystallization). ^{13}C NMR (193 K, CD_2Cl_2, 125.80 MHz): 193.9 (s, Cq, Zr-*C*), 186.0 (s, Cq, *C*N), 144.9 (Cq, C_6H_4), 144.4 (Cq, $CC_6H_4CF_3$), 140.0 (C_6H_4), 137.0 (br

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q, $^1J_{CF}$ 280 Hz, CF_3), 133.0 (C_6H_4), 128.8 (C_6H_4), 128.7 (C_6H_4-CF_3), 128.8 (d, $^2J_{CF}$ 100 Hz, C_5H_5), 125.4 (s, C_5H_5), 125.4 (C_6H_4-CF_3), 125.1 ($C_6H_4CF_3$), 124.4 (C_6H_4), 122.3 ($C_6H_4CF_3$), (toluene: 138.1, 129.1, 128.3, 125.4, 21.5; carbons of the C_6F_5 groups are broad peaks found at 152.0, 150.3, 148.9, 148.4, 147.5, 146.9, 145.6). ^{19}F NMR (298 K, CD_2Cl_2, 188.298 MHz): −69.9 (3F, CF_3), −129.0 (d, 1F, *o*-F-C_6F_5), −131.7 (br, 4F, *o*-F-C_6F_5), −157.1 (m, 1F, *m*-F-C_6F_5), −159.2 (t, 1F, *p*-F-C_6F_5), −160.0 (br, 2F, *p*-F-C_6F_5), −163.2 (m, 1F, *m*-F-C_6F_5), −165.9 (br, 4F, *m*-F-C_6F_5), −166.8 (d, 1F, *o*-F-C_6F_5). ^{19}F NMR (193 K, CD_2Cl_2, 376.441 MHz) −63.4 (s, 3F, CF_3), −128.3 (app t, 1F, *o*-F-C_6F_5), −129.6 (app t, 1F, *o*-F-C_6F_5), −131.1 (d, 1F, *o*-F-C_6F_5), −131.7 (d, 1F, *o*-F-C_6F_5), −132.2 (d, 1F, *o*-F-C_6F_5), −156.4 (t, 1F, *p*-F-C_6F_5), −158.9 (t, 1F, *p*-F-C_6F_5), −159.4 (t, 1F, *p*-F-C_6F_5), −160.0 (m, 1F, *m*-F-C_6F_5), −162.2 (m, 1F, *m*-F-C_6F_5), −165.0 (m, 1F, *m*-F-C_6F_5), −165.2 (m, 1F, *m*-F-C_6F_5), −165.7 (m, 1F, *m*-F-C_6F_5), −166.4 (m, 1F, *m*-F-C_6F_5), −168.0 (d, 1F, *o*-F-C_6F_5). ^{11}B NMR (CD_2Cl_2, 160.52 MHz): −7.1.

Synthesis of [$Cp_2Zr\{\eta^2$-C,N-$C_6H_4C(CH_3)NH\}\{NCCHC(CH_3)NH\cdot B(C_6F_5)_3\}$] (4) and [$Cp_2Zr\{\eta^2$-C,N-$C_6H_4C(CD_3)ND\}\{NCCDC(CD_3)ND\cdot B(C_6F_5)_3\}$] (4′). To a toluene solution (10 mL) of [Cp_2ZrPh_2] (75 mg, 0.2 mmol) and $B(C_6F_5)_3$ (102 mg, 0.2 mmol) was added 3 equiv of nitrile CH_3CN (120 μL) (note that using only 2 equiv of CH_3CN afforded the same complex). The resulting solution was heated for 15 h at 80 °C and evaporated to dryness to give an oil. The oil was dissolved in a small amount of toluene and layered with pentane to give yellow crystals of **4**. Crystals of **4** were filtered from the solution and were washed with toluene and small portions of pentane. Yield: 150 mg (80%). Anal. Calcd for $C_{40}H_{23}BF_{15}N_3Zr$ (932.64): C 51.51, H 2.49, N 4.51. Found: C 51.35, H 2.36, N 4.33. IR: ν(NH) 3435; 3346 cm^{-1}, ν(CN) 2174 cm^{-1}. ^{1}H NMR (THF-d_8, 500.33 MHz): 9.07 (s, 1H, ZrN(*H*)), 7.73, 7.67 (d, 1H, *J*(CH) 10 Hz, C_6H_4); 7.38, 7.19 (t, 1H, *J*(CH) 5 Hz, C_6H_4); 6.92 (s, 1H, C(CH_3)=N*H*); 6.11 (s, 10H, C_5H_5); 3.73 (s, 1H, C*H*); 2.61 (s, 3H, ($C_6H_4CCH_3$); 2.41 (s, 3H, CHC(CH_3)). ^{1}H NMR (CD_2Cl_2, 500.33 MHz): 8.04 (s, 1H, ZrN(*H*)), 7.57 (d, 1H, *J*(CH) 10 Hz, C_6H_4), 7.45 (d, 1H, *J*(CH) 10 Hz, C_6H_4), 7.29 (t, 1H, ^1J(CH) 5 Hz, C_6H_4), 7.12 (t, 1H, ^1J(CH) 5 Hz, C_6H_4), 5.95 (s, 10H, C_5H_5), 5.72 (s, 1H, C(CH_3)=N*H*), 3.58 (s, 1H, C*H*), 2.52 (s, 3H, $C_6H_4CCH_3$), 2.24 (s, 3H, CHC(CH_3)). ^{1}H NMR (toluene-d_8, 200 MHz): 7.65 (s, 1H, ZrN(*H*)), 7.10−6.8 (m, 4H, (C_6H_4), 5.92 (s, 1H, C(CH_3)=N*H*), 5.39 (s, 10H, C_5H_5), 4.07 (s, 1H, C*H*), 2.00 (s, 3H, CHC(CH_3)), 1.67 (s, 3H, $C_6H_4NCCH_3$). ^{13}C NMR (THF-d_8, 100.62 MHz): 195.18 (s, Cq Zr-*C*), 191.53 (s, Cq, $C_6H_4C(CH_3)$=NH), 169.83 (s, Cq, CH*C*(CH_3)NH), 148.4 (d, $^1J_{CF}$ 240 Hz, *o*-F-C_6F_5), 143.15 (s, Cq, C*ipso* C_6H_4), 140.33 (d, $^1J_{CH}$ 154 Hz, C_6H_4), 139.56 (s, Cq, CH*C*N), 138.80 (d, $^1J_{CF}$ 252 Hz, *p*-F-C_6F_5), 136.51 (d, $^1J_{CF}$ 248 Hz, *m*-F-C_6F_5), 129.62 (d, $^1J_{CH}$ 157 Hz, C_6H_4), 128.19 (d, $^1J_{CH}$ 156 Hz, C_6H_4), 123.48 (d, $^1J_{CH}$ 160 Hz, C_6H_4), 121.6 (br s, $\Delta_{1/2}$ 200 Hz, C*ipso* C_6F_5) 110.3 (d, $^1J_{CH}$ 174 Hz, C_5H_5), 51.52 (d, $^1J_{CH}$ 178 Hz, *C*H), 22.49 (q, $^1J_{CH}$ 128 Hz, C(*C*H$_3$)NH), 21.29 (q, $^1J_{CH}$ 126 Hz, CHC*C*H$_3$). ^{11}B NMR (THF-d_8, 128.37 MHz): −11 ppm. ^{19}F NMR (THF-d_8, 188.298 MHz): −134.1 (*o*-F-C_6F_5); −163.0 (*p*-F-C_6F_5); −167.4 (*m*-F-C_6F_5). ^{19}F NMR (CD_2Cl_2 188.298 MHz): −134.9 (*o*-F-C_6F_5); −161.6 (*p*-F-C_6F_5); −166.5 (*m*-F-C_6F_5).

The deuterated congener **4′** was prepared using the procedure described above for **4** but with CD_3CN instead of CH_3CN. IR: ν(ND) 2245, 2180. ^{2}H NMR (THF-d_8, 76.80 MHz): 9.07 (br s, ZrN-*D*), 6.80 (br s, C(CD_3)=N*D*), 3.65 (br s, C-*D*), 2.52 (s, $C_6H_4C(CD_3)$), 2.48 (s, CDC*C*D$_3$).

Synthesis of [$Cp_2Zr\{\eta^3$-C,N,N′-$C_6H_4C(F_3CC_6H_4)$N-C($F_3CC_6H_4$)N$\cdot B(C_6F_5)_3\}$] (5). To a toluene solution (10 mL) of [Cp_2ZrPh_2] (36 mg, 0.1 mmol) were added 2−4 equiv of nitrile $F_3CC_6H_4CN$ (35 mg, 0.2 mmol) and $B(C_6F_5)_3$ (51 mg, 0.1 mmol). The resulting solution was heated for 15 h at 80 °C without stirring and left at room temperature. Yellow crystals were separated by filtration from the solution, washed with toluene and small portions of pentane, and dried under vacuum. Yield: 68 mg (59%). Anal. Calcd for $C_{50}H_{22}BF_{21}N_2Zr$ (1151.72): C 52.14, H 1.93, N 2.43. Found: C 52.08, H 1.95, N 2.47. ^{1}H NMR (THF-d_8, 400.13 MHz): 7.90 (d, $^1J_{CH}$ 8 Hz, 1H, ZrC_6H_4), 7.56 (d, $^1J_{CH}$ 8 Hz, 2H, $F_3CC_6H_4$), 7.40 (dd, $^1J_{CH}$ 8 Hz, 1H, ZrC_6H_4), 7.30 (d, $^1J_{CH}$ 8 Hz, 2H, C_6H_4CN), 7.27 (dd, $^1J_{CH}$ 8 Hz, 1H, ZrC_6H_4), 7.21 (d, $^1J_{CH}$ 8 Hz, 1H, ZrC_6H_4), 7.13 (d, $^1J_{CH}$ 8 Hz, 2H, C_6H_4CN), 7.05 (d, $^1J_{CH}$ 8 Hz, 2H, C_6H_4CN), 6.33 (s, 10H, C_5H_5) (toluene of crystallization: 7.36−7.22 obscured Ph, 2.44 CH_3). ^{13}C NMR (THF-d_8, 100.62 MHz): 207.1 (s, Cq, Zr-*C*C_6H_4), 184.6 (s, Cq, Zr*NC*(C_6H_4)($C_6H_4CF_3$), 169.4 (s, Cq, Zr*NC*(NB(C_6F_5)$_3$)($C_6H_4CF_3$), 149.5 (br d, $^1J_{CF}$ 240 Hz, *o*-C_6F_5), 143.6 (d, $^1J_{CH}$ 158 Hz, Zr(C_6H_4)), 143.6 (s, Cq, Zr(C_6H_4)), 140.3 (s, Cq, N*ipso*C $C_6H_4CF_3$), 140.6 (br d, $^1J_{CF}$ 245 Hz, *p*-C_6F_5), 138.3 (s, Cq, N*ipso*C $C_6H_4CF_3$), 135.9 (d, $^1J_{CH}$ 159 Hz, ZrC_6H_4), 131.7 (d, $^1J_{CH}$ 159 Hz, ZrC_6H_4), 130.4 (d, $^1J_{CH}$ 159 Hz, ZrC_6H_4), 138.2 (br d, $^1J_{CF}$ 233 Hz, *m*-C_6F_5), 132.5 (q, $^1J_{CF}$ 33 Hz, *C*CF_3), 131.6 (q, $^1J_{CF}$ 33 Hz, *C*CF_3), 129.6 (d, $^1J_{CH}$ 166 Hz, $C_6H_4CF_3$), 126.2 (d, $^1J_{CH}$ 166 Hz, $C_6H_4CF_3$), 126.1 (d, $^1J_{CH}$ 166 Hz, $C_6H_4CF_3$), 125.5 (d, $^1J_{CH}$ 166 Hz, $C_6H_4CF_3$), 124.9 (q, $^1J_{CF}$ 272 Hz, *C*F_3), 124.7 (q, $^1J_{CF}$ 272 Hz, *C*F_3), 112.8 (d, $^1J_{CH}$ 175 Hz, C_5H_5), *ipso*C−B not observed (toluene of crystallization 138.93, 130.16, 129.56, 126.53, 20.90). ^{19}F NMR (THF-d_8, 188.298 MHz): −64.5 (3F, CF_3), −65.0 (3F, CF_3), −122.5 (1F, C_6F_5), −131.0 (br, 4F, C_6F_5), −132.7 (1F, C_6F_5), −159.6 (1F, C_6F_5), −161.4 (2F, C_6F_5), −165.2 (1F, C_6F_5), −166.7 (5F, C_6F_5). ^{11}B NMR (THF-d_8, 128.37 MHz): −7.40.

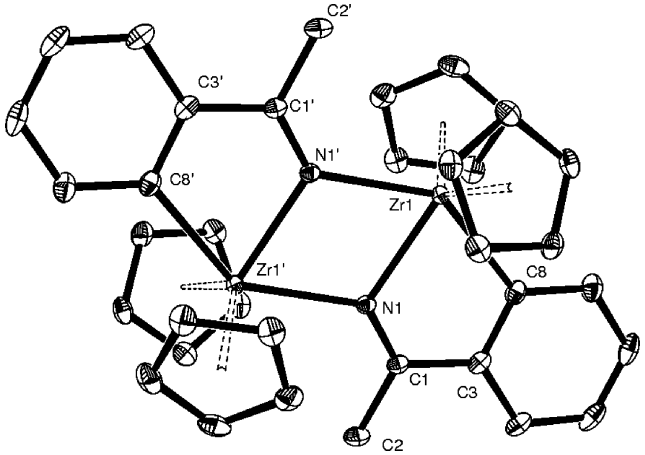


Figure 1. Molecular structure of **1**, showing 50% probability ellipsoids and partial atom-labeling scheme. Hydrogen atoms are omitted for clarity. Zr(1)−N(1) 2.2980(15); Zr(1)−C(8) 2.3480(18); Zr(1′)−N(1) 2.3564(14); N(1)−C(1) 1.292(2); C(1)−C(3) 1.480(2); C(3)−C(8) 1.398(3); N(1)−Zr(1)−C(8) 71.39(6); Zr(1)−N(1)−Zr(1′) 111.32(6).

Results and Discussion

1. Reactivity of Cp_2ZrPh_2 with Nitriles RCN (R = CH_3, *p*-F_3C-C_6H_4). Reactions of acetonitrile (CH_3CN) and trifluoro-*p*-tolunitrile (*p*-F_3C-C_6H_4CN) with Cp_2ZrPh_2 were first evaluated, as templates for comparison purposes to further studies within the present work. The thermolysis of Cp_2ZrPh_2 with CH_3CN or *p*-F_3C-C_6H_4CN in toluene at 80 °C afforded bright yellow crystals of compounds **1** and **2**, respectively, for CH_3CN and *p*-F_3C-C_6H_4CN. The structure of the two complexes was ascertained by X-ray diffraction analysis and is shown in Figures 1 and 2. These complexes are formulated as [$Cp_2Zr\{C_6H_4(RCN)\}]_2$ (**1**, R = CH_3; **2** *p*-F_3C-C_6H_4) and consist of a dimer structure with an azametallacycle. Both solid-state structures are similar to the one previously published on the analogous complex [$Cp_2Zr\{C_6H_4(PrCN)\}]_2$, resulting from the insertion of PrCN in the Cp_2Zr(benzyne) complex.[4a] The amido Zr−N bond lengths (average: 2.30 and 2.37 Å respectively for **1** and

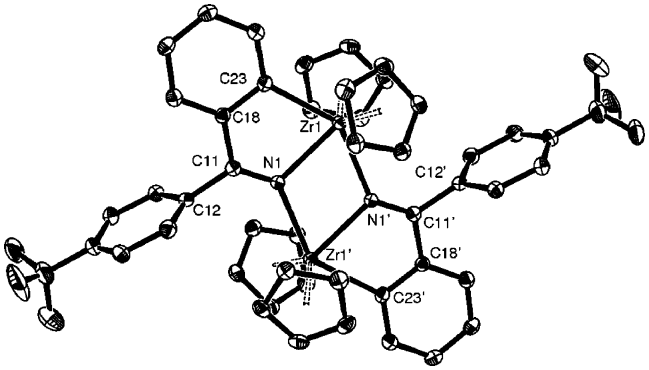
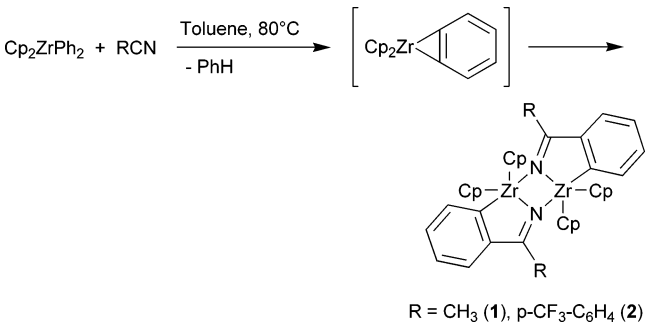


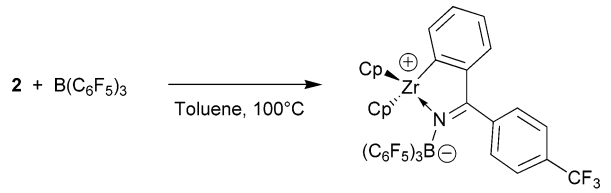
Figure 2. Molecular structure of **2**, showing 50% probability ellipsoids and partial atom-labeling scheme. Hydrogen atoms are omitted for clarity. Zr(1)−N(1) 2.308(2); Zr(1)−C(23) 2.347(3); Zr(1′)−N(1) 2.380(2); N(1)−C(11) 1.289(4); C(11)−C(18) 1.484(4); C(18)−C(23) 1.405(4); N(1)−Zr(1)−C(23) 72.21(9); Zr(1)−N−Zr(1′) 110.09(9).

Scheme 1. Synthesis of Complexes 1 and 2



R = CH_3 (**1**), p-CF_3-C_6H_4 (**2**)

Scheme 2. Synthesis of Complex 3



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2) are in the expected range for a bridging amido group, and the C═N distance (average 1.29 Å) corresponds to an imine group.[11] Compounds **1** and **2** are insoluble in usual solvents (THF, CH_2Cl_2, CH_3CN, toluene) even at high temperature (**2** decomposes in boiling toluene), which precluded their characterization by NMR spectroscopy.

2. Reactivity of Compounds 1 and 2 with $B(C_6F_5)_3$. In contrast to compound **1**, which is unreactive toward $B(C_6F_5)_3$ (probably for solubility reasons) even when heated in toluene, the addition of 1 equiv of $B(C_6F_5)_3$ to a toluene solution of complex **2** and heating at 100−110 °C (see Scheme 2) produced the yellow crystalline, monomeric, borane adduct [$Cp_2Zr\{\eta^2$-C,N-$C_6H_4C(F_3CC_6H_4)N{\cdot}B(C_6F_5)_3\}$] (**3**), as revealed by an X-ray structure determination. An ellipsoid plot is presented in Figure 3 (the compound crystallized with 1.5 molecule of toluene, which is not represented). Coordination of one $B(C_6F_5)_3$ molecule at the imine nitrogen atom of the azametallacycle in compound **2** has induced the breaking of the bimetallic frame (in **2**) into the monomer borane adduct **3**. The Zr−N(1) distance

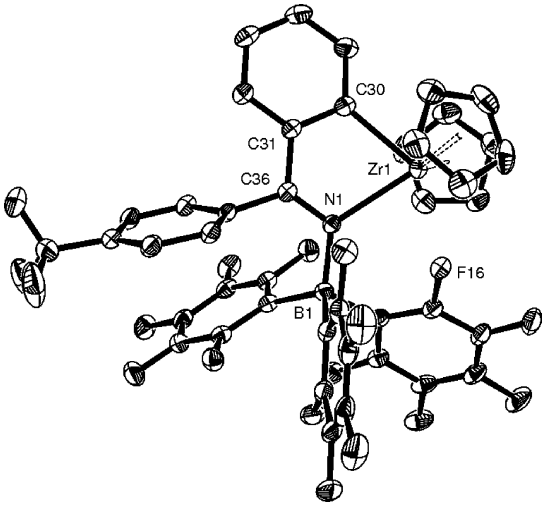


Figure 3. Molecular structure of **3**, showing 50% probability ellipsoids and partial atom-labeling scheme. Hydrogen atoms and solvent (1.5 toluene) of crystallization are omitted for clarity. Zr(1)−N(1) 2.4219(19); Zr(1)−C(30) 2.269(3); N(1)−C(36) 1.303(3); N(1)−B(1) 1.616(3); C(30)−C(31) 1.405(3); F(16)−Zr(1) 2.4497(14); C(36)−N(1)−B(1) 119.94(19); C(36)−N(1)−Zr(1) 111.17(14); B(1)−N(1)−Zr(1) 128.89(14); C(31)−C(30)−Zr(1) 114.12(17); C(30)−C(31)−C(36) 117.7(2); N(1)−C(36)−C(31) 121.0(2); C(30)−Zr(1)−N(1) 73.65(8); C(30)−Zr(1)−F(16) 142.03(7); N(1)−Zr(1)−F(16) 69.40(6).

(2.4219(19) Å) is comparable to Zr−N distances in related Zr(IV) compounds containing a neutral N donor ligand.[12] Atoms of the metallacycle Zr, C(30), C(31), C(36), N(1), B(1), and the ortho-fluorine atom F(16) of one C_6F_5 group of the borane are contained in the same plane. The bond length C(36)−N(1) (1.303(3) Å) is typical of an imine −C═N− function and supports a high degree of double-bond character. The N(1)−B(1) distance (1.606(3) Å) is in the same range as in a nitrile-borane adduct. The resulting Zr−F(16) distance of 2.4497(14) Å implies a weak intramolecular Zr−(μ-F)−C situation with one ortho-fluorine atom of that C_6F_5 group.[13,14] Noteworthy, this Zr−F interaction is also observed in solution by NMR spectroscopy. Complex **3** decomposes in THF solvent, as shown by ^{19}F NMR spectroscopic experiments, in which different sets of peaks were observed with formation of the $THF{\cdot}B(C_6F_5)_3$ adduct. Nevertheless, in CD_2Cl_2, complex **3** exhibits in its room-temperature (298 K) ^{19}F NMR spectrum several sets of signals. First, it presents five well-resolved peaks (each integrating for one fluorine), attributed to the five fluorine atoms of a pentafluorophenyl group that is further coordinated to the zirconium center. The resonance of the ortho-fluorine atom in contact with the zirconium center is a doublet shifted at −166.8 ppm, by comparison to the other *o*-F of the same C_6F_5 group, which appears in the normal range as a doublet at −129.0 ppm (others peaks are *m*-F, m, −157.1; *p*-F, t, −159.2; *m*-F, m, −163.2 ppm). This would support that the weak Zr−F interaction observed in the solid state is retained in solution. The other

(11) (a) Chisholm, M. H.; Hammond, C. E.; Huffman, J. C. *Polyhedron* **1988**, *7*, 2515−2520. (b) Wu, Z.; Diminnie, J. B.; Xue, Z. *Inorg. Chem.* **1998**, *37*, 2570−2574.

(12) (a) Moore, E. J.; Strauss, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc*. **1983**, *105*, 2068−2070. (b) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1995**, *14*, 371−386.

(13) (a) Pintado, G. J.; Thornton-Pett, M.; Bouwkamp, M.; Meetsma, A.; Hessen, B.; Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2358−3831. (b) Pintado, G. J.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M *J. Am. Chem. Soc*. **1998**, *120*, 6816−6817. (c) Siedle, A. R.; Newmark, R. A.; Lamanna, W. N. *Organometallics* **1993**, *12*, 1491−1492.

(14) The Zr···F van der Waals interaction is ca. 3.0 Å; see: Bondi, A. *J. Phys. Chem*. **1964**, *68*, 441−451.

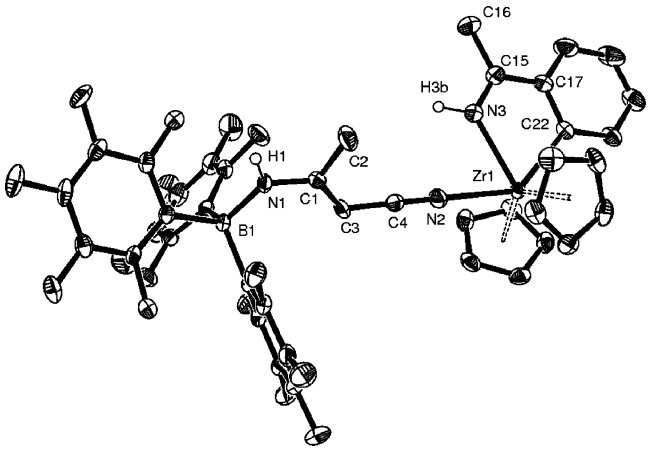
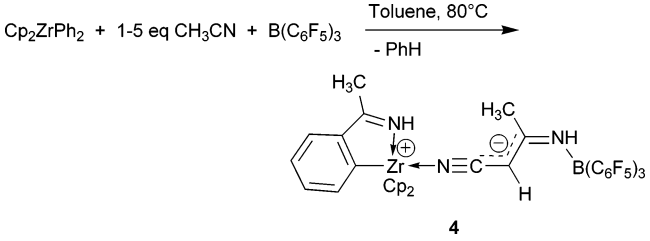


Figure 4. Molecular structure of **4**, showing 50% probability ellipsoids and partial atom-labeling scheme. Hydrogen atoms are omitted for clarity. Zr(1)−N(3) 2.295(4); Zr(1)−N(2) 2.312(4); N(1)−C(1) 1.328(5); N(1)−B(1) 1.541(6); C(1)−C(3) 1.376(6); C(3)−C(4) 1.402(6); N(2)−C(4) 1.158(6); C(1−C(2) 1.511(6); N(3)−Zr(1)−N(2) 70.95(14); C(1)−N(1)−B(1) 130.6(4); C(1)−C(3)−C(4) 121.3(4); C(4)−N(2)−Zr(1) 172.2(4); N(1)−C(1)−C(3) 123.2(4); N(1)−C(1)−C(2) 115.9(4); C(3)−C(1)−C(2) 120.9(4); N(2)−C(4)−C(3) 177.5(5).

Scheme 3. Synthesis of Complex 4



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peaks, corresponding to the two noncoordinated C_6F_5 substituents of the borane, appear as broad peaks (−131.7, −160.0, and −165.9 ppm, respectively for *o*-, *p*-, *m*-F). In addition, complex **3** exhibits a dynamic behavior in solution, and at 193 K, all 15 fluorine atoms become inequivalent under these conditions.[13c,15] At that temperature (193 K), the two Cp ligands become inequivalent, which is reflected in the ^{1}H NMR spectrum by the presence of a doublet at 6.28 ppm (the five protons of that Cp are coupled to the Zr−F with $^3J_{HF} = 3.6$ Hz) and a singlet at 6.21 ppm (5H). The ^{11}B NMR spectrum shows a resonance at −7.1 ppm, a value between a borate-type boron (as for **4**, vide infra) and a neutral, four-coordinate center. Nevertheless, a zwitterionic zirconium complex could be drawn on this basis as depicted in Scheme 2.

3. Reactivity of Cp_2ZrPh_2 with RCN (R = CH_3, *p*-F_3C−C_6H_4,) in Presence of $B(C_6F_5)_3$. The thermolysis of Cp_2ZrPh_2 with RCN (R = CH_3, *p*-F_3C-C_6H_4,) in the presence of $B(C_6F_5)_3$ proceeds differently.

When Cp_2ZrPh_2 is treated with CH_3CN (1 to 5 equiv) in the presence of $B(C_6F_5)_3$ in toluene at 80 °C, a yellow crystalline product **4** is formed in good yield (Scheme 3). The molecular structure of compound **4** has been determined by an X-ray diffraction analysis, and an ORTEP view is presented in Figure 4. Complex **4** shows the Cp_2Zr unit with the expected insertion of a nitrile CN bond into the benzyne moiety, resulting in the formation of a metallacycle-imine fragment, as observed for **1**, but with the unexpected formation of a NH bond (−C═NH: C(15)−N(3) 1.304(6) Å). Interestingly, in the second part of the molecule, a coupling between an αC and a *β*C carbon atom of two acetonitrile molecules has occurred. At one side of the resulting new crotonylamido ligand, the nitrogen atom [N(1)−H] of an imine functionality [the CN bond distance is in agreement with a double bond: C(1)═N(1) 1.328(5) Å] is connected to a distorded tetrahedral tris(pentafluorophenyl)-borane molecule. The B(1)−N(1) distance (1.541(6) Å) is shorter than the typical B−N distance found in $RCN{\cdot}B(C_6F_5)_3$ adducts (1.59−1.61 Å).[7a,16] The second side of the ligand contains a nitrile skeleton, by which it is coordinated to the zirconium center. The C≡N bond distance of 1.158 (6) Å is consistent with a triple-bond character (for acetonitrile (α-phase at 208 K) a value of 1.141(2) Å was obtained for the C≡N triple bond[16] and a nearly linear N(2)−C(4)−C(3) angle (177.5-(5)°). As a result, this crotonylamido fragment can be considered as a donor ligand to the cationic moiety $[Cp_2Zr(\eta^2\text{-}C_6H_4\text{-}NCCH_3)]^+$. Indeed, the Zr−N distances (Zr−N(2) 2.312(4) Å and Zr−N(3) 2.295(4) Å) are similar to those found in the cationic benzyl complex $[Cp_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)]^+$ (Zr−N = 2.295(5) Å).[18] The C−C bond parameters within the crotonylamido fragment are the following: C(1)−C(3) and C(3)−C(4) bond distances of 1.376(6) and 1.402(6) Å, respectively, with a C(1)−C(3)−C(4) angle of 121.3(4)°). Although no hydrogen atom was located in the X-ray structure on the C(3) atom, the NMR studies (vide infra) established the presence of a methine hydrogen atom at this C(3) carbon atom. All atoms of the chain (B(1), N(1), C(1), C(2), C(3) C(4), N(2), Zr) are nearly contained in the same plane [for example, dihedral angle between N(1)−C(1)−C(3) and C(1)−C(3)−C(4)−N(2) is approximately 1.77(0.86)°], and the bond distances suggest a succession of a double bond (N(1)−C(1)), a partial double bond (C(1)−C(3)−C(4)) and a triple bond (C(4)−N(2)). Therefore, significant delocalization within the *π*-system of this crotonitrileamido fragment and a carbanionic character is suspected for the latter C(3) atom. Likewise, compound **4** is better described by the resonance structures shown in Figure 5.

A similar reactivity was observed in organoyttrium chemistry between $Y(NO)_2(CH(SiMe_3)_2$ (*NO* = $[Me_2Si(NCMe_3)OCMe_3]$) and CH_3CN that gave the dimer $[(NO)_2YN(H)C(Me)CHCN)]_2$. The crotonitrileamido ligand in this yttrium system has similar bonding parameters to those found in **4**.[19]

The NMR spectroscopic data of **4** (^{1}H, ^{13}C, ^{19}F, ^{11}B) are consistent with the solid-state structure. In the ^{1}H NMR (THF-d_8) spectrum, three singlets at 8.98, 6.83, and 3.64 ppm, each integrating for one proton, are characteristic of two NH groups and the hydrogen of the methine group, although the latter was not observed in the X-ray structure determination. The corresponding ^{13}C NMR spectrum showed the chemical shift of the methine carbon as a doublet at 51.5 ppm, with a C−H coupling constant of 171 Hz. To ascertain the presence of a methine hydrogen in the molecule and to eliminate all ambiguities for that, a coupling reaction with CD_3CN was carried out. The deuterated orange crystalline compound **4′** $[Cp_2Zr\{\eta^2\text{-}C,N\text{-}C_6H_4C(CD_3)ND\}\{NCC(D)C(CD_3)ND{\cdot}B(C_6F_5)_3\}]$ was obtained from Cp_2ZrPh_2, $B(C_6F_5)_3$, and CD_3CN. The ^{2}H NMR spectro-

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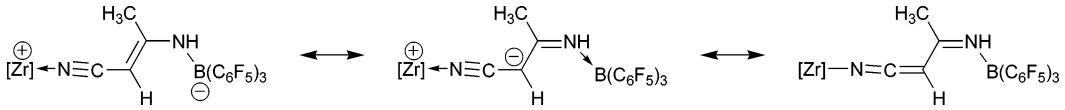
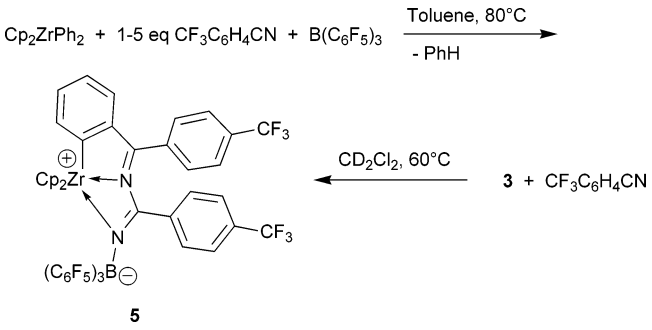


Figure 5. Canonic formulas for **4**.

Scheme 4. Synthesis of Complex 5



scopic data confirmed the presence of deuterated N−D and C−D methine protons as well as the deuterated CD_3 groups. Consistently, in the $^{13}C\{^1H\}$ NMR spectrum of deuterated **4′**, the carbon atom associated with the deuterated methine gave a 1:1:1 triplet with $^1J(C-D) = 27$ Hz. This high-field shift position of the methine carbon atom is in agreement with a formal negative charge on this carbon, indicating a considerable charge delocalization within the crotonitrileamido fragment [N(H)═C(CH_3)-C(H)-C≡N]. The spectroscopic and structural data of this fragment are in close agreement with those reported for the above-mentioned organoyttrium crotononitrileamido complex $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}N,N'\text{-NH-CMe═CH-C≡N})\}_2$. In addition, ^{11}B NMR spectroscopic studies of **4** exhibit a resonance at −11.0 ppm, indicative of a borate-type boron rather than a neutral, four-coordinate center. The presence of both NH and CN bonds in **4** was also evidenced by IR spectroscopic measurements (**4**: ν(NH) = 3435; 3346 cm^{-1}; ν(CN) = 2174 cm^{-1}, **4′**: ν(ND) = 2245; 2180 cm^{-1}).

The reaction of Cp_2ZrPh_2 with *p*-F_3C-C_6H_4CN (1 to 5 equiv) in the presence of $B(C_6F_5)_3$ (1 to 2 equiv) in toluene at 80 °C affords compound **5** (Scheme 4) as yellow crystals that were suitable for an X-ray structure analysis. The molecular structure of complex **5** is presented in Figure 6. The complex crystallized with 1.5 molecule of toluene in the lattice. This structure shows the Cp_2Zr unit with the expected insertion of the CN bond of the nitrile into the benzyne moiety to form a metallacycle−imine fragment as observed for **2** and a C,N coupling between the carbon atom C(25) of the nitrile of a second Lewis acid adduct $F_3CC_6H_4CN{\cdot}B(C_6F_5)_3$ and the nitrogen atom N(1) of the nitrile of the metallacycle-imine. The Zr−N(1) and Zr−C(11) distances (2.233(3) and 2.346(5) Å, respectively) are comparable with those observed for the metallacycle in **2**. The Zr−N(2) distance (2.589 Å) is significantly longer than Zr−N(1) and is comparable to Zr−N distances in related Zr(IV) compounds containing neutral N donor ligand.[12] Atoms of the metallacycle (C11)−C(16), C(17), N(2), B(1)) are almost contained in the same plane (the distance of atoms N(1), C(25), and Zr to the mean plane is deviated by −0.137, −0.299, and 0.358 Å, respectively). The imine bond lengths C(17)−N(1) (1.315(6) Å) and C(25)−N(2) (1.287(6) Å) support a high degree of double-bond character. The N(1)−C(25) distance of 1.408(5) Å for the N−C bond resulting from the coupling between the two nitrile molecules is in agreement with a weak double-bond character. The situation of the nitrogen atom N(2) is quite puzzling. Careful investigations demonstrated that no electronic residue around the N(2) atom is observed in the crystal structure

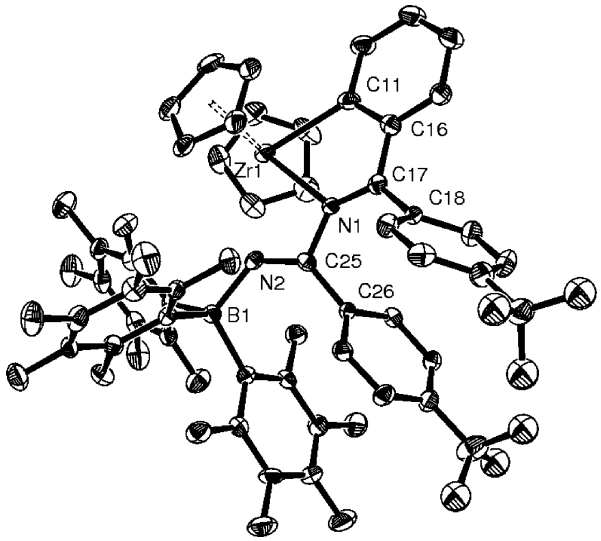


Figure 6. Molecular structure of **5**, showing 50% probability ellipsoids and partial atom-labeling scheme. Hydrogen atoms and solvent (1.5 toluene) of crystallization are omitted for clarity. Zr(1)−N(1) 2.230(3); Zr(1)−C(11) 2.344(4); N(1)−C(17) 1.307(5); C(16)−C(17) 1.458(6); N(1)−C(25) 1.408(5); N(2)−C(25) 1.282(5); N(2)−B(1) 1.597(6); N(1)−Zr(1)−C(11) 68.71(13); C(17)−N(1)−C(25) 131.6(4); C(17)−N(1)−Zr(1) 123.8(3); C(25)−N(1)−Zr(1) 103.8(3); C(25)−N(2)−B(1) 126.1(4); C(25)−N(2)−Zr(1) 90.3(3); B(1)−N(2)−Zr(1) 143.5(3).

data and that no N(2)−H bond is present. The latter was also confirmed by the absence of NH absorption in the IR spectrum of **5**. This implies a connectivity between the nitrogen atom N(2) of the imine group and both zirconium and boron centers (Zr−N(2) 2.589 Å; B−N(2) 1.595(6) Å; the sum of the angles around N(2) connected to Zr, B(1), and C(25) is 359.9°). This is similar to the distances observed in compound **3**, in which the tris(perfluorophenyl)borane is connected to the nitrogen atom of the [Zr−N(1)═C−$C_6H_4CF_3$] moiety with very similar structural features. Additionally, the angle between the C_6H_4 planes of the two nitriles is 18.10°, and the one between C_6H_4 and one C_6F_5 of the borane is 23.13°, excluding overlapping aromatic rings.

Compound **5** was also fully characterized by multinuclear NMR spectroscopic studies. A spatial correlation between the quaternary carbon C(11) attached to the zirconium and the cyclopentadienyl rings as well as to the C_6H_4 group of the metallacycle allowed to locate its chemical shift at the lowest field (207 ppm). It is worth noting that ^{13}C NMR and ^{19}F NMR data show the inequivalency of the two CF_3 groups, and the ^{19}F NMR data show the inequivalency of five fluorine atoms of a C_6F_5 group in the borane. We suspect that the rotation of a C_6F_5 group around the B−C axis is restricted by the proximity of the $-C_6H_4CF_3$ ligand. The ^{11}B NMR spectrum of **5** exhibits a single signal at −7.4 ppm (as observed in **3**). A zwitterionic zirconium complex could be drawn on this basis that is depicted in Scheme 4.

Importantly, the reaction of complex **3** with 1 equiv of *p*-F_3C-C_6H_4CN was monitored by ^1H and ^{19}F NMR in CD_2Cl_2 (60 °C for 24 h in a sealed NMR tube). Again, complex **5** was formed, via insertion of the CN bond of the nitrile into the Zr−N bond.

This observation indicates that decoordination of the $B(C_6F_5)_3$ in **3** is possible.

To explain the formation of compounds **4** and **5**, we propose the intermediacy of the dimers **1** and **2**. The dimers would be broken by π-coordination of a $RCN{\cdot}B(C_6F_5)_3$ adduct to generate a monomeric intermediate $[Cp_2Zr\{\eta^2\text{-}C,N\text{-}C_6H_4(RCN)\}\{RCN{\cdot}B(C_6F_5)_3\}]$. This species could further evolve, but depending on the nature of the nitrile: (i) either by C,C coupling between two acetonitrile molecules or (ii) C,N coupling between the benzylic carbon atom of a second Lewis acid adduct $p\text{-}F_3C\text{-}C_6H_4CN{\cdot}B(C_6F_5)_3$ and the nitrogen atom of the azazirconacycle. Indeed, we have verified that complexes **4** and **5** can be readily prepared from precursors **1** and **2** and isolated $RCN{\cdot}B(C_6F_5)_3$ ($R = CH_3$, $C_6H_4CF_3$) in toluene at 80 °C. More studies will be necessary to clarify these assumptions.

Conclusions

In conclusion, these investigations present new developments in the chemistry of $B(C_6F_5)_3$-"activated" nitriles. In the reported zirconium systems, CN and CC coupling are obtained, which demonstrates that $RCN{\cdot}B(C_6F_5)_3$ is not a spectator ligand.[2a,20] Further studies on related zirconium compounds will be reported in due course.

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Supporting Information Available: CIF files and tables of atomic coordinates, bond distances, and angles for the X-ray crystal structures of complexes **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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