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Reactions of Pendant Boryl Groups in Cp–Metal Complexes: Heterocyclic Ring Annelation in a CpIr System

Christoph Herrmann,[a] Gerald Kehr,[a] Roland Fröhlich,[a][‡] and Gerhard Erker*[a]

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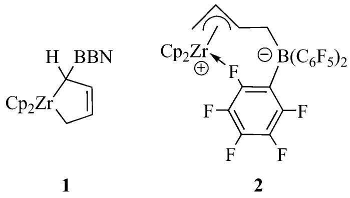
Treatment of (cod)IrCl dimer with Li(allyl)cyclopentadienide gave (C_5H_4–CH_2–CH=CH_2)Ir(cod) (**11**). At 100 °C, **11** isomerizes cleanly into its ring-conjugated (*trans*-CH_3–CH=CH–C_5H_4)Ir(cod) isomer (**13**). Subsequent addition of $HB(C_6F_5)_2$ results in the formation of a product (**16**) that contains an annelated five-membered borata heterocycle at the Cp ring. This is probably formed by means of a reaction sequence involving regioselective hydroboration, followed by an electrophilic substitution reaction at the Cp ring by the strongly Lewis acidic $–B(C_6F_5)_2$ group, in which the iridium metal base acts as the proton abstractor. Products **13** and **16** were characterized by X-ray diffraction.

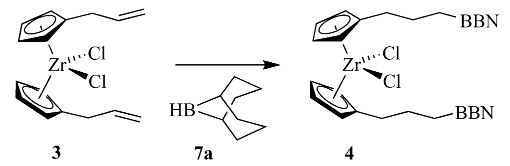
Introduction

Boron-containing functionalities can be attached directly to transition-metal centers.[1] They can also be bound to ligand systems that are coordinated to d metal centers. Some such systems have made interesting bifunctional d-metal/main-group systems. There are quite a number of examples described in literature where boron-containing functionalities were directly bonded to cyclopentadienide ring systems.[2] Other examples include borylated conjugated diene metal complexes such as **1**[3] (Scheme 1) or borane addition products to the butadiene ligand[4] in group 4 metal chemistry such as **2**.[5] The latter system has turned out to be of interest in single-component homogeneous Ziegler–Natta catalysis.[6]

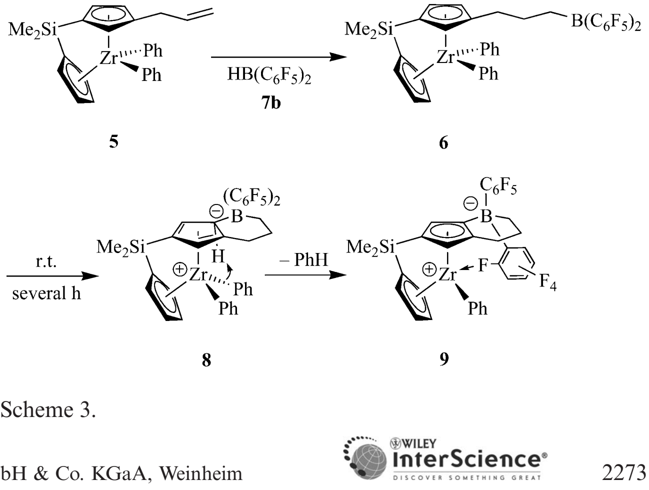


Scheme 1.

Hydroboration of pendant alkenyl groups on the Cp rings of group 4 metal systems has been a convenient route to, for example, bifunctional Zr/B systems. Formation of **4** by the addition of 9-BBN (**7a**) to **3** represents an early example[7] (Scheme 2). Similarly, bifunctional complex **6** was obtained from **5** by a related hydroboration route[8] by employing the strongly electrophilic hydroboration reagent $HB(C_6F_5)_2$ (**7b**).[9] However, in this case the resulting bifunctional Zr/B system was only stable for a limited period of time at ambient temperature. Keeping it in toluene solution for 16 h resulted in clean conversion into complex **9** with formation of one molar equivalent of benzene. We assume that this annelation reaction at the Cp ring of **6** was initiated by intramolecular electrophilic addition of the strongly electron-deficient $–B(C_6F_5)_2$ moiety to the electron-rich Cp system to give the reactive intermediate **8** (Scheme 3). The two-step electrophilic aromatic substitu-



Scheme 2.



Scheme 3.

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[a] Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, 48149 Münster, Germany
[‡] X-ray crystal structure analysis.
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tion reaction sequence was then completed by proton abstraction by the [Zr]Ph carbon base to eventually yield complex **9**.[8]

We have now prepared a remotely related group 9 metal complex, namely (Cp–CH=CH–CH$_3$)Ir(cod) (see below), and treated it with HB(C$_6$F$_5$)$_2$. This led to some observations that bear resemblance to the group 4 metal/borane chemistry that we had observed earlier.

Results and Discussion

We started this study by treating the (cyclooctadiene)iridium chloride dimer [(cod)IrCl]$_2$ (**10**) with (allyl-Cp)Li **11**.[10] This gave the expected (cod)Ir(Cp-allyl) product (**12**) in >80% yield as a colorless oil. It features typical NMR spectroscopic data of the η^5-C$_5$H$_4$–CH$_2$–CH=CH$_2$ ligand [Cp ^{1}H NMR signals at δ = 4.85, 4.76 ppm; allyl group ^{1}H NMR resonances at δ = 5.83 (HC=), 4.96 (=CH$_{2(Z)}$), 4.94 (=CH$_{2(E)}$), 2.77 (–CH$_2$–) ppm]. The stabilizing cod ligand ^{13}C NMR resonances show up at δ = 47.3 and 34.5 ppm.

Heating of complex **12** for 1.5 h at 100 °C resulted in complete conversion into the conjugated 1-propenyl-Cp isomer. Only *trans* isomer **13** was identified. It shows a single set of ^{1}H NMR resonances of the η^5-Cp–CH=CH–CH$_3$ ligand at δ = 5.79/5.50 (–CH=CH–, ^3J = 15.6 Hz), 5.09/4.80 (C$_5$H$_4$), 1.54 (CH$_3$, ^3J = 6.6 Hz) ppm. The corresponding ^{13}C NMR signals of the *trans*-CH=CH–CH$_3$ substituent on the Cp ring were observed at δ = 123.2/124.7 (–CH=CH–), 18.2 (CH$_3$) ppm [^{13}C NMR cod ligand signals at δ = 48.6 (–CH=CH–), 34.4 (–CH$_2$–CH$_2$–) ppm].

After several weeks, the yellow oil crystallized and complex **13** (Figure 1) was characterized by X-ray crystal structure analysis. Complex **13** contains two independent molecules (A) and (B) in the crystal, which represent equivalent structures. Data of molecule (B) are given in square brackets below. The iridium metal in complex **13** is coordinated to the pair of –CH=CH– double bonds of the cod ligand. The Ir–C11/C12/C15/C16 distances were found in a narrow range between 2.107(6) to 2.129(6) Å [2.112(6) to 2.127(6) Å]. The substituted cyclopentadienide ligand is rather uniformly η^5-coordinated to the central metal atom with Ir–C1 to C5 bond lengths being in a narrow range between 2.208(6) and 2.301(6) Å [2.197(6) and 2.296(6) Å]. The 1-propenyl substituent at the cyclopentadienyl C1 carbon atom is oriented coplanar with the adjacent Cp ring {dihedral angles [°]: C5–C1–C6–C7 163.0(7) [175.3(6)], C2–C1–C6–C7 –15.2(11) [–3.0(10)]}. The bond angles around C1 were found at 105.7(6)° [106.5(6)°] (C2–C1–C5), 125.2(6)° [127.4(6)°] (C5–C1–C6), and 129.2(6)° [126.1(6)°] (C2–C1–C6). The bond lengths [Å] at the substituent are in the typical range: C1–C6 1.446(10) [1.470(9)], C6–C7 1.333(11) [1.1340(10)], C7–C8 1.477(11) [1.483(9)], with bond angles [°] of C1–C6–C7 123.8(7) [125.3(7)] and C6–C7–C8 124.6(8) [124.3(7)]. The complex attains a conformation in the crystal that orients the Cp(C1)–substituent (C6) vector in the direction of C11 [θ C11–Ir–Cp(centroid)–C1 13.2° (31.9°)].

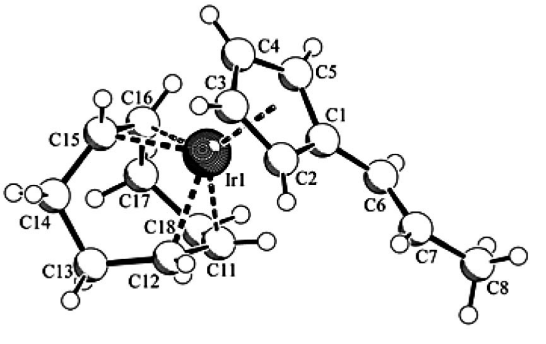
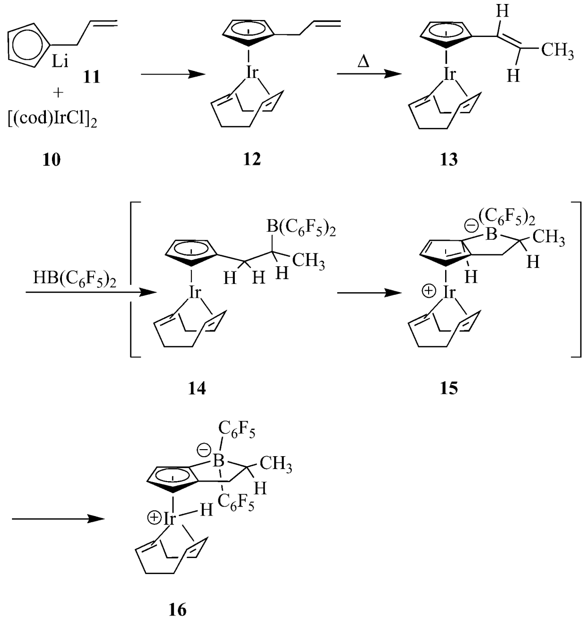


Figure 1. Molecular geometry of complex **13**.

Complex **13** was then treated with HB(C$_6$F$_5$)$_2$ in pentane at room temperature. Within 5 min, a white precipitate began to form. After 2 h, the reaction was complete and product **16** was isolated. Hydroboration of the pendant C=C bond of the 1-propenyl substituent had apparently occurred with the expected anti-Markovnikov orientation.[11] However, the simple hydroboration product **14** was not isolated or observed. It had apparently undergone a subsequent cyclization reaction to eventually yield **16** (Scheme 4). The presence of an iridium hydride is clearly proved by a broad singlet at δ = –12.23 ppm in the ^{1}H NMR spectrum. Only the NMR resonances of three remaining CH(Cp) units were detected [δ(^{1}H/^{13}C) = 5.60/92.7, 5.55/84.3, 5.45/76.3 ppm]. The ^{11}B chemical shift (δ = –13.0 ppm) is characteristic of tetracoordination at the boron center. The two diastereotopic C$_6$F$_5$ substituents give rise to two sets of three ^{19}F signals each. At –30 °C, the rotation of the C$_6$F$_5$ group around the B–C$_{ipso}$(C$_6$F$_5$) vectors is slow on the NMR timescale. Consequently, 10 ^{19}F signals were monitored, 5 of each C$_6$F$_5$ subunit [δ = –129.7 (*o*), –131.0 (*o*), –162.5 (*p*), –165.9 (*m*), –166.2 (*m*) (C$_6$F$_5$^{A}); –131.5 (*o*), –135.8 (*o*), –162.4 (*p*), –165.2 (*m*), –165.4 (*m*) (C$_6$F$_5$^{B}) ppm]. Upon in-



Scheme 4.

creasing the temperature to 25 °C, only one of the two C_6F_5 group showed complete coalescence. The rotational barrier around the B–C_{ipso}(C_6F_5) vector was estimated to $\Delta G^{\neq}$ = 11.9 ± 0.2 kcal mol^{-1} (for details see the Supporting Information). Compound **16** was characterized by C and H elemental analysis and by an X-ray crystal structure analysis (single crystals were obtained from an in situ generated sample in [D_2]dichloromethane).

Complex **16** features a typical Ir–cod arrangement, and the Ir–C11/C12/C15/C16 distances are in the narrow range of 2.191(3) to 2.205(3) Å. The iridium metal in complex **16** carries a hydride ligand [d(Ir–H) = 1.57(4) Å]. The Ir–H vector is oriented towards the C13–C14 sector of the molecule. The coordination sphere of Ir is completed by η^5-bonding to a *doubly substituted* Cp ring [Ir–C(Cp) bond lengths within 2.196(3) and 2.246(3) Å]. The cyclopentadienyl core carries a carbon substituent [C5–C6 1.501(5) Å] and *ortho* to it a boron substituent [C1–B1 1.633(4) Å]. Both are part of a newly formed annelated five-ring boron heterocycle [remaining bond lengths: C1–C5 1.433(4) Å, C6–C7 1.570(5) Å, C7–B1 1.659(4) Å] (see Figure 2 and Scheme 4).

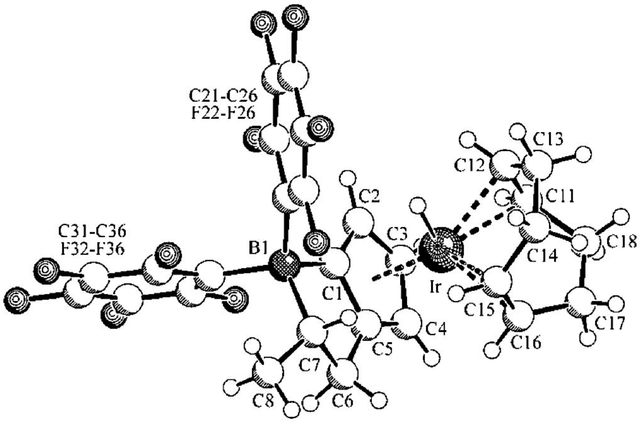
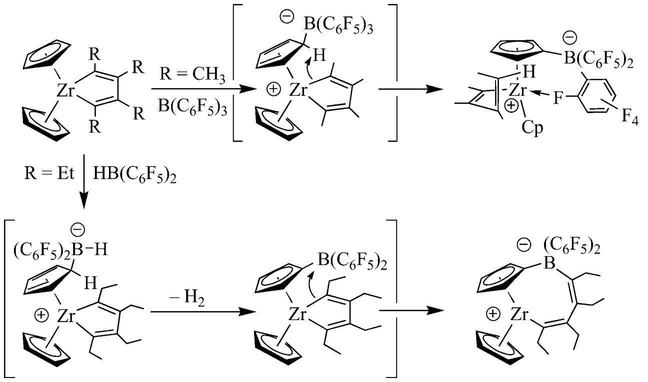


Figure 2. A view of the molecular structure of zwitterionic complex **16**.

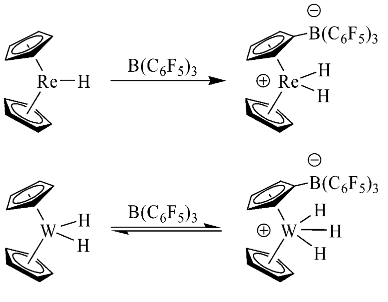
The saturated ring carbon atom C7 bears a methyl substituent [C7–C8 1.519(4) Å] that is oriented *away* (*anti*) from the metal center [dihedral angle Ir–Cp(centroid)–C7–C8 –162.1°]. The adjacent boron atom is tetracoordinate [B1–C21 1.643(4) Å, B1–C31 1.659(4) Å] and hence of a borate anion type. The five-membered heterocycle of the formally zwitterionic borate anion/ligIrH cation complex **16** is oriented *syn* to the Ir–H vector.

The structure of the obtained product **16** suggests that the primary hydroboration product **14** undergoes intramolecular electrophilic attack of the Lewis acidic boron center at an *ortho* position of the Cp ring to which it is attached by a short two-carbon chain. This would lead to intermediate **15**, which is presumably prone to rapid internal deprotonation by the iridium metal base[12] to restore the aromatic Cp ligand system with formation of **16**. Actually, this route could have led to two isomers of **16**, but only the one featuring the CH_3 substituent at carbon atom C7 of the five-membered ring in the *anti* position was so far identified as a product of this reaction sequence, possibly because of steric hindrance.

Actually, related electrophilic intramolecular substitution reactions of borane moieties bearing strongly electron-withdrawing C_6F_5 substituents had previously been observed, for example, in early transition-metal chemistry (Schemes 3 and 5)[8,13] or for systems derived from d elements from the middle section of the periodic table.[1,14] The group 6 and group 7 metal systems depicted in Scheme 6 are typical examples.



Scheme 5.



Scheme 6.

Conclusions

We conclude that a pendant $B(C_6F_5)_2$ group can readily undergo electrophilic aromatic substitution at the Cp ring of the CpIr(cod) system. In the case of the described example, this seems to be a convenient method of annelation of a boron-containing heterocycle to yield a corresponding zwitterionic iridium hydride complex.

Experimental Section

General Information: All syntheses were performed with the use of dried solvents in an inert gas atmosphere (argon) by using Schlenk-type glassware or a glove box. Solvents were dried and distilled prior to use. NMR spectra were recorded with Bruker AC 200 P (^{11}B: 64.2 MHz), Bruker AMX400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz), and a Varian UNITYplus 600 (^{1}H: 599.6 MHz, ^{13}C: 150.8 MHz, ^{19}F: 564.2 MHz). ^{11}B NMR spectra were referenced to an external $Et_2O{\cdot}BF_3$ (neat) sample, ^{19}F NMR spectra were referenced to external $CFCl_3$ (neat). NMR assignments were supported by additional 2D experiments. IR spectra were recorded with a Varian 3100 FTIR (Excalibur Series) spectrometer. Elemental analyses were obtained with a Foss-Heraeus CHNO-Rapid. Melting points were determined with a DSC 2010 (TA-Instruments) apparatus. The data was analyzed by using the baseline method. (Allyl)cyclopentadienyllithium,[15] bis(pentafluorophenyl)borane,[9] and chloro(1,5-cyclooctadiene)iridium dimer[16] were prepared according to literature procedures.

X-ray Crystal Structure Analyses: Data sets were collected with a Nonius KappaCCD diffractometer, a rotating anode generator was used. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[17] absorption correction Denzo,[18] structure solution SHELXS-97,[19] structure refinement SHELXL-97,[20] graphics SCHAKAL.[21] CCDC-663982 and -663983 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Complex 12: Chloro(1,5-cyclooctadiene)iridium dimer (980 mg, 1.46 mmol) in THF (10 mL) was added to a solution of (allyl)cyclopentadienyllithium (340 mg, 3.03 mmol) in THF (10 mL) at room temperature. The solution was heated at reflux for 1 h, and the volatiles were then removed in vacuo and the residue taken up in pentane (100 mL). Short-column chromatography over neutral alumina with pentane yielded **12** after removal of the solvent as a colorless oil (969 mg, 82%). ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ = 5.83 (ddt, $^3J_{H,H}$ = 16.8, 10.1, 6.8 Hz, 1 H, 7-H), 4.96 (dm, $^3J_{H,H}$ = 16.8 Hz, 1 H, 8-H), 4.94 (dm, $^3J_{H,H}$ = 10.1 Hz, 1 H, 8-H′), 4.85 (m, 2 H, 2,5-H), 4.76 (m, 2 H, 3,4-H), 3.74 (m, 4 H, 9-H), 2.77 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H, 6-H), 2.21 (m, 4 H, 10-H), 1.96 (m, 4 H, 10-H′) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 25 °C): δ = 137.4 (C-7), 115.6 (C-8), 100.3 (C-1), 82.3 (C-2,5), 80.7 (C-3,4), 47.3 (C-9), 34.5 (C-10), 31.9 (C-6) ppm. IR (KBr): $\tilde{\nu}$ = 3461 (br.), 3076 (w), 2967 (s), 2921 (s), 2872 (s), 2325 (s), 1637 (w), 1429 (w), 1318 (m), 1236 (w), 991 (m), 910 (s), 838 (s), 567 (w), 497 (m) cm^{-1}. $C_{16}H_{21}Ir$ (405.6): calcd. C 47.38, H 5.22; found C 47.84, H 5.29.

Complex 13: Chloro(1,5-cyclooctadiene)iridium dimer (972 mg, 1.45 mmol) and (allyl)cyclopentadienyllithium (324 mg, 2.90 mmol) were combined according to the procedure described above for **12**. The colorless oil was then heated under vacuum in a Schlenk tube at 100 °C for 1.5 h. A yellow oil formed, which crystallized after 5 weeks (1.05 g, 90%). M.p. 62 °C. ^1H NMR (599.6 MHz, C_6D_6, 298 K): δ = 5.79 (dqm, $^3J_{H,H}$ = 15.6 Hz, $^4J_{H,H}$ = 1.7 Hz, 1 H, 6-H), 5.50 (dq, $^3J_{H,H}$ = 15.6 Hz, $^3J_{H,H}$ = 6.6 Hz, 1 H, 7-H), 5.09 (m, 2 H, 2,5-H), 4.80 (m, 2 H, 3,4-H), 3.74 (m, 4 H, 9-H), 2.22 (m, 4 H, 10-H), 1.97 (m, 4 H, 10-H′), 1.54 (dd, $^3J_{H,H}$ = 6.6 Hz, $^4J_{H,H}$ = 1.7 Hz, 3 H, 8-H) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, C_6D_6, 298 K): δ = 124.7 (C-7), 123.2 (C-6), 100.3 (C-1), 80.8 (C-3,4), 80.1 (C-2,5), 48.6 (C-9), 34.4 (C-10), 18.2 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3086 (w), 2965 (s), 2922 (s), 2871 (s), 2825 (s), 2360 (m), 1471 (m), 1438 (m), 1317 (m), 1261 (w), 1234 (w), 1084 (m), 1020 (m), 958 (s), 911 (s), 804 (vs) cm^{-1}. $C_{16}H_{21}Ir$ (405.6): calcd. C 47.38, H 5.22; found C 47.12, H 5.34.

X-ray Crystal Structure Analysis for 13: Formula $C_{16}H_{21}Ir$, M = 405.53, colorless crystal 0.40 × 0.25 × 0.15 mm, a = 8.384(1) Å, b = 12.611(1) Å, c = 13.447(1) Å, α = 96.69(1)°, β = 99.93(1)°, γ = 107.12(1)°, V = 1317.1(2) $Å^3$, $\rho_{calcd.}$ = 2.045 $g\,cm^{-3}$, μ = 10.112 mm^{-1}, empirical absorption correction ($0.107 \leq T \leq 0.312$), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 13582 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.67 $Å^{-1}$, 6198 independent (R_{int} = 0.045) and 5538 observed reflections [$I \geq 2\sigma(I)$], 309 refined parameters, R = 0.034, wR^2 = 0.096, max. residual electron density 2.35 (–2.51) $e\,Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Complex 16: Complex **13** (81.1 mg, 0.19 mmol) was dissolved in pentane (10 mL). At room temperature a solution of bis(pentafluorophenyl)borane (69.2 mg, 0.19 mmol) in pentane (10 mL) was added. The solution turned to a glowing orange color instantly. After 5 min, a white precipitate formed. After stirring for 2 h, the solution was completely decolorized and a white precipitate had formed. After removing the solvent, the remaining powder was washed with pentane (10 mL) and dried in vacuo. A white powder was isolated (117.2 mg, 0.16 mmol, 78.0%). Crystals suitable for X-ray diffraction could be obtained by generating **16** in [D_2]dichloromethane instead of pentane. M.p. 138.7 °C. ^1H NMR (599.6 MHz, CD_2Cl_2, 253 K): δ = 5.60 (m, 1 H, 3-H), 5.55 (br., 1 H, 4-H), 5.45 (m, 1 H, 2-H), 4.50, 4.45, 3.95, 3.80 (each m, each 1 H, $=CH^{COD}$), 2.24/2.12, 2.24 (×2), 2.22/2.01, 2.21/2.04 (m, Σ 8 H, $-CH_2^{COD}$), 2.23, 2.02 (each m, each 1 H, 6-H), 1.61 (br., 1 H, 7-H), 0.86 (br. d, $^3J_{HH}$ = 6.6 Hz, 3 H, 8-H), –12.23 (s, 1 H, Ir-H) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 253 K): δ = 126.8 (C-1), 92.7 (C-3), 84.3 (C-4), 76.3 (C-2), 69.3, 67.4, 66.7, 66.0 ($=CH^{COD}$), 33.6 (C-6), 33.0, 32.3, 31.8, 31.2 ($4\times$ $-CH_2^{COD}$), 17.0 (C-8), n.o. (C-7), n.o. (C-5) ppm. [22] ^{19}F NMR (564.2 MHz, CD_2Cl_2, 243 K): δ = –129.7, –131.0 (each br., each 1 F, o-$C_6F_5^A$), –131.5, –135.8 (each m, each 1 F, o-$C_6F_5^B$), –162.4 (t, $^3J_{FF}$ = 20.6 Hz, 1 F, p-$C_6F_5^B$), –162.5 (t, $^3J_{FF}$ = 21.5 Hz, 1 F, p-$C_6F_5^A$), –165.2, –165.4 (each m, each 1 F, m-$C_6F_5^B$), –165.9, –166.2 (each br., each 1 F, m-$C_6F_5^A$) ppm. $^{11}B\{^1H\}$ NMR (64.2 MHz, CD_2Cl_2, 300 K): δ = –13.0 ($\nu_{1/2}$ = 40 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3039 (w), 2961 (m), 2921 (s), 2901 (sh), 2858 (m), 2829 (w), 2371 (w), 2345 (w), 2157 (m), 1643 (s), 1512 (vs), 1463 (vs), 1269 (s), 1088 (s), 965 (s), 771 (s), 748 (m), 701 (m), 681 (m), 641 (m), 603 (w) cm^{-1}. $C_{28}H_{22}BF_{10}Ir$ (751.5): calcd. C 44.75, H 2.95; found C 44.88, H 2.89.

X-ray Crystal Structure Analysis of 16: Formula $C_{28}H_{22}BF_{10}Ir$, M = 751.47, colorless crystal 0.25 × 0.15 × 0.10 mm, a = 10.3710(1) Å, b = 13.9206(2) Å, c = 17.6004(2) Å, β = 102.083(1)°, V = 2484.68(5) $Å^3$, $\rho_{calcd.}$ = 2.009 $g\,cm^{-3}$, μ = 5.467 mm^{-1}, empirical absorption correction ($0.342 \leq T \leq 0.611$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 19865 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.67 $Å^{-1}$, 6081 independent (R_{int} = 0.034) and 5387 observed reflections [$I \geq 2\sigma(I)$], 366 refined parameters, R = 0.023, wR^2 = 0.057, max. residual electron density 1.08 (–0.99) $e\,Å^{-3}$, hydrogen atom at the iridium atom from difference Fourier calculation, others calculated and refined as riding atoms.

Supporting Information (see footnote on the first page of this article): Additional experimental and NMR spectroscopic data for complexes **12**, **13**, and **16**. DNMR spectroscopic details for complex **16**.

Acknowledgments

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[1] Early review: H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882–1898; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1786–1801; for more recent examples, see, for example: A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams, *Angew. Chem.* **1999**, *111*, 2920–2923; *Angew. Chem. Int. Ed.* **1999**, *38*, 2759–2761; G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright,

Angew. Chem. **2000**, *112*, 978–980; *Angew. Chem. Int. Ed.* **2000**, *39*, 948–950; A. A. Dickinson, D. J. Willock, R. J. Calder, S. Aldridge, *Organometallics* **2002**, *21*, 1146–1157; D. L. Coombs, S. Aldridge, C. Jones, D. J. Willock, *J. Am. Chem. Soc.* **2003**, *125*, 6356–6357; H. Braunschweig, K. Radacki, F. Seeler, G. R. Whittell, *Organometallics* **2004**, *23*, 4178–4180; H. Braunschweig, K. Radacki, D. Scheschkewitz, G. R. Whittell, *Angew. Chem.* **2005**, *117*, 1685–1688; *Angew. Chem. Int. Ed.* **2005**, *44*, 1658–1661; S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu, D. Bourissou, *Angew. Chem.* **2006**, *118*, 1641–1644; *Angew. Chem. Int. Ed.* **2006**, *45*, 1611–1614; S. Aldridge, C. Jones, T. Gans-Eichler, A. Stasch, D. L. Kays, N. D. Coombs, D. J. Willock, *Angew. Chem.* **2006**, *118*, 6264–6268; *Angew. Chem. Int. Ed.* **2006**, *45*, 6118–6122 and references cited in these articles.

[2] See, for example: M. B. Hossain, D. van der Helm, *Inorg. Chem.* **1978**, *17*, 2893–2900; M. T. Reetz, H. Brummer, M. Kessler, J. Kuhnigk, *Chimia* **1995**, *49*, 501–503; M. Bochmann, S. J. Lancaster, O. B. Robinson, *J. Chem. Soc., Chem. Commun.* **1995**, 2081–2082; S. A. Larkin, J. T. Golden, P. J. Shapiro, G. P. A. Yap, D. M. J. Foo, A. L. Rheingold, *Organometallics* **1996**, *15*, 2393–2398; K. A. Rufanov, V. V. Kotov, N. B. Kazennova, D. A. Lemenovskii, E. V. Avtomonov, J. Lorberth, *J. Organomet. Chem.* **1996**, *525*, 287–289; E. Barday, B. Frange, B. Hanquet, G. E. Herberich, *J. Organomet. Chem.* **1999**, *572*, 225–232; A. Appel, F. Jäkle, T. Priermeier, R. Schmid, M. Wagner, *Organometallics* **1996**, *15*, 1188–1194; A. J. Ashe III, X. Fang, J. W. Kampf, *Organometallics* **1999**, *18*, 2288–2290; Y. Sun, R. E. v. H. Spence, W. E. Piers, M. Parvez, G. P. A. Yap, *J. Am. Chem. Soc.* **1997**, *119*, 5132–5143; S. J. Lancaster, S. Al-Benna, M. Thornton-Pett, M. Bochmann, *Organometallics* **2000**, *19*, 1599–1608; N. Kleigrewe, T. Brackemeyer, G. Kehr, R. Fröhlich, G. Erker, *Organometallics* **2001**, *20*, 1952–1955.

[3] G. Erker, R. Noe, D. Wingbermühle, J. L. Petersen, *Angew. Chem.* **1993**, *105*, 1216–1218; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1213–1215; R. Noe, D. Wingbermühle, G. Erker, C. Krüger, J. Bruckmann, *Organometallics* **1993**, *12*, 4993–4999.

[4] Reviews: G. Erker, G. Kehr, R. Fröhlich, *J. Organomet. Chem.* **2004**, *689*, 4305–4318; G. Erker, G. Kehr, R. Fröhlich, *Adv. Organomet. Chem.* **2004**, *51*, 109–162.

[5] B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, *Angew. Chem.* **1995**, *107*, 1867–1869; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1755–1757; D. D. Devore, F. J. Timmers, D. L. Hasha, R. K. Rosen, T. J. Marks, P. A. Deck, C. L. Stern, *Organometallics* **1995**, *14*, 3132–3134; Y. Sun, W. E. Piers, S. J. Rettig, *Organometallics* **1996**, *15*, 4110–4112; Y. Sun, W. E. Piers, S. J. Rettig, *Chem. Commun.* **1998**, 127–128; W. E. Piers, *Chem. Eur. J.* **1998**, *4*, 13–18; L. W. M. Lee, W. E. Piers, M. Parvez, S. J. Rettig, V. G. Young Jr., *Organometallics* **1999**, *18*, 3904–3912; A. H. Cowley, G. S. Hair, B. G. McBurnett, R. A. Jones, *Chem. Commun.* **1999**, 437–438; Y. H. Kim, T. H. Kim, B. Y. Lee, D. Woodmansee, X. Bu, G. C. Bazan, *Organometallics* **2002**, *21*, 3082–3084; G. J. Pindado, M. Thornton-Pett, M. Bouwkamp, A. Meetsma, B. Hessen, M. Bochmann, *Angew. Chem.* **1997**, *109*, 2457–2460; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2358–2361; G. J. Pindado, M. Thornton-Pett, M. Bochmann, *J. Chem. Soc., Dalton Trans.* **1997**, 3115–3127; M. Schreuder Goedheijt, T. Nijbacker, A. D. Horton, F. J. J. de Kanter, O. S. Akkerman, F. Bickelhaupt, *Eur. J. Inorg. Chem.* **2003**, 638–643; D. A. Kissounko, J. C. Fettinger, L. R. Sita, *J. Organomet. Chem.* **2003**, *683*, 29–38; R. Choukroun, C. Lorber, C. Lepetit, B. Donnadieu, *Organometallics* **2003**, *22*, 1995–1997.

[6] G. Erker, *Acc. Chem. Res.* **2001**, *34*, 309–317; G. Erker, G. Kehr, R. Fröhlich, *J. Organomet. Chem.* **2005**, *690*, 6254–6262.

[7] G. Erker, R. Aul, *Chem. Ber.* **1991**, *124*, 1301–1310; R. E. v. H. Spence, W. E. Piers, *Organometallics* **1995**, *14*, 4617–4624; W. E. Piers, Y. Sun, L. W. M. T. Lee, *Top. Catal.* **1999**, *7*, 133–143; D. Kunz, G. Erker, R. Fröhlich, G. Kehr, *Eur. J. Inorg. Chem.* **2000**, 409–416; A. Kestel-Jakob, H. G. Alt, *Z. Naturforsch., B* **2007**, *62*, 314–322.

[8] M. Hill, G. Kehr, G. Erker, O. Kataeva, R. Fröhlich, *Chem. Commun.* **2004**, 1020–1021; M. Hill, G. Erker, G. Kehr, R. Fröhlich, O. Kataeva, *J. Am. Chem. Soc.* **2004**, *126*, 11046–11057; M. Hill, G. Kehr, R. Fröhlich, G. Erker, *Eur. J. Inorg. Chem.* **2003**, 3583–3589.

[9] D. J. Parks, R. E. v. H. Spence, W. 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, S. J. Rettig, *Angew. Chem.* **1995**, *107*, 1337–1340; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1230–1233; W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345–354; R. E. v. H. Spence, W. E. Piers, Y. Sun, M. Parvez, L. R. MacGillivray, M. J. Zaworotko, *Organometallics* **1998**, *17*, 2459–2469; D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492–5503.

[10] For a related reaction, see: E. J. Miller, M. J. Naughton, C. A. Weigelt, J. E. Bradt, J. A. Serth, C. L. Ofslager, W. J. O'Brian, *Macromol. Chem. Macromol. Symp.* **1992**, *59*, 135–153.

[11] See, however: L. Chen, G. Kehr, R. Fröhlich, G. Erker, *Eur. J. Inorg. Chem.* **2008**, 73–83.

[12] H. Werner, *Pure Appl. Chem.* **1982**, *54*, 177–188; H. Werner, *Angew. Chem.* **1983**, *95*, 932–954; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 927–949; H. Werner, F. Lippert, K. Peters, H. G. von Schnering, *Chem. Ber.* **1992**, *125*, 347–352 and references cited therein.

[13] J. Ruwwe, G. Erker, R. Fröhlich, *Angew. Chem.* **1996**, *108*, 108–110; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 80–82; W. H. Sun, G. Erker, G. Kehr, *unpublished*.

[14] H. Braunschweig, T. Wagner, *Chem. Ber.* **1994**, *127*, 1613–1614; for a related reaction, see, for example: L. H. Doerrer, A. J. Graham, D. Haussinger, M. L. H. Green, *J. Chem. Soc., Dalton Trans.* **2000**, 813–820; V. V. Burlakov, S. I. Troyanov, A. V. Letov, L. I. Strunkina, M. K. Minacheva, G. G. Furin, U. Rosenthal, V. B. Shur, *J. Organomet. Chem.* **2000**, *598*, 243–247; V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, A. V. Letov, K. A. Lyssenko, A. A. Korlyukov, L. I. Strunkina, M. K. Minacheva, V. B. Shur, *Organometallics* **2001**, *20*, 4072–4079; P.-J. Sinnema, P. J. Shapiro, D. M. J. Foo, B. Twamley, *J. Am. Chem. Soc.* **2002**, *124*, 10996–10997; R. Choukroun, C. Lorber, B. Donnadieu, *Organometallics* **2004**, *23*, 1434–1437.

[15] M. F. Lappert, C. J. Pickett, P. I. Riley, P. I. W. Yarrow, *J. Chem. Soc., Dalton Trans.* **1981**, 805–813; R. Riemschneider, *Z. Naturforsch., B* **1963**, *18*, 641; B. H. Chang, R. H. Grubbs, C. H. Brubaker Jr., *J. Organomet. Chem.* **1985**, *280*, 365–376.

[16] J. L. Herde, J. C. Lambert, C. V. Senoff, M. A. Cushing, *Inorg. Synth.* **1974**, *15*, 18–20.

[17] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.

[18] Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr., Sect. A* **2003**, *59*, 228–234.

[19] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[20] G. M. Sheldrick, University of Göttingen, **1997**.

[21] E. Keller, University of Freiburg, **1997**.

[22] ^{13}C and ^{1}H NMR chemical shifts were determined by ^{1}H,^{1}H COSY, ^{1}H,^{13}C GHSQC and ^{1}H,^{13}C GHMBC experiments.

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