Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Carbene-induced synthesis of the first borironium cations using the $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]^-$ anion as unlikely leaving group

Holger Braunschweig, Rian D. Dewhurst, Katharina Ferkinghoff

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg

General Procedures. All manipulations were performed under an inert atmosphere of argon by using standard Schlenk and glovebox techniques. Solvents were distilled over alkali metal, degassed and stored over molecular sieves (4Å) under argon. Deuterated solvents were degassed by three freeze-pump-thaw cycles and stored under argon over molecular sieves. NMR experiments were performed on Bruker Avance 500 (^{1}H: 500.1 MHz; ^{11}B{^{1}H}: 160.5 MHz; ^{13}C{^{1}H}: 125.8 MHz) or Bruker Avance 400 (^{1}H: 400.1 MHz; ^{11}B{^{1}H}: 128.4 MHz; ^{13}C{^{1}H}: 100.6 MHz) spectrometers. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were calibrated to TMS. Elemental analysis were performed at an Elementar Vario Micro Tube elemental analyzer and Leco Instruments CHNS 932 elemental analyzer. Precursor materials **1**,[1] IMe,[2] and IMeMe[3] were prepared by published procedures.

Synthesis of [(IMe)$_2$BC$_2$(SiMe$_3$)$_2$][(η^5-C$_5$Me$_5$)Fe(CO)$_2$] (2a). To a solution of [(η^5-C$_5$Me$_5$)Fe(CO)$_2${BC$_2$(SiMe$_3$)$_2$}] (20.0 mg, 0.047 mmol) in toluene (0.5 mL), *N,N´*-dimethylimidazol-2-ylidene (9.0 mg, 0.094 mmol) was added at room temperature. An orange precipitate and a clear solution immediately formed. After filtration of the solution, the orange residue was washed with pentane and dried in vacuo to yield [(IMe)$_2$BC$_2$(SiMe$_3$)$_2$][(η^5-C$_5$Me$_5$)Fe(CO)$_2$] as an orange solid. Crystals suitable for X-ray diffraction were grown by slow evaporation of a THF solution stored at –35 °C for one day.

Yield: 20.4 mg (0.033 mmol, 70%).

^{1}H NMR (400.13 MHz, C$_6$D$_6$): δ = 7.45 (s, 4H, (C(NMe)$_2$C$_2$*H$_2$*), 3.54 (s, 12H, (NC*H$_3$*)$_4$) 1.85 (s, 15H, C$_5$*Me$_5$*), 0.14 (s, 18H, Si*Me$_3$*) ppm.

^{11}B{^{1}H} NMR (128.38 MHz, C$_6$D$_6$): δ = –32.6 (s) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$): δ = 231.9 (CO), 163.3 (Cq), 160.7 (s, C), 122.8 (CH), 87.4 (s, Fe*C$_5$*Me$_5$), 36.1 (s, N*Me$_2$*), 12.9 (s, FeC$_5$*Me$_5$*), 0.37 (Si*Me$_3$*) ppm.

Elemental analysis [%]: calcd. for C$_{30}$H$_{49}$BFeN$_4$O$_2$Si$_2$: C 58.06, H 7.95, N 9.02; found: C 58.02, H 7.82, N 9.02.

Synthesis of [(IMeMe)$_2$BC$_2$(SiMe$_3$)$_2$][(η^5-C$_5$Me$_5$)Fe(CO)$_2$] (2b). To a solution of [(η^5-C$_5$Me$_5$)Fe(CO)$_2${BC$_2$(SiMe$_3$)$_2$}] (30.0 mg, 0.070 mmol) in toluene (0.5 mL), *N,N´*-dimethyl(3,4-dimethyl)imidazol-2-ylidene (17.4 mg, 0.140 mmol) was added at room temperature. Thereby the color changed from light orange to dark red. The solvent and volatile compounds of the reaction were removed in vacuo and the red residue was washed with pentane. After the crude red product was extracted with THF, the solution was stored at –35 °C for a few days to isolate **2b** as red crystals. Crystals suitable for X-ray diffraction were grown by slow evaporation of a THF solution stored at –35 °C for one day.

Yield: 23.7 mg (0.035 mmol, 50%).

^{1}H NMR (400.13 MHz, C$_6$D$_6$): δ = 3.41 (s, 12H, (N*Me*)$_4$), 2.16 (s, 12H, (C*Me*)$_4$) 1.84 (s, 15H, C$_5$*Me$_5$*), 0.11 (s, 18H, Si*Me$_3$*) ppm.

^{11}B{^{1}H} NMR (128.38 MHz, C$_6$D$_6$): δ = –33.3 (s) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$): δ = 232.1 (CO), 162.7 (Cq), 125.6 (C), 122.8 (CH), 87.3 (s, Fe*C$_5$*Me$_5$), 32.9 (s, N*Me$_2$*), 13.0 (s, FeC$_5$*Me$_5$*), 8.70 (s, C*C*H$_3$) 0.57 (Si*Me$_3$*) ppm.

Elemental analysis [%]: calcd. for C$_{34}$H$_{57}$BFeN$_4$O$_2$Si$_2$: C 60.35, H 8.49, N 8.28; found: C 59.90, H 8.16, N 8.03.

Crystal structure determination

The crystal data of **2a** and **2b** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $\mathrm{Mo}_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the Shelx software package[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystal data for **2a**: $C_{30}H_{49}BFeN_4O_2Si_2$, $M_r = 620.57$, orange needle, 0.40×0.20×0.10 mm^3, monoclinic space group $P2_1/n$, $a = 16.807(7)$ Å, $b = 12.849(6)$ Å, $c = 17.795(8)$ Å, $\beta = 114.070(6)°$, $V = 3509(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.175$ g·cm^{-3}, $\mu = 0.528$ mm^{-1}, $F(000) = 1328$, $T = 100(2)$ K, $R_1 = 0.0476$, $wR^2 = 0.0873$, 7177 independent reflections [$2\theta \leq 52.74°$] and 376 parameters.

Crystal data for **2b**: $C_{34}H_{57}BFeN_4O_2Si_2$, $M_r = 676.68$, orange block, 0.60×0.40×0.20 mm^3, monoclinic space group $P2_1/c$, $a = 10.5605(6)$ Å, $b = 17.2867(10)$ Å, $c = 20.8645(12)$ Å, $\beta = 99.455(2)°$, $V = 3757.2(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.196$ g·cm^{-3}, $\mu = 0.499$ mm^{-1}, $F(000) = 1456$, $T = 100(2)$ K, $R_1 = 0.0323$, $wR^2 = 0.0782$, 8022 independent reflections [$2\theta \leq 53.56°$] and 416 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-1422335 (**2a**) and -1422336 (**2b**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

References

1. H. Braunschweig, I. Fernández, G. Frenking, K. Radacki and F. Seeler, *Angew. Chem. Int. Ed.*, 2007, **46**, 5215.
2. T. Schaub, M. Backes and U. Radius, *Organometallics*, 2006, **25**, 4196.
3. N. Kuhn and T. Kratz, *Synthesis*, 1993, **1993**, 561.
4. G. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.