

Electronic Supplementary Information

Synthesis and Structure of the First Heterodinuclear Bis(borylene) Complexes

Holger Braunschweig,* Qing Ye, Alexander Damme and Krzysztof Radacki

[*] Prof. Dr. Holger Braunschweig
Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany.
E-mail: h.braunschweig@mail.uni-wuerzburg.de.
Fax: + 49 931 31 85260.

1) Crystal structure determinations of **7** and **8**

The crystal data of **7** and **8** were collected on a Bruker X8-APEX II 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-940839, 940840. 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 **7**

Data	7
Empirical formula	C ₃₇ H ₆₄ B ₂ FeNO ₃ PPtSi ₂
Formula weight (g·mol ⁻¹)	930.60
Temperature (K)	100(2)
Radiation, λ (Å)	MoKα 0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	21.750(16)
<i>b</i> (Å)	12.337(9)
<i>c</i> (Å)	15.479(12)
α (°)	90.00
β (°)	94.824(15)
γ (°)	90.00
Volume (Å ³)	4139(5)
Z	4
Calculated density (Mg·m ⁻³)	1.493
Absorbtion coefficient (mm ⁻¹)	3.858
<i>F</i> (000)	1896
Theta range for collection	0.94 to 26.78°
Reflections collected	43855
Independent reflections	8727
Minimum/maximum transmission	0.5480/0.7454
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / parameters / restraints	8727 / 443 / 0
Goodness-of-fit on <i>F</i> ²	1.013
Final R indices [<i>I</i> >2σ(<i>I</i>)]	R ₁ = 0.0267, wR ² = 0.0532
R indices (all data)	R ₁ = 0.0370, wR ² = 0.0567
Maximum/minimum residual electron density (e·Å ⁻³)	0.836 / -0.830

Crystal data for **8**

Data	8
Empirical formula	C ₃₈ H ₆₃ B ₂ FeNO ₄ PPtSi ₂
Formula weight (g·mol ⁻¹)	957.60
Temperature (K)	100(2)
Radiation, λ (Å)	MoKα 0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>Unit cell dimensions</i>	

a (Å)	9.4922(6)
b (Å)	11.7168(7)
c (Å)	20.7030(13)
α (°)	78.249(2)
β (°)	81.135(2)
γ (°)	76.416(2)
Volume (Å ³)	2177.5(2)
Z	2
Calculated density (Mg·m ⁻³)	1.460
Absorbtion coefficient (mm ⁻¹)	3.670
$F(000)$	974
Theta range for collection	1.82 to 26.37°
Reflections collected	23988
Independent reflections	8880
Minimum/maximum transmission	0.6119/0.7455
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restraints	8880 / 461 / 0
Goodness-of-fit on F^2	0.964
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0423$, $wR^2 = 0.0767$
R indices (all data)	$R_1 = 0.0629$, $wR^2 = 0.0814$
Maximum/minimum residual electron density (e·Å ⁻³)	1.241 / -2.227

2) Experimental section

General Remarks: All manipulations were performed either under dry argon or in Vacuo using standard Schlenk line and glovebox techniques. Solvents (benzene and hexane) were purified by distillation under dry argon from sodium and stored under the same inert gas over molecular sieves. 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. $[(\text{OC})_3\text{Fe}(\text{BDur})\{\text{BN}(\text{SiMe}_3)_2\}]$ (**3**)¹ and $[\text{Pt}(\text{PCy}_3)_2]$ (**6**)² were prepared according to the literature. NMR spectroscopic experiments were performed in young NMR tubes.

$[(\text{CO})_2(\text{PMe}_3)\text{Fe}\{\mu\text{-BN}(\text{SiMe}_3)_2\}(\mu\text{-BDur})\text{Pt}(\text{PCy}_3)]$ (**7**): Compound $[\text{Pt}(\text{PCy}_3)_2]$ (**6**) (38 mg, 0.05 mmol) was added to a solution of $[(\text{OC})_3\text{Fe}(\text{BDur})\{\text{BN}(\text{SiMe}_3)_2\}]$ (**3**) (23 mg, 0.05 mmol) in 1 mL hexane. The colour of the solution changed immediately from red to deep brown. The solution was concentrated to ca. 0.5 mL, stored at -35°C overnight, yielding **7** as brown crystals (33 mg, 71% yield).

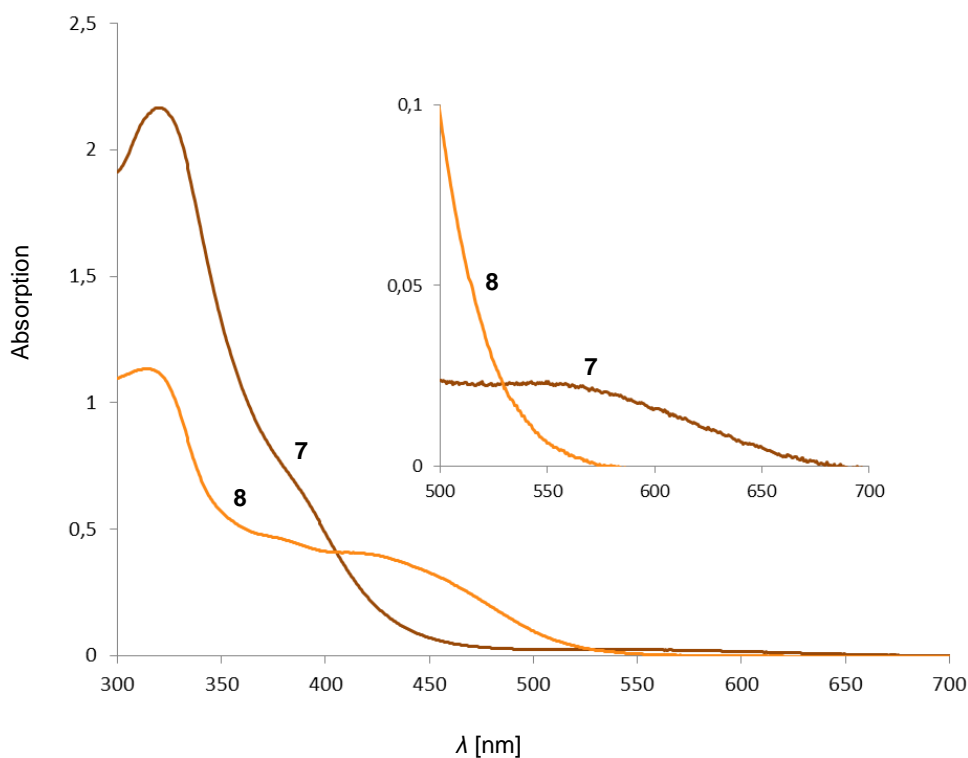
^1H NMR: δ = 6.83 (s, 1H, *p*-H of Dur), 2.64 (s, 6H, Me of Dur), 2.06 (s, 6H, Me of Dur), 0.47 (s, 18H, SiMe_3), 1.01-1.87 (m, 33H, Cy); $^{13}\text{C}\{^1\text{H}\}$ NMR: signal for boron-bound carbon was not detected, δ = 218.93 (s, CO), 218.90 (s, CO), 19.80 (s, CH_3 of Dur), 19.55 (s, CH_3 of Dur), 2.23 (s, SiMe_3), 132.99 (s, *p*-CH of Dur), 134.38 (s, CCH_3 of Dur), 133.62 (s, CCH_3 of Dur), 30.61 (s, CH_2 of Cy), 27.57 (d, $^2J_{\text{C-P}}$ = 11.2 Hz, CH_2 of Cy), 26.21 (bs, CH_2 of Cy), 35.22 (d, $^1J_{\text{C-P}}$ = 22.8 Hz, CH of Cy); $^{11}\text{B}\{^1\text{H}\}$ NMR: δ = 121.8(bs), 97.6 (bs); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = 74.39 (d, $^1J_{\text{Pt-P}}$ = 4021.6

Hz); elemental analysis (%) calcd. For $B_2C_{37}FeH_{64}NO_3PPtSi_2$: C 47.75, H 6.93, N 1.51; found: C 47.81, H 7.14, N 1.47.

$[(CO)_2(PMe_3)Fe\{\mu-BN(SiMe_3)_2\}(\mu-BDur)Pt(PCy_3)(CO)]$ (8): A deep brown C_6D_6 solution of **7** was exposed to CO (1.2 bar) in a sealed Young NMR tube. The colour of the solution turned immediately orange.

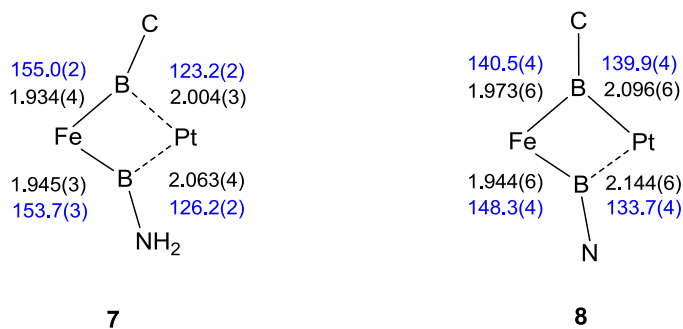
1H NMR: δ = 6.87 (s, 1H, *p*-H of Dur), 2.35 (s, 6H, Me of Dur), 2.10 (s, 6H, Me of Dur), 0.44 (s, 18H, SiMe₃), 2.24 (m, 3H, CH of Cy), 0.90-1.80 (m, 30H, Cy); $^{13}C\{^1H\}$ NMR: signal for boron-bound carbon was not detected, δ = 219.60 (bs, CO), 214.42 (s, CO), 20.64 (s, CH₃ of Dur), 19.66 (s, CH₃ of Dur), 2.98 (s, SiMe₃), 132.13 (s, *p*-CH of Dur), 133.56 (s, CCH₃ of Dur), 132.02 (s, CCH₃ of Dur), 30.39 (s, CH₂ of Cy), 27.47 (d, $^2J_{C-P}$ = 10.7 Hz, CH₂ of Cy), 26.48 (bs, CH₂ of Cy), 36.20 (bs, CH of Cy); $^{11}B\{^1H\}$ NMR: δ = 134(bs), 98 (bs); $^{31}P\{^1H\}$ NMR: δ = 31.4 (bs).

3) UV-Vis Spectra of **7** and **8**



UV-vis spectra of **7** and **8** were recorded in benzene solution, featuring similar absorption maximum ($\lambda_{\text{max}} = 320 \text{ nm}$ (**7**), 315 nm (**8**)). The first absorption band of **7** was observed at $\lambda = 550 \text{ nm}$, while that of **8** was blue-shifted to $\lambda = 415 \text{ nm}$.

4) Comparison of the central Fe-B-Pt-B geometry between **7** and **8**



Bond lengths are shown in black (Å), bond angles in blue (°).

5) References

- [1] H. Braunschweig, Q. Ye, A. Vargas, R. D. Dewhurst, K. Radacki and A. Damme, *Nat. Chem.*, 2012, **4**, 563.
- [2] T. Yoshida, S. Otsuka, *Inorg. Synth.*, 1990, **28**, 113.