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Formation of a bifunctional zirconocene complex that favours intramolecular $-B(C_6F_5)_2$ addition to a Cp ring over σ-ligand abstraction

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The diphenyl-*ansa*-zirconocene complex 2 adds $HB(C_6F_5)_2$ at the C=C double bond of its pendent Cp-allyl functional group to yield 3. During 3 days at room temperature the $-B(C_6F_5)_2$ group takes part in an electrophilic substitution reaction at the adjacent Cp-ring to form 5 with formation of one equivalent of benzene. Complex 5 was characterized by X-ray diffraction

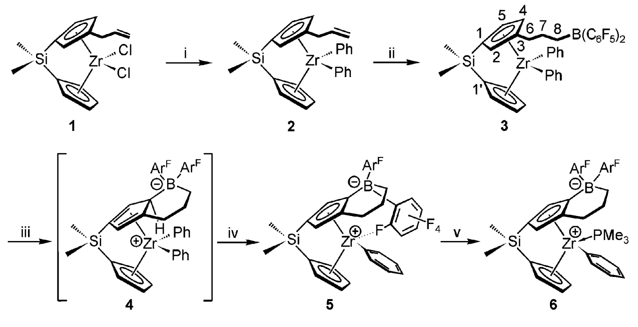
Abstraction of a σ-alkyl ligand from zirconocene complexes $^RCp_2ZrR_2$ by strong *Lewis* acids such as *e.g.* $B(C_6F_5)_3$ to generate $[^RCp_2ZrR^+]$ cations constitutes a major activation pathway in homogeneous *Ziegler–Natta* catalysis.[1] In the literature, examples of such σ-ligand abstractions are so numerous, that alternative competing reaction pathways of the $^RCp_2ZrR_2/B(C_6F_5)_3$ systems may become underestimated. Addition reactions of $B(C_6F_5)_3$ to π-ligands at zirconium have been described.[2,3] There are even a few examples known where $B(C_6F_5)_3$ has added to a Cp ligand at zirconium leaving an adjacent σ-ligand untouched,[4] although these rare cases have admittedly involved sterically very demanding σ-ligand environments. We have now found a system where a strongly electrophilic boron *Lewis* acid has avoided abstracting a simple σ-phenyl group at zirconium in favour of entering into a reaction sequence that is initiated by electrophilic attack at the framework of a substituted η^5-cyclopentadienyl π-ligand.

Treatment of the allyl-functionalized *ansa*-zirconocene dichloride (**1**)[5] with two molar equivalents of phenyl lithium in ether gave the corresponding diphenyl zirconocene complex **2** (96% isolated). Subsequent treatment with $HB(C_6F_5)_2$[6] resulted in a selective hydroboration reaction of the pendent α-olefin moiety to give **3**. The bifunctional product shows three ^{13}C NMR signals of the connecting trimethylene unit (C6–C8: δ 32.3, 26.9, and 31.8) and a ^{11}B NMR resonance at δ 79.2, which is typical of tricoordinate boron of a $RB(C_6F_5)_2$ unit [corresponding ^{19}F NMR signals at δ −129.7 (*o*), −147.5 (*p*), and −160.9 (*m*)]. Complex **3** is not stable for a prolonged time at room temperature. During 3 days it reacted further with liberation of one equivalent of benzene to yield **5a** (89% isolated).[7]

Complex **5a** was characterized by X-ray diffraction. In the crystal it features a slightly strained Me_2Si-bridged *ansa*-zirconocene system with typical general structural parameters [averaged proximal Zr–C(Cp) distances (Zr–C9/C10/C13) 2.459 Å; (Zr–C1/C2/C5) 2.428 Å; distal Zr–C(Cp) distances (Zr–C11/C12) 2.550 Å, (Zr–C3/C4) 2.537 Å; angle C1–Si–C9 93.81(9)°]. The most noteworthy structural feature is the presence of a newly formed B–C(sp^2) bond between the boron atom and its adjacent Cp–ring (B–C3: 1.627(3) Å, angle C3–B–C8 106.7(2)°). The $B(C_6F_5)_2$ group has become part of a substituted borata-tetrahydroindenyl-type ligand (see Fig. 1). Only a single σ-C_6H_5 ligand has remained bonded to zirconium (Zr–C14: 2.203(2) Å) with the phenyl plane being conformationally oriented in the major σ-ligand plane of the bent metallocene framework. The other σ-coordination site at Zr has become occupied by an *ortho*-fluorine centre from the C_6F_5 substituent at boron (C14–Zr–F23: 113.0(1)°) that is axially oriented at the half-chair shaped newly formed six-ring heterocycle (θ C6–C7–C8–B: 66.9(2)°). The resulting (C)F–Zr bond length (Zr–F23: 2.250(1) Å) is one of the shortest encountered in such a situation.[8] The corresponding C–(μF) bond (C23–F23 1.410(2) Å) is markedly elongated relative to the three remaining C_6F_5 *ortho* C–F bonds (Δd > 0.05 Å). The C23–F23–Zr angle in complex **5a** amounts to 142.8(1)°.

The low temperature NMR spectra have revealed an analogous structure of **5a** in solution. The ^{13}C NMR spectrum shows three CH_2 resonances of the newly formed anellated heterocycle at δ 27.8, 22.8, and 24.3 (C6–C8). The low temperature ^{19}F NMR spectrum features a total of 10 different resonances: the equatorially oriented C_6F_5 ring, whose B–C(aryl) rotation is "frozen" at 203 K, shows resonances at δ −131.2/−132.1 (*o*), δ −160.0 (*p*) and δ −162.8/−164.6 (*m*). The other C_6F_5 ring is locked into a rigid orientation by the presence of the strong (C)F–Zr interaction. Consequently, we have observed a pair of typically differentiated ^{19}F NMR *o*-(C)F signals for this ring at δ −126.2 and δ −175.4 (μ-F)[2,8] in addition to signals at δ −156.8 (*p*) and δ −155.6/−164.2 (*m*). The low temperature ^{19}F NMR spectra have also revealed the presence of a minor conformational isomer (**5b**) at < *ca*. 280 K, that does not show the characteristic (C)F–Zr interaction. We assume that it is formed by equilibration between the two possible half-chair conformations of the Cp-anellated six-membered heterocyclic framework (see Scheme 2).

Complex **5** adds one equivalent of PMe_3 to form the adduct **6** as a single isomer (*ca*. 90% isolated).[9] The ^{11}B NMR spectrum of **6** features a typical tetracoordinated borate resonance at δ −13.0 and



Scheme 1 i) + PhLi, 0 °C, Et_2O, – LiCl, 96% yield; ii) + $HB(C_6F_5)_2$, toluene, r.t.; iii+iv) toluene, 3d, r.t., $-C_6H_6$, 89% yield; v) + PMe_3, toluene, r.t.

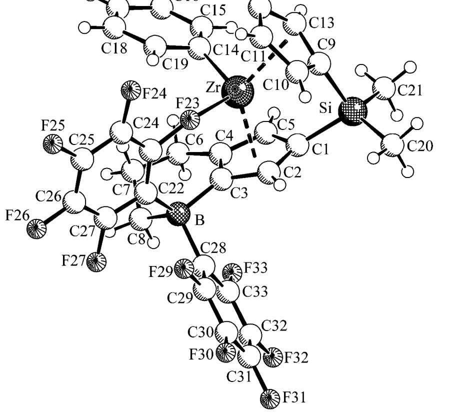


Fig. 1 Molecular structure of compound **5a**.

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† X-ray crystal structure analyses.

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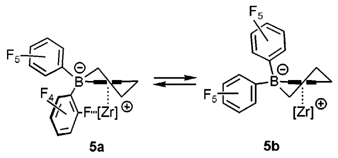

Scheme 2

a ^{31}P NMR signal of the [Zr]–PMe$_3$ unit at $\delta\,-9.4$. Below 213 K the rotation of both C$_6$F$_5$ rings at boron is slow on the NMR time scale [^{19}F NMR: $\delta\,-105.0/-110.0$ (*o*), -157.4 (*p*), $-162.6/-162.7$ (*m* of ring A), $\delta\,-120.7/129.8$ (*o*), -157.8 (*p*), $-162.8/-164.2$ (*m* of ring B).

We must assume that the strongly *Lewis* acidic –B(C$_6$F$_5$)$_2$ group in the bifunctional diphenylzirconocene complex **3** undergoes an intramolecular addition to its adjacent substituted Cp ring system[10] to form the reactive intermediate **4** (see Scheme 1). Addition of the –B(C$_6$F$_5$)$_2$ functional group from the outside consequently results in an orientation of the remaining *ipso*-(Cp)C–H vector towards the central [Zr]Ph$_2$ moiety, thus enabling one of the zirconium bound phenyl groups to act as an internal base. Deprotonation with formation of one equivalent of benzene then reforms the (substituted) η^5-cyclopentadienyl π-ligand system to yield the observed product **5**. Our study has shown that the addition of a strongly electrophilic borane to a Zr-coordinated cyclopentadienide can successfully compete with or even be favoured over the ubiquitous σ-ligand abstraction reaction. We will see whether electrophilic attack at such nucleophilic π-ligand systems may follow similar selectivity rules as they were previously established for the complementary addition of nucleophilic reagents to the π-ligands of strongly electrophilic transition metal complexes (the "Davies, Green, Mingos rules").[11]

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Notes and references

1 X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015–10031,Reviews: H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem.*, 1995, **107**, 1255–1283 (*Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143–1170); M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255–270; E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391–1434.

2 B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich and S. Kotila, *Angew. Chem.*, 1995, **107**, 1867–1869 (*Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1755–1757); G. Erker, *Chem. Commun.*, 2003, 1469–1476 (feature article).

3 G. J. Pindado, M. Thornton-Pett and M. Bochmann, *Chem. Commun.*, 1997, 609–610; G. J. Pindado, M. Thornton-Pett, M. Bouwkamp, A. Meetsma, B. Hessen and M. Bochmann, *Angew. Chem.*, 1997, **109**, 2457–2460 (*Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2358–2361); G. J. Pindado, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1997, 3115–3127; G. J. Pindado, M. Thornton-Pett, M. B. Hursthouse, S. J. Coles and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1999, 1663–1668.

4 J. Ruwwe, G. Erker and R. Fröhlich, *Angew. Chem.*, 1996, **108**, 108–110 (*Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 80–82); Y. Sun, W. E. Piers and S. J. Rettig, *Organometallics*, 1996, **15**, 4110–4112; P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, V. V. Burlakov and V. B. Shur, *Angew. Chem.*, 2003, **114**, 1455–1458 (*Angew. Chem., Int. Ed. Engl.*, 2003, **42**, 1414–1418) and references cited therein. G. Erker, G. Kehr and R. Fröhlich, *J. Organomet. Chem.*, 2004, in press.

5 J. Cano Sierra, D. Hüerländer, M. Hill, G. Kehr, G. Erker and R. Fröhlich, *Chem. Eur. J.*, 2003, **9**, 3618–3622; M. Hill, G. Kehr, R. Fröhlich and G. Erker, *Eur. J. Inorg. Chem.*, 2003, 3583–3589.

6 D. J. Parks, R. E. v. H. Spence and W. E. Piers, *Angew. Chem.*, 1995, **107**, 895–897 (*Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 809–811); R. E. v. H. Spence, D. J. Parks, W. E. Piers, M. A. MacDonald, M. J. Zaworotko and S. J. Rettig, *Angew. Chem.*, 1995, **107**, 1337–1340 (*Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1230–1234); W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, **26**, 345–354.

7 A mixture of **2** (125 mg, 265 μmol) and HB(C$_6$F$_5$)$_2$ (92 mg, 265 μmol) was dissolved in toluene and stirred for 3 days at room temperature. Removal of the solvent *in vacuo* gave 196 mg of **5** (89%) as a yellow solid. ^{1}H NMR (293 K, d$_8$-toluene, 600 MHz): δ 7.21, 7.20, 7.04 (m, 5H, *o*-, *m*-, *p*-Ph), 6.44 (m, 2H, 4′-H, 5-H), 6.35 (m, 1H, 5′-H), 5.95 (m, 1H, 3′-H), 5.80 (m, 1H, 2-H), 5.79 (m, 1H, 2′-H), 2.32/1.68 (m, each 1H, 6-H, 6-H′), 1.56/1.23 (m, each 1H, 8-H, 8-H′), 1.46/1.30 (m, each 1H, 7-H, 7-H′), 0.65/0.61 (s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (293K, d$_8$-toluene, 150 MHz): δ 189.3, 128.6, 128.3, 127.6 (*ipso*-, *o*-, *m*-, *p* -Ph), 151.9 (C3), 125.0 (C5′), 121.6 (C4′), 119.8 (C5), 118.8 (C2), 115.2 (C2′), 112.4 (C3′), 105.0 (C1), 99.9 (C1′), 27.8 (C6), 24.3 (C8), 22.8 (C7), $-5.5/-5.6$ (Si(CH$_3$)$_2$), (^{13}C$_6$F$_5$ signals not cleanly resolved). X-ray crystal structure analysis of complex **5a** (single crystals from toluene at −20 °C): Crystal data for C$_{33}$H$_{23}$BF$_{10}$SiZr * C$_7$H$_8$, M, = 831.77, triclinic, space group $P\bar{1}$ (No. 2), a = 9.766(1), b = 10.662(1), c = 18.675(1) Å, α = 104.46(1), β = 96.15(1), γ = 109.47(1)°, V = 1736.2(3) Å^3, D_c = 1.591 g cm^{-3}, μ = 4.36 cm^{-1}, Z, = 2, λ = 0.71073 Å, T, = 198 K, 16169 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 8376 independent (R_{int} = 0.037) and 7283 observed reflections [I, ≥ 2 σ(I)], 480 refined parameters, R, = 0.035, wR^2 = 0.086. CCDC 229733. See http://www.rsc.org/suppdata/cc/b4/b400228h/ for crystallographic data in .cif or other electronic format.

8 M. Dahlmann, G. Erker, R. Fröhlich and O. Meyer, *Organometallics*, 2000, **19**, 2956–2967; J. Karl, G. Erker and R. Fröhlich, *J. Am. Chem. Soc.*, 1997, **119**, 11165–11173; N. Kleigrewe, T. Brackemeyer, G. Kehr, R. Fröhlich and G. Erker, *Organometallics*, 2001, **20**, 1952–1955 and references cited therein.

9 A sample of **2** (162 mg, 344 μmol) was reacted with HB(C$_6$F$_5$)$_2$ (119 mg, 344 μmol) in toluene for 3 days at room temperature to generate **5**. A slight excess of PMe$_3$ was then added. Removal of all volatiles *in vacuo* gave 250 mg (89%) of **6** as a yellow solid, mp = 168 °C (decomp.). Anal. calcd. for C$_{36}$H$_{32}$BF$_{10}$PSiZr (815.7): 53.01% C, 3.95% H, found: 52.53% C, 3.69% H. ^{1}H NMR (293 K, d$_8$-toluene, 600 MHz): δ 7.15, 7.12, 7.00 (m, 5H, Ph), 6.71 (m, 1H, 4′-H), 6.09 (m, 1H, 5-H), 5.97 (m, 1H, 3′-H), 5.79 (m, 1H, 2-H), 5.74 (m, 1H, 5′-H), 5.53 (m, 1H, 2′-H), 2.30/1.96 (m, each 1H, 6-H, 6-H′), 1.66/0.96 (m, each 1H, 7-H, 7-H′), 1.31/0.85 (m, each 1H, 8-H, 8-H′), 0.35/0.31 (s, each 3H, Si(CH$_3$)$_2$, 0.22 (d, $^2J_{\text{PH}}$ = 10 Hz, 9H, PMe$_3$). ^{13}C{^{1}H} NMR (293 K, d$_8$-toluene, 150 MHz): δ 186.7, 131.4, 127.0, 126.0 (Ph), 149.0 ($^1J_{\text{CF}}$ = 238 Hz), 139.5 ($^1J_{\text{CF}}$ = 261 Hz), 137.7 ($^1J_{\text{CF}}$ = 263 Hz, *o*-, *p*-, *m*- of C$_6$F$_5$) 144.3 (C3), 120.2 (C4′), 125.0 (C3′), 119.4 (C2), 116.3 (C5), 115.4 (C2′), 109.6 (C5′), 99.7 (C1), 97.4 (C1′), 28.5 (C6), 24.3 (C7), 16.2 (C8), 8.9 (d, $^1J_{\text{CP}}$ = 30 Hz, PMe$_3$), $-4.9/-5.8$ (Si(CH$_3$)$_2$), (^{13}C$_6$F$_5$ resonances not cleanly resolved). ^{11}B{^{1}H} NMR (293K, d$_8$-toluene, 64 MHz): $\delta\,-13.0$ ($\nu_{1/2}$ = 224 Hz), ^{31}P{^{1}H} NMR (293 K, d$_8$-toluene, 81 MHz): $\delta\,-9.4$.

10 For related boryl-substituted Cp-systems see e.g.: S. J. Lancaster, A. J. Mountford, D. L. Hughes, M. Schormann and M. Bochmann, *J. Organomet. Chem.*, 2003, **680**, 193–205 and references cited therein.

11 S. G. Davies, M. L. H. Green and D. M. P. Mingos, *Tetrahedron Report, no 57, Tetrahedron*, 1978, **34**, 3047–3077.