

Electronic Supplementary Information

High Yield Synthesis of a Neutral and Carbonyl-rich Terminal Arylborylene Complex

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1) Crystal structure determinations of **3**, **5** and **7**

The crystal data of **3**, **5** and **7** were collected on a Bruker X8APEX diffractometer with a CCD area detector and multi-layer mirror monochromated Mo_Kα radiation. The structure was solved using direct methods, refined with the Shelx software package (G. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112–122) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-855614 (**3**), CCDC- 855615 (**5**) and CCDC- 855616 (**7**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **3**

Data	3
Empirical formula	C ₁₆ H ₂₂ BFeO ₃ P
Formula weight (g·mol ⁻¹)	359.97
Temperature (K)	103(2)

Radiation, λ (Å)	Mo _K α 0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>Unit cell dimensions</i>	
a (Å)	8.7378(6)
b (Å)	12.5147(8)
c (Å)	16.5294(10)
α (°)	90.00
β (°)	99.597(3)
γ (°)	90.00
Volume (Å ³)	1782.2(2)
Z	4
Calculated density (Mg·m ⁻³)	1.342
Absorption coefficient (mm ⁻¹)	0.943
$F(000)$	752
Theta range for collection	2.05 to 30.54°
Reflections collected	82607
Independent reflections	5191
Minimum/maximum transmission	0.6662/0.7461
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restraints	5191 / 206 / 0
Goodness-of-fit on F^2	1.047
R_{int}	0.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0243$, $wR^2 = 0.0620$
R indices (all data)	$R_1 = 0.0304$, $wR^2 = 0.0648$
Maximum/minimum residual electron density (e·Å ⁻³)	0.394 / -0.212

Crystal data for **5**

Data	5
Empirical formula	C ₇₅ H ₁₁₈ B ₂ Fe ₂ O ₆ P ₄ Pt ₂
Formula weight (g·mol ⁻¹)	1763.07
Temperature (K)	100(2)
Radiation, λ (Å)	Mo _K α 0.71073
Crystal system	Triclinic
Space group	$P-1$
<i>Unit cell dimensions</i>	
a (Å)	8.9521(5)
b (Å)	10.0878(6)
c (Å)	22.4284(14)
α (°)	97.278(4)
β (°)	95.272(4)

γ (°)	107.887(3)
Volume (Å ³)	1893.57(19)
Z	1
Calculated density (Mg·m ⁻³)	1.546
Absorbtion coefficient (mm ⁻¹)	4.191
<i>F</i> (000)	894
Theta range for collection	2.20 to 25.99°
Reflections collected	55524
Independent reflections	7363
Minimum/maximum transmission	0.5686/0.7453
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / parameters / restraints	7363 / 401 / 0
Goodness-of-fit on <i>F</i> ²	1.168
<i>R</i> _{int}	0.0488
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0256, <i>wR</i> ² = 0.0698
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0267, <i>wR</i> ² = 0.0703
Maximum/minimum residual electron density (e·Å ⁻³)	1.775 / -1.133

Crystal data for **7**

Data	7
Empirical formula	C ₂₉ H ₃₂ BFeO ₄ P
Formula weight (g·mol ⁻¹)	542.18
Temperature (K)	100(2)
Radiation, λ (Å)	MoKα 0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	9.1705(8)
<i>b</i> (Å)	16.2856(16)
<i>c</i> (Å)	18.7869(17)
α (°)	79.362(4)
β (°)	89.368(4)
γ (°)	84.646(4)
Volume (Å ³)	2745.5(4)
Z	4
Calculated density (Mg·m ⁻³)	1.312
Absorbtion coefficient (mm ⁻¹)	0.640
<i>F</i> (000)	1136
Theta range for collection	1.10 to 30.53°
Reflections collected	163239
Independent reflections	14709

Minimum/maximum transmission	0.6935/0.7461
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restraints	14709 / 663 / 0
Goodness-of-fit on F^2	1.029
R_{int}	0.0422
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0318$, $wR^2 = 0.0741$
R indices (all data)	$R_1 = 0.0442$, $wR^2 = 0.0797$
Maximum/minimum residual electron density ($e \cdot \text{\AA}^{-3}$)	0.603 / -0.323

2) Experimental section

General Remarks: All manipulations were performed either under dry argon or in Vacuo using standard Schlenk line and glovebox techniques. Solvents (toluene, ether, benzene and hexane) were purified by distillation under dry argon from sodium and stored under the same inert gas over molecular sieves. Acetonitrile was purified by distillation under dry argon from CaH_2 and stored under the same inert gas over molecular sieves in absence of light. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. NMR spectra were acquired on Varian Unity 500 (^1H : 499.834; ^{11}B : 160.364; ^{13}C : 125.697 MHz) or Bruker Avance 500 (^1H : 500.133; ^{11}B : 160.472; ^{13}C : 125.777 MHz) NMR spectrometers. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to external TMS via the residual protio solvent (^1H) or the solvent itself (^{13}C). $^{11}\text{B}\{^1\text{H}\}$ spectra were referenced to external $\text{BF}_3 \cdot \text{OEt}_2$ and TMS, respectively. NMR probe temperatures were calibrated using a MeOH standard for VT NMR spectroscopic studies. Microanalyses were performed on a Leco CHNS-932 Elemental Analyzer. $[(\text{CO})_4\text{Fe}(\text{PMe}_3)]^1$, $[(\text{CO})_3(\text{PMe}_3)\text{Fe}(\text{H})(\text{SiMe}_3)]^2$, $\text{K}[(\text{CO})_3(\text{PMe}_3)\text{Fe}(\text{SiMe}_3)]$ (**1**)², DurBr^3 , DurLi^4 and $[\text{Pt}(\text{PCy}_3)_2]$ (**4**)⁵ were prepared according to the literature. NMR spectroscopic experiments were performed in young NMR tubes. Infrared data were acquired on a JASCO FT/IR-6200typeA apparatus.

DurBBr₂ (2): The colorless DurLi (9.47 g, 67.57 mmol) was suspended in hexane

(200 mL) at $-70\text{ }^{\circ}\text{C}$. BBr_3 (16.93 g, 6.4 mL, 67.57 mmol) was added dropwise by a syringe. The reaction mixture was allowed to warm to ambient temperature very slowly. After overnight stirring, the colorless suspension was filtered. The colorless residue was extracted with warm hexane (3 x 50 mL). All volatile materials were removed under high vacuum then. **2** was obtained as colorless crystalline solide (12.10 g, 59%). $^1\text{H-NMR}$: $\delta = 1.90$ (s, 6H, Me of Dur), 2.07 (s, 6H, Me of Dur), 6.75 (s, 1H, *p*-H of Dur); $^{11}\text{B}\{^1\text{H}\}$ -NMR: $\delta = 62.68$ (s).

[(PMe₃)(OC)₃Fe=BDur] (3): In a centrifuge schlenk, a hexane solution (30 mL) of **2** (936 mg, 3.08 mmol) was added to a grey-colored suspension of $\text{K}[(\text{CO})_3(\text{PMe}_3)\text{Fe}(\text{SiMe}_3)]$ (**1**) (1 g, 3.05 mmol) in hexane (30 mL) at RT. The reaction mixture was stirred for 1 h at ambient temperature and was subsequently centrifuged. The obtained yellow hexane solution containing **3** was concentrated to ca. 20 mL and stored at $-30\text{ }^{\circ}\text{C}$ overnight, yielding **3** as yellow crystals (666 mg, 61% yield). $^1\text{H-NMR}$: $\delta = 6.78$ (s, 1H, *p*-H of Dur), 2.71 (s, 6H, Me of Dur), 1.87 (s, 6H, Me of Dur), 1.10 (d, $^2J_{\text{H-P}} = 9.24$ Hz, 9H, PMe_3); $^{13}\text{C}\{^1\text{H}\}$ -NMR: signal for boron-bound carbon was not detected, $\delta = 216.26$ (d, $^2J_{\text{C-P}} = 23.33$ Hz, CO), 18.71 (s, CH_3 of Dur), 18.97 (s, CH_3 of Dur), 20.32 (d, $^1J_{\text{P-C}} = 28.60$ Hz, $\text{P}(\text{CH}_3)_3$), 137.19 (s, *p*-CH of Dur), 134.11 (s, CCH_3 of Dur), 140.49 (s, CCH_3 of Dur); $^{11}\text{B}\{^1\text{H}\}$ -NMR: $\delta = 145.67$ (bs); $^{31}\text{P}\{^1\text{H}\}$ -NMR: $\delta = 17.63$ (s); elemental analysis (%) calcd. for $\text{C}_{16}\text{H}_{22}\text{BFeO}_3\text{P}$: C 53.39, H 6.16; found: C 53.43, H 6.03.

[(CO)₂(PMe₃)Fe(μ -CO)(μ -BDur)Pt(PCy₃)] (5): Compound **4** (42 mg, 0.056 mmol) was added to a solution of **3** (20 mg, 0.056 mmol) in 0.4 mL toluene. The color of the solution immediately changed from yellow to deep red. The solution was concentrated to ca. 0.1 mL, layered with 0.3 mL hexane, stored at $-35\text{ }^{\circ}\text{C}$, yielding deep red crystals (35 mg, 75% yield). $^1\text{H-NMR}$: $\delta = 6.86$ (s, 1H, *p*-H of Dur), 2.84 (s, 6H, Me of Dur), 2.11 (s, 6H, Me of Dur), 1.37 (d, $^2J_{\text{H-P}} = 9.56$ Hz, 9H, PMe_3), 1.01-1.87 (m, 33H, Cy); $^{13}\text{C}\{^1\text{H}\}$ -NMR: signal for boron-bound carbon was not detected, $\delta = 220.20$ (m, CO), 19.71 (s, CH_3 of Dur), 19.48 (s, CH_3 of Dur), 19.64 (d, $^1J_{\text{P-C}} = 30.61$ Hz,

$P(CH_3)_3$), 133.56 (s, *p*-CH of Dur), 132.98 (s, CCH_3 of Dur), 140.49 (s, CCH_3 of Dur), 27.51 (d, $^2J_{C-P} = 11.45$ Hz, $C_{2,6}$ of Cy), 30.72 (d, $^3J_{C-P} = 1.17$ Hz, $C_{3,5}$ of Cy), 26.28 (d, $^4J_{C-P} = 1.08$ Hz, C_4 of Cy), 35.03 (d, $^1J_{C-P} = 25.34$ Hz, C_1 of Cy); $^{11}B\{^1H\}$ -NMR: $\delta = 125.19$ (bs); $^{31}P\{^1H\}$ -NMR: $\delta = 66.84$ (d, $^3J_{P-P} = 14.56$ Hz, $1J_{Pt-P} = 4964.38$ Hz, Pt-*P*), 36.10 (d, $^3J_{P-P} = 14.56$ Hz, Fe-*P*); elemental analysis (%) calcd. For $BC_{34}FeH_{55}O_3P_2Pt + 0.5 \times (C_6H_5CH_3)$: C 51.09, H 6.75; found: C 51.31, H 7.23.

[(CO)₂(PMe₃)Fe{B(Dur)OC(Ph)₂}] (7): Benzophenone (**6**) was added to a solution of **3** (30 mg, 0.083 mmol) in 0.4 mL toluene. The color of the solution immediately changed from yellow to pale yellow. The solution was concentrated to ca. 0.1 mL, layered with 0.3 mL hexane, stored at -35 °C, yielding colorless crystals (52 mg, 85% yield). 1H -NMR: $\delta = 0.57$ (d, $^2J_{H-P} = 8.94$ Hz, 9H, PMe_3), 6.86 (s, 1H, *p*-H of Dur), 2.39 (s, 6H, Me of Dur), 2.07 (s, 6H, Me of Dur), 8.13 (d, 4H, $^3J_{H-H} = 7.55$ Hz, *o*-H of Ph), 7.31 (t, 4H, $^3J_{H-H} = 7.59$ Hz, *m*-H of Ph), 6.99 (t, 2H, $^3J_{H-H} = 7.50$ Hz, *p*-H of Ph); $^{13}C\{^1H\}$ -NMR: signal for boron-bound carbon was not detected, $\delta = 212.02$ (d, $^2J_{C-P} = 23.20$ Hz, CO), 20.32 (s, CH_3 of Dur), 19.64 (s, CH_3 of Dur), 18.41 (d, $^1J_{P-C} = 28.51$ Hz, $P(CH_3)_3$), 131.90 (s, *p*-CH of Dur), 133.71 (s, CCH_3 of Dur), 133.86 (s, CCH_3 of Dur), 124.91 (s, *p*-CH of Ph), 125.00 (s, *o*-CH of Ph), 128.42 (s, *m*-CH of Ph), 129.27 (s, *C* of Ph), 155.13 (s, Fe-C-O-B); $^{11}B\{^1H\}$ -NMR: $\delta = 72.82$ (bs); $^{31}P\{^1H\}$ -NMR: $\delta = 12.42$ (s); elemental analysis (%) calcd. For $BC_{29}FeH_{32}O_4P$: C 64.24, H 5.95; found C 64.28, H 5.98.

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