Supporting Information

for

Platinum Substituted Boroles

Holger Braunschweig*, Ching-Wen Chiu, Krzysztof Radacki, Peter Brenner

Institute of Inorganic Chemistry, University of Wuerzburg, Am Hubland, D-97074 Wuerzburg, Germany

General consideration: All syntheses were carried out under an argon atmosphere with standard Schlenk and glovebox techniques. [Pt(PCy$_3$)$_2$] and C$_4$Ph$_4$BCl were prepared according to the published procedures.[1] Solvents were dried by distillation over drying reagents (Na/K alloy for hexane and benzene; P$_2$O$_5$ for CH$_2$Cl$_2$) under argon and stored over molecular sieves. Deuterated solvents were degassed with three freeze-pump-thaw cycles and stored over molecular sieves. Elemental analyses were obtained from a Elementar Vario MICRO cube instrument. Electronic absorption spectra were measured on JASCO-V-600 UV-vis spectrometer. NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer (500 MHz for ^{1}H, 202 MHz for ^{31}P{^{1}H}, 160 MHz for ^{11}B{^{1}H}, 126 MHz for ^{13}C{^{1}H}). Chemical shifts *d* are given in ppm, and are referenced against external Me$_4$Si (^{1}H, ^{13}C), BF$_3$·Et$_2$O (^{11}B), and 85% H$_3$PO$_4$ (^{31}P).

Synthesis of [(Cy$_3$P)$_2$Pt(Cl)(BC$_4$Ph$_4$)] (1): [Pt(PCy$_3$)$_2$] (29 mg, 0.038 mmol) was dissolved in 0.5 mL benzene and slowly added into a 1 mL benzene solution of C$_4$Ph$_4$BCl (28 mg, 0.072 mmol) in glove box. After stirring at room temperature for 30 minutes, solvents were removed under vacuum to afford a red solid residue. Extraction of the residue with hexane (0.5 mL, 3 times) gives a bright red solution, which was allowed to slowly evaporate to afford red crystalline product as a 0.5 hexane solvate (9.4 mg, yield = 20%). ^{1}H NMR (500 MHz, C$_6$D$_6$, 297 K): 1.15-1.44 (m, 18H, Cy), 1.56-1.67 (m, 30H, Cy), 2.18 (bs, 12H, Cy), 2.67 (bs, 6H, Cy), 6.91-7.05 (m, 12H, Ph), 7.16-7.22 (m, 10H, Ph), 7.93 (d, $^3J_{H\text{-}H}$= 7.9 Hz, 4H, Ph). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$, 297 K): 35.7 ($^1J_{P\text{-}Pt}$=2947 Hz). ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 297 K): 14.9 (hex), 23.61 (hex), 27.4 (Cy), 28.7 (Cy), 31.5 (Cy), 32.5 (hex), 37.5 (Cy), 126.3 (p-Ph), 127.3 (p-Ph), 128.0 (m-Ph), 130.5 (o-Ph), 132.9 (o-Ph), 139.0 (ipso-Ph), 142.2 (ipso-Ph), 143.6 (C=C-B), 155.2 (C=C-C). ^{11}B{^{1}H} NMR (160 MHz, C$_6$D$_6$, 297 K): 91.1 ppm. Anal. Calcd. for C$_{67}$H$_{93}$BClP$_2$Pt: C 66.96; H 7.80. Found: C 67.31; H 8.33.

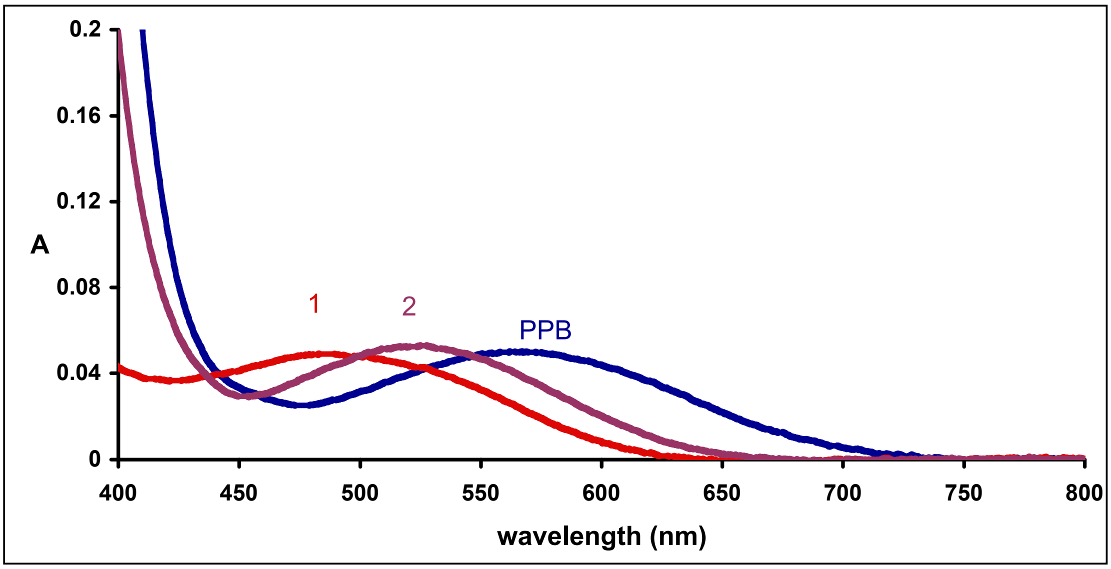
Synthesis of [(Cy$_3$P)$_2$Pt(BC$_4$Ph$_4$)]$^+$[BAr^F$_4$]$^-$ (2): Compound 1 (10 mg, 0.0083 mmol) and Na[BAr^F$_4$] (10 mg, 0.0086 mmol) were mixed and dissolved in 1 mL of CH$_2$Cl$_2$. After standing at ambient temperature for 30 minutes, the white precipitates were filtered off in glove box. By cooling a CH$_2$Cl$_2$/hexane solution to -30°C for 2 days, compound **2** was obtained as purplish-red crystals (9.3 mg, yield = 49 %). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 297 K): 1.15-1.43 (m, 30H, Cy), 1.79-1.87 (m, 18H, Cy), 2.00 (bs, 12H, Cy), 2.22 (bs, 6H, Cy), 6.66 (d, ${}^3J_{H\text{-}H}$= 8.0 Hz, 4H, Ph), 7.06 (d, ${}^3J_{H\text{-}H}$= 7.5 Hz, 4H, Ph), 7.16-7.25 (m, 12H, Ph), 7.48 (s, 4H, $[BAr^F_4]^-$), 7.64 (s, 8H, $[BAr^F_4]^-$). ${}^{31}P\{{}^1H\}$ NMR (202 MHz, CD_2Cl_2, 297 K): 53.5 (${}^1J_{P\text{-}Pt}$=2850.6 Hz). ${}^{13}C\{{}^1H\}$ NMR (126 MHz, CD_2Cl_2, 297 K): 26.1 (Cy), 27.3 (Cy), 27.4 (Cy), 27.5 (Cy), 30.9 (Cy), 35.1 (Cy), 35.2 (Cy), 35.3 (Cy), 117.8 ($[BAr^F_4]^-$), 123.9, 126.1, 127.2, 128.1, 128.2, 128.5, 129.4, 130.2, 135.2, 135.5, 138.9, 158.2, 162.1 (q, ${}^1J_{C\text{-}B}$=50 Hz, $[BAr^F_4]^-$). ${}^{11}B\{{}^1H\}$ NMR (160 MHz, CD_2Cl_2, 297 K): -7.6 ppm ($BAr^F_4{}^-$). Anal. Calcd. for $C_{96}H_{98}B_2F_{24}P_2Pt$: C 58.05; H 4.97. Found: C 58.00; H 5.09.

Crystal structure determination: The crystal data of **1** and **2** were collected on a Bruker X8APEX diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ 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 assigned to idealised positions and were included in structure factors calculations. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-749579 for **1** and CCDC-749580 for **2**. 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 **1**• ${}^1/_2(C_6H_{14})$: $C_{67}H_{93}BClP_2Pt$, M_r = 1201.70, red block, 0.37×0.20×0.19 mm³, Triclinic space group P-1, a = 14.4237(11) Å, b = 14.8407(11) Å, c = 16.0189(13) Å, α = 82.627(3)°, β = 69.204(3)°, γ = 68.636(3)°, V = 2985.3(4) Å³, Z = 2, ρ_{calcd} = 1.337 g·cm⁻³, μ = 2.488 mm⁻¹, $F(000)$ = 1250, T = 100(2) K, R_1 = 0.0249, wR^2 = 0.0562, 16842 independent reflections [$2\theta \leq 61.08°$] (R_{int} = 0.0689) and 649 parameters.

Crystal data for **2**• $3(CH_2Cl_2)$: $C_{99}H_{104}B_2Cl_6F_{24}P_2Pt$, M_r = 2241.17, red plate, 0.21×0.11×0.04 mm³, Triclinic space group P-1, a = 13.1946(15) Å, b = 19.388(2) Å, c = 21.575(3) Å, α = 80.879(2)°, β = 77.509(2)°, γ = 89.330(2)°, V = 5319.0(11) Å³, Z = 2, ρ_{calcd} = 1.399 g·cm⁻³, μ = 1.585 mm⁻¹, $F(000)$ = 2268, T = 100(2) K, R_1 = 0.0533, wR^2 = 0.1252, 26224 independent reflections [$2\theta \leq 56.66°$] (R_{int} = 0.0000) and 1223 parameters.

UV-vis spectrum of 1, 2 and PPB in CH_2Cl_2:



Computational details: All calculations carried out on model complexes **3** and **4** were performed using the Gaussian 03 suite of programs.[2] Geometries of molecules were optimized in DFT method with B3LYP[3] functional and 6-31g* basis set[4] for all atoms and Stuttgart RSC 1997 ECP for the Pt center.[5] The geometry of the molecules was fully optimized and the frequency calculation of the optimized geometry indicates the absence of imaginary frequencies. Time-dependent DFT calculation[6] and Natural Bond Orbital analysis (NBO 3.1)[7] were performed over the optimized geometry at the same level of theory.

Cartesian coordinates for **3**:

		X	Y	Z
1	B	0	0	0
2	C	0	0	1.605699
3	C	1.289733	0	1.993192
4	C	2.229929	0.002219	0.814451
5	C	1.565391	0.003964	-0.356871
6	P	-1.632814	-2.347035	-1.322576
7	C	-0.402251	-3.324648	-0.355601

8	C	-3.253539	-3.016617	-0.764039
9	C	-1.446403	-2.989413	-3.037138
10	P	-1.68251	2.310983	-1.324483
11	C	-0.482139	3.316969	-0.348779
12	C	-1.496355	2.955727	-3.038275
13	C	-3.322248	2.945281	-0.780426
14	H	0.609581	-3.063241	-0.680132
15	H	-3.400114	-2.784876	0.295329
16	H	-2.189726	-2.493419	-3.66686
17	H	-0.578766	3.07378	0.713726
18	H	-4.09283	2.433858	-1.363246
19	Cl	-3.585745	-0.040567	-2.8425
20	Pt	-1.562952	-0.016592	-1.242678
21	H	-0.558062	-4.400999	-0.490045
22	H	-0.491149	-3.077432	0.706716
23	H	-0.44906	-2.74323	-3.414133
24	H	-1.588659	-4.075682	-3.068629
25	H	-3.302646	-4.101932	-0.90854
26	H	-4.040137	-2.523409	-1.34117
27	H	-0.491952	2.728159	-3.408067
28	H	-1.659138	4.039043	-3.071966
29	H	-2.225697	2.445466	-3.67296
30	H	-3.472466	2.711625	0.278008
31	H	-3.394373	4.029052	-0.927103
32	H	-0.657578	4.389277	-0.49113
33	H	0.538295	3.073901	-0.660332
34	H	2.059855	0.00654	-1.324189
35	H	3.311371	0.003059	0.949228
36	H	1.661568	-0.000796	3.017608
37	H	-0.833227	-0.000957	2.302803

Cartesian coordinates for **4**:

		X	Y	Z
1	B	0.000747	1.504225	-0.000098
2	C	0.000805	2.442703	1.272243
3	C	0.002105	3.68854	0.756996
4	C	0.002801	3.688683	-0.756821
5	C	0.002072	2.442943	-1.27229
6	P	2.349729	-0.630823	0.000283
7	C	3.187336	0.111984	-1.457923
8	C	3.185403	0.110373	1.460409
9	C	2.882249	-2.395121	-0.000451
10	P	-2.350443	-0.629042	0.000124
11	C	-3.185538	0.112686	1.460308
12	C	-3.187464	0.114404	-1.458101
13	C	-2.884439	-2.392901	-0.000672
14	H	2.810861	-0.35115	-2.374682
15	H	2.969913	1.182068	1.50433
16	H	2.497975	-2.904885	0.888331
17	H	-2.807686	-0.351373	2.37603
18	H	-2.502113	-2.901683	-0.890852
19	Pt	-0.000341	-0.467923	-0.000514
20	H	4.27071	-0.036844	-1.397806
21	H	2.971978	1.183742	-1.500952
22	H	2.498914	-2.903771	-0.890275
23	H	3.975853	-2.460324	0.000104
24	H	4.268871	-0.038305	1.401592
25	H	2.807728	-0.353802	2.376144
26	H	-2.971342	1.186007	-1.501109
27	H	-4.270951	-0.033657	-1.398117

28	H	-2.81122	-0.348996	-2.374823
29	H	-2.500091	-2.903213	0.887762
30	H	-3.978101	-2.457099	0.000549
31	H	-4.269051	-0.035784	1.401842
32	H	-2.969809	1.184344	1.50394
33	H	0.002415	2.219271	-2.332626
34	H	0.00385	4.617958	-1.322728
35	H	0.002676	4.61771	1.323079
36	H	0.000173	2.218857	2.332546

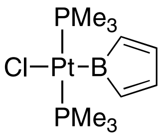
Selected structural parameters for **3**,**1**, **4**, and **2** (bondlength in Å):

	3 (DFT)	**1** (X-ray)	**4** (DFT)	**2** (X-ray)
Pt-B	1.997	1.9860(9)	1.972	1.952(3)
B-C1	1.606	1.624(2)	1.581	1.584(4)
B-C4	1.606	1.622(2)	1.581	1.586(4)
C1-C2	1.347	1.359(2)	1.348	1.349(4)
C2-C3	1.508	1.514(2)	1.514	1.519(4)
C3-C4	1.347	1.353(2)	1.348	1.356(4)

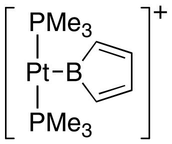
Selected Wiberg bond index output from NBO analysis of **3** and **4**:

	3	**4**
Pt-B	0.81	0.93
B-C1	0.88	0.92
B-C4	0.88	0.92
C1-C2	1.88	1.86
C2-C3	1.03	1.02
C3-C4	1.88	1.86

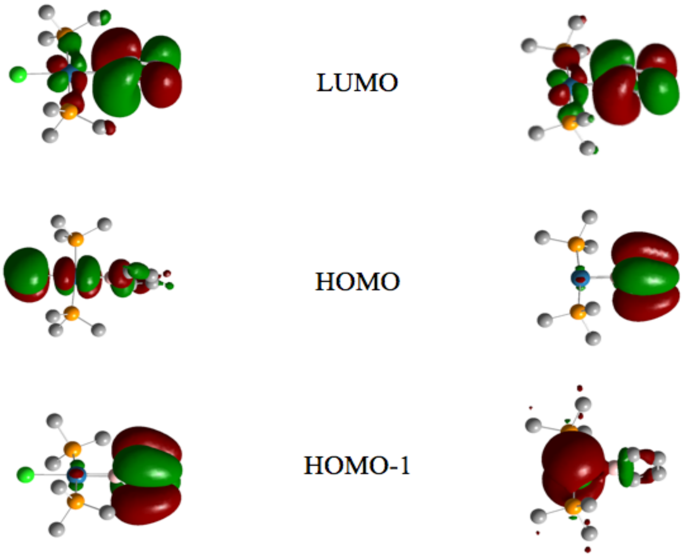
Selected frontier molecular orbital of **3** and **4**:



3



4



Selected outputs from TD-DFT calculation of **3** and **4**:

Excitation energies and oscillator strengths for **3**:

```
 Excited State   1:   Singlet-A      2.7633 eV  448.69 nm  f=0.0000
      71 -> 77         0.14970
      76 -> 77         0.68279
 Excited State   2:   Singlet-A      2.7978 eV  443.14 nm  f=0.0000
      74 -> 77         0.69896
 Excited State   3:   Singlet-A      2.8204 eV  439.59 nm  f=0.0035
      75 -> 77         0.64226
```

Excitation energies and oscillator strengths for **4**:

```
 Excited State   1:   Singlet-A      2.6415 eV  469.38 nm  f=0.0019
      67 -> 68         0.64502
Excited State   2:   Singlet-A      3.2248 eV  384.47 nm  f=0.0000
```

```
      67 -> 69         0.70180
 Excited State   3:   Singlet-A      3.2833 eV  377.62 nm  f=0.0004
      66 -> 68         0.70198
```

References:

(1) (a) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 342. (b) Braunschweig, H.; Kupfer, T. *Chem. Commun.* **2008**, 4487.

(2) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian* 03 revision *E01*, Inc., Wallingford CT, **2004**.

(3) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R.G. *Physical Review B* **1988**, *37*, 785. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200

(4) Hehre, W.J. ; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, 56, 2257

(5) Stuttgart RSC 1997 ECP Basis Set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy.

---

(6) (a) Casida, M. E. *Recent Developments and Applications of Modern Density Functional Theory*; Elsevier: Amsterdam, 1996; Vol. 4. (b) Casida, M. E.; Chong, D. P. *Recent AdVances in Density Functional Methods*; World Scientific: Singapore, 1995; Vol. 1, p 155.

(7) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Reed, A. E.; Weinhold, F. J. *J. Chem. Phys.* **1985**, *83*, 1736. (c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (d) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Re*V. **1988**, *88*, 899