Electronic Supplementary Information

Borido Complexes *via* Intermetallic Metalloborylene Transfer**

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1) Experimental details on the crystal structure determinations of compound 2 and 4:

The crystal data for **2** and **4** were collected on a Bruker X8Apex diffractometer with a CCD area detector and a multi-layer mirror with monochromated $\mathrm{Mo_{K\alpha}}$ radiation. The structures were solved using direct methods, refined with Shelx software package (G. Sheldrick, *Acta Cryst.*, *A*, **2008**, *64*, 112–122), and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically.

‡Crystal data for **2**: $C_{23}H_{30}BFeIrO_3$, $M_r = 613.33$, yellow plate, $0.30\times0.34\times0.36$ mm^3, Triclinic space group $P{-}1$, $a = 8.398(3)$ Å, $b = 9.349(4)$ Å, $c = 15.567(5)$ Å, $\alpha = 80.62(2)°$, $\beta = 89.08(2)°$, $\gamma = 72.57(2)°$, $V = 1149.8(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.772$ g·cm^{-3}, $\mu = 6.432$ mm^{-1}, $F(000) = 600$, $T = 100(2)$ K, $R_1 = 0.0210$, $wR_2 = 0.0755$, 7009 independent reflections [$2\theta \leq 61.2°$] and 272 parameters

Crystal data for **4**: $C_{36}H_{45}BFe_2O_6Rh_2$, $M_r = 902.05$, brown plate, $0.29\times0.14\times0.03$ mm^3, Triclinic space group $P{-}1$, $a = 8.8386(7)$ Å, $b = 11.5497(9)$ Å, $c = 18.0410(14)$ Å, $\alpha = 88.332(4)°$, $\beta = 79.256(3)°$, $\gamma = 83.798(3)°$, $V = 1798.7(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.665$ g·cm^{-3}, $\mu = 1.735$ mm^{-1}, $F(000) = 912$, $T = 100(2)$ K, $R_1 = 0.0357$, $wR_2 = 0.0457$, 10273 independent reflections [$2\theta \leq 61.02°$] and 439 parameters.

2) Experimental section

General Remarks: All manipulations were performed either under dry argon or in vacuo using standard Schlenk line and glovebox techniques. Solvents were purified by distillation under dry argon from sodium and stored under the same inert gas over molecular sieves. NMR spectra were acquired on Varian Unity 500 (^{1}H: 499.834; ^{11}B: 160.364; ^{13}C: 125.697 MHz) or Bruker Avance 500 (^{1}H: 500.133; ^{11}B: 160.472; ^{13}C: 125.777 MHz) NMR spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS via the residual protio solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B{^{1}H} spectra were referenced to external $BF_3{\cdot}OEt_2$ and TMS, respectively. Microanalyses were performed on a Leco CHNS-932 Elemental Analyzer. The borylene complex [{(η^5–C_5Me_5)Fe(CO)$_2$}(μ-B){Cr(CO)$_5$}] (**1**) was synthesized as reported in the literature.[1]

Synthesis of [{(η^5-C_5Me_5)Fe(CO)$_2$}(μ-B){(η^5-C_5Me_5)Ir(CO)}] (2): A solution of [{(η^5–C_5Me_5)Fe(CO)$_2$)}(μ^2-B){Cr(CO)$_5$}] (1) (37.0 mg, 0.082 mmol) in C_6D_6 (4 mL) was added to solid [(η^5–C_5Me_5)Ir(CO)$_2$] (26.8 g, 0.070 mmol) and heated for 80° C for 2 days. The solvent was removed in vacuo; then the residue was extracted with hexane (4 mL). The insoluble components were removed by filtration and the resulting filtrate was stored at –30 C to yield the product **2** as yellow crystals (21 mg, 49%).

IR (hexane): ν = 2012(s, CO), 1962 (s, CO), 1935 (m, CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 296.2 K): δ = 2.19 (s, 15H, IrC$_5$*Me*$_5$), 1.54 (s, 15H, FeC$_5$*Me*$_5$); ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 296.2 K): δ = 139.6 (br s); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 296.2 K): δ = 211.5 (CO), 97.2 (s, Fe*C*$_5$Me$_5$), 96.2 (s, Ir*C*$_5$Me$_5$), 11.4 (s, IrC$_5$*Me*$_5$), 9.8 (s, FeC$_5$*Me*$_5$); C, H analysis (%) calcd. for $C_{23}H_{30}O_3FeBIr$: C 52.58; H 4.65; found: C 53.14; H 4.87.

Synthesis of [{(η^5–C_5Me_5)Fe(CO))}(μ–CO)$_4$(μ^3–B)Rh{(η^5–C_5Me_5)Fe(CO)} {(η^5–C_5Me_5)Rh(CO)}] (4)

Solid [(η^5–C_5Me_5)Rh(CO)$_2$] (10 mg, 34 mmol) was added to a solution of [{(η^5–C_5Me_5)Fe(CO)$_2$}(μ^2–B){Cr(CO)$_5$}] (**1**) (16 mg, 36 mmol) in C_6D_6 (4 mL) and heated for 80 °C for 4 days. After removing the solvent in vacuo, the residue was extracted with hexane (5 mL). The insoluble components were removed by filtration and the resulting filtrate was stored at –30 C to yield the product **4** as dark yellow crystals (8 mg, 53%).

IR (hexane): $\nu = 1984, 1952, 1824, 1796, 1776$ cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 296.2 K): $\delta = 1.99$ (s, 15H, RhC_5*Me*$_5$), 1.62 (s, 15H, FeC_5*Me*$_5$), 1.49 (s, 15H, FeC_5*Me*$_5$) ppm. ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 296.2 K): $\delta = 186.4$ (br s); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 296.2 K): $\delta = 210.0$ (CO), 203.3 (CO), 181.2 (CO), 99.5 (RhC_5*Me*$_5$), 96.5 (FeC_5*Me*$_5$), 11.0 (Rh*C*$_5$Me$_5$), 9.61 (Fe*C*$_5$Me$_5$) ppm. C, H analysis (%) calcd. for $C_{36}H_{45}BFe_2Rh_2O_5$: C 48.10, H 5.20; found: C 48.61, H 5.45.

[1] H. Braunschweig, K. Radacki, D. Scheschkewitz, und G. R. Whittell, *Angew. Chem. Int. Ed.* **2005**, *44*, 1658–1660.