1

**Chemical Communications** 

# A bidentate boryl ligand: syntheses of platinum and iridium complexes



H. Schubert, W. Leis, H. A. Mayer and L. Wesemann\*

Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany. E-mail: 1.wesemann@uni-tuebingen.de

Supporting Information 1) X-Ray crystal structure data 2) Experimental details

|  | 2 x hexane                     | 3                              |
|--|--------------------------------|--------------------------------|
| Empirical formula                            | $C_{25}H_{21}BN_2PPt_{0.50}$   | $C_{56}H_{56}B_2ClIrN_4P_2$    |
| Formula weight                               | 488.76                         | 1096.26                        |
| Crystal system                               | monoclinic                     | triclinic                      |
| Space group                                  | $P2_1/c$                       | <i>P</i> -1                    |
| Unit cell dimensions                         |                                |                                |
| a  | 12.2156(4)                     | 11.1350(3)                     |
| b  | 12.5195(5)                     | 14.5868(4)                     |
| С  | 13.8368(5)                     | 15.8347(4)                     |
| α  |                                | 93.1110(10)                    |
| β  | 104.242(2)                     | 103.1490(10)                   |
| γ  |                                | 95.7580(10)                    |
| Volume                                       | 2051.07(13)                    | 2483.97(11)                    |
| Z, Calculated density                        | 4, 1.583                       | 2, 1.466                       |
| Absorption coefficient                       | 3.541                          | 2.848                          |
| Refl. collected / unique                     | 36846 / 5100                   | 26695 / 10184                  |
| <i>R</i> <sub>int</sub>                      | 0.0401                         | 0.0328                         |
| Goodness-of-fit on $F^2$                     | 1.088                          | 1.029                          |
| Data / restraints /                          | 5100 / 0 / 267                 | 10184 / 0 / 597                |
| parameters                                   |                                |                                |
| Final R indices                              | $R_1 = 0.0195, wR_2 = 0.0440$  | $R_1 = 0.0328, wR_2 = 0.0682$  |
| [I>2sigma(I)]<br><b>R</b> indices (all data) | $R_1 = 0.0216 \ wR_2 = 0.0440$ | $R_1 = 0.0438 \ wR_2 = 0.0717$ |
| CCDC   | $n_1 = 0.0210, wn_2 = 0.0440$  | $n_1 = 0.0430, wn_2 = 0.0717$  |
|  | 215025                         | 273024                         |

1) Table. X-Ray crystal structure data of 2 and 3.

## 2) Experimental section



Scheme1. Formation of the ligand molecule 1.



Scheme2. Formation of the transition metal complexes 2 and 3.

### **General Procedures**

Unless otherwise stated, all materials were handled under Argon using either standard Schlenk techniques or an inert-atmosphere glove box. All starting materials were purchased from Aldrich Chemical Co. and used without further purification. Solvents were dried and distilled before use by standard methods. Tris(bicyclo[2.2.1.]heptene)platinum(0) (Pt(nbe)<sub>3</sub>) was prepared by using the published procedures.<sup>1</sup>

*Synthesis of* [o-C<sub>6</sub>H<sub>4</sub>(NHCH<sub>2</sub>PPh<sub>2</sub>)(NHPh)]: A suspension of Ph<sub>2</sub>PH (12,10 g, 65 mmol) and *para*formaldehyde (1.95 g, 65 mmol) in 20 mL CH<sub>2</sub>Cl<sub>2</sub> was stirred at 60 °C for 12 h. After cooling the suspension to room temperature, a solution of *N*-phenyl-*o*-phenylenediamine (11.98 g, 65 mmol) in 100 mL CH<sub>2</sub>Cl<sub>2</sub> was added and the resulting solution was stirred for 2 days at room temperature. Finally, all volatiles were removed under reduced pressure and the residue was purified by column chromatography (silica, petrol ether/ethyl acetate 80/20) to yield [*o*-C<sub>6</sub>H<sub>4</sub>(NHCH<sub>2</sub>PPh<sub>2</sub>)(NHPh)] as a colorless oil (20,08 g, 81 %). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.95 (d, 2H, CH<sub>2</sub>-P, <sup>2</sup>J<sub>1H-31P</sub> = 4.5 Hz), 4.8 (br, s, 1H,N-H), 6.2 (br, s, 1H,N-H), 6.65-6.76 (4H, C-H<sub>aromatic</sub>), 6.97-7.01 (1H, C-H<sub>aromatic</sub>), 7.08-7.20 (4H, C-H<sub>aromatic</sub>), 7.25-7.36 (6H, C-H<sub>aromatic</sub>), 7.40-7.51 (4H, C-H<sub>aromatic</sub>).<sup>13</sup>C{<sup>1</sup>H} NMR (100.60 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  43.5 (d, CH<sub>2</sub>-P, <sup>1</sup>J<sub>13C-31P</sub> = 12.5 Hz), 111.72, 111.73, 115.0, 117.6, 119.0, 125.2, 125.3, 126.2, 128.2, 128.4, 128.61, 128.67, 128.9, 129.1, 131.0, 131.1, 132.8, 132.9, 133.0, 133.1, 136.5, 136.6, 144.1, 144.2, 145.8. <sup>31</sup>P{<sup>1</sup>H} NMR (161.96 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -19.5 (s). *Synthesis of* [(*o*-C<sub>6</sub>H<sub>4</sub>)Ph<sub>2</sub>PCH<sub>2</sub>NBHNPh] (**1**). To a stirred CH<sub>2</sub>Cl<sub>2</sub> solution (50 mL) of [*o*-C<sub>6</sub>H<sub>4</sub>(NHCH<sub>2</sub>PPh<sub>2</sub>)(NHPh)] (5,95 g, 15.6 mmol) at 0°C a solution of BH<sub>3</sub>\*SMe<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (1 M, 31.2 mL, 31.2 mmol) was added via syringe. After stirring this mixture for 1 h at room temperature all volatiles were removed in vacuo. The resulting oil was dissolved in HN(*n*-Pr)<sub>2</sub> (20 mL) and refluxed for 24 h. After evaporating all volatiles, the raw product was purified by column chromatography (silica, petrol ether/ethyl acetate 80/20) to yield compound **1** as a white powder (4.21 g, 69 %). Elemental analysis: (Found: C, 76.68; H, 5.68; N, 7.13. Calc for C<sub>25</sub>H<sub>22</sub>PN<sub>2</sub>B: C, 76.55; H, 5.65; N, 7.14). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 4.42 (d, 2H, CH<sub>2</sub>-P, <sup>2</sup>J<sub>1H-31P</sub> = 4.5Hz), 4.75 (s, 1H, B-H), 7.0-7.5 (m, 19H, C-H<sub>Aromatic</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (80.25 MHz, C<sub>6</sub>D<sub>6</sub>): δ 25.8. <sup>31</sup>P{<sup>1</sup>H} NMR (161.96 MHz, C<sub>6</sub>D<sub>6</sub>): δ -22.5 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (100.60 MHz, C<sub>6</sub>D<sub>6</sub>): δ 44.7 (d, CH<sub>2</sub>-P, <sup>1</sup>J<sub>13H-31P</sub> = 14.2 Hz), 110.3, 111.5, 116.6, 120.3, 120.5, 127.0, 128.5, 128.6, 129.1, 129.4, 129.4, 133.4, 133.6, 136.2, 136.5, 136.7, 137.3, 139.1.

Synthesis of  $[Pt{(o-C_6H_4)Ph_2PCH_2NBNPh}_2]$  (2). To a stirred toluene solution (20 mL) of 1 (400 mg, 1.02 mmol), solid Pt(nbe)<sub>3</sub> (240 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 2 h, concentrated under reduced pressure and filtered through a plug of cotton. The filtrate was carefully layered with hexane which yields light yellow green crystals of 2 (413 mg, 83 %) after one day. Elemental analysis: (Found: C, 61.67; H, 4.19; N, 5.69. Calc for C<sub>50</sub>H<sub>42</sub>P<sub>2</sub>N<sub>4</sub>B<sub>2</sub>Pt: C, 61.43; H, 4.33; N, 5.73.) <sup>1</sup>H NMR (500 MHz, thf-d<sub>8</sub>):  $\delta$  4.48 (m, 2H, P-CH<sub>axial</sub>), 4.76 (m, 2H, P-C-H<sub>equat</sub>), 6.60 (m, 2H, *meta*-H<sub>Ar-NBN</sub>), 6.67 (m, 2H, *para*-H<sub>Ph-N</sub>), 6.73 (m, 2H, *meta*-H<sub>Ar-NBN</sub>), 6.90 (m, 2H, *ortho*-H<sub>Ar-NBN</sub>), 6.97 (m, 4H, *ortho*-H<sub>Ph-N</sub>), 7.01 (m, 2H, *ortho*-H<sub>Ar-NBN</sub>), 7.04 (m, 2H, *para*-H<sub>axial</sub> Ph-P), 7.16 (m, 4H, *meta*-H<sub>axial</sub> Ph-P), 7.25 (m, 4H, *ortho*-H<sub>axial</sub> Ph-P), 7.30 (m, 4H, *meta*-H<sub>Ph-N</sub>), 7.33 (m, 4H, *meta*-H<sub>equat</sub> Ph-P), 7.40 (m, 2H, *para*-H<sub>equat,Ph-P</sub>), 7.67 (m, 4H, *ortho*-H<sub>equat</sub> Ph-P),  $^{31}P{}^{1}H$  NMR (202.45 MHz, thf-d<sub>8</sub>):  $\delta$  62.8 (br. s, <sup>1</sup>J<sub>31P-195Pt</sub> = 1248 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (160.46 MHz, thf-d<sub>8</sub>):  $\delta$  49.0 (br, s). <sup>195</sup>Pt NMR (thf-d<sub>8</sub>):  $\delta$  -4970. <sup>13</sup>C{<sup>1</sup>H} NMR (125.75 MHz, thf-d<sub>8</sub>):  $\delta$  49.6 (P-CH<sub>2</sub>-N), 107.8 (*ortho*-C-H<sub>Ar-NBN</sub>), 108.1 (*ortho*-C-H<sub>Ar-NBN</sub>), 117.2 (*meta*-C-H<sub>Ar-NBN</sub>), 118.0 (*meta*-C-H<sub>Arial</sub> Ph-P), 128.2 (*meta*-C-H<sub>axial</sub> Ph-P), 128.4 (*meta*-C-H<sub>equat,Ph-P</sub>), 129.9 (*para*-C-H<sub>equat,Ph-P</sub>), 132.5 (*ortho*-C-H<sub>axial</sub> Ph-P), 130.0 (*ortho*-C-H<sub>axial</sub> Ph-P), 129.9 (*para*-C-H<sub>equat,Ph-P</sub>), 132.5 (*ortho*-C-H<sub>axial</sub> Ph-P), 130.0 (*ortho*-C-H<sub>axial</sub> Ph-P), 128.4 (*meta*-C-H<sub>equat,Ph-P</sub>), 129.9 (*para*-C-H<sub>equat,Ph-P</sub>), 132.5 (*ortho*-C-H<sub>axial</sub> Ph-P), 133.0 (*ortho*-C-H<sub>axial</sub> Ph-P), 128.4 (*meta*-C-H<sub>equat,Ph-P</sub>), 129.9 (*para*-C-H<sub>equat,Ph-P</sub>), 132.5 (*ortho*-C-H<sub>axial</sub> Ph-P), 133.0 (*ortho*-C-H<sub>axial</sub> Ph-P), 128.4 (*meta*-C-H<sub>equat,Ph-P</sub>), 129.9 (*para*-C-H<sub>equat,Ph-P</sub>), 132.5 (*ortho*-C-H<sub>axial</sub> P

H<sub>equat.Ph-P</sub>), 135.0 (*ipso*-C-H<sub>equat.Ph-P</sub>), 135.8 (*ipso*-C-H<sub>axial Ph-P</sub>), 138.1 (*ipso*-C- H<sub>Ar-NBN</sub>), 138.4 (*ipso*-C- H<sub>Ar-NBN</sub>), 142.6 (*ipso*-C- H<sub>Ph-N</sub>).

Synthesis of  $[IrCl{(o-C_6H_4)Ph_2PCH_2NBNPh}_2]$  (3). To a stirred toluene solution (20 mL) of 1 (400 mg, 1.02 mmol), solid [(coe<sub>2</sub>IrCl)<sub>2</sub>] (228 mg, 0.25 mmol) was added. The reaction mixture was stirred at room temperature for 2 h, concentrated under reduced pressure and filtered through a plug of cotton. The filtrate was carefully layered with hexane to yield light yellow crystals of 3 (375 mg, 73 %) after several days. Recrystallization of 3 can also be achieved by cooling a saturated THF solution to  $-24^{\circ}$ C for several days. Elemental analysis: (Found: C, 60.53; H, 4.72; N, 5.02. Calc for  $C_{50}H_{42}P_2N_4B_2IrCl^*2$  THF: C, 60.35; H, 4.85; N, 5.06.) (The inclusion of THF was also confirmed by single crystal structure analysis). <sup>1</sup>H NMR (500 MHz, thf-d<sub>8</sub>): δ 2.07 (m, 2H, P-CH), 3.76 (m, 2H, P-CH), 6.15-6.24 [(m, 2H, ortho-H<sub>Ar-NBN</sub>) (bs, 2H, meta-H<sub>Ph-N</sub>)], 6.39 (br, s, 2H, ortho-H<sub>Ph-N</sub>), 6.56 (m, 2H, meta-H<sub>Ar-NBN</sub>), 6.65 (br, s, 2H, ortho-H<sub>Ph-N</sub>), 6.70 (m, 2H, ortho-H<sub>Ar-NBN</sub>), 6.77 (m, 2H, meta-H<sub>Ar-</sub> NBN), 7.03 (m, 2H, para-H<sub>Ph-N</sub>), 7.13-7.25 [(m, 4H, meta-H<sub>Ph-P</sub>) (m, 4H, ortho-H<sub>Ph-P</sub>) (br. s, 2H, meta-H<sub>Ph-N</sub>) (m, 2H, para-H<sub>Ph-P</sub>)], 7.55 (m, 4H, ortho-H<sub>Ph-P</sub>), 7.66 (m, 2H, para-H<sub>Ph-P</sub>), 7.85 (m, 4H, meta- $H_{Ph-P}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (202.45 MHz, thf-d<sub>8</sub>):  $\delta$  47.7 (s). <sup>11</sup>B{<sup>1</sup>H} NMR (160.46 MHz, thf-d<sub>8</sub>):  $\delta$  30.0 (br, s). <sup>13</sup>C{<sup>1</sup>H} NMR (125.75 MHz, thf-d<sub>8</sub>): δ 43.5 (P-CH<sub>2</sub>-N), 107.5 (*ortho*-C-H<sub>Ar-NBN</sub>), 108.1 (*ortho*-C-H<sub>Ar-NBN</sub>), 117.5 (meta-C-H<sub>Ar-NBN</sub>), 118.4 (meta-C-H<sub>Ar-NBN</sub>), 125.2 (para-C-H<sub>Ar-N</sub>), 127.4 (meta-C-H<sub>Ph-</sub> P), 128.2 (meta-C-H<sub>Ph-P</sub>), 128.6 (para-C-H<sub>Ph-N</sub>), 128.9 (para-C-H<sub>Ph-P</sub>), 129.6 (ortho-C-H<sub>Ph-N</sub>), 130.9 (para-C-H<sub>Ph-P</sub>), 131.6 (ortho-C-H<sub>Ph-P</sub>), 135.7 (ortho-C-H<sub>Ph-P</sub>), 137.4 (ipso-C-H<sub>Ar-NBN</sub>), 141.8 (ipso-C-H<sub>Ar-NBN</sub>).

#### **Computational Details**

All calculations were performed with version 3.0.0 of the electronic structure program Orca using KS-DFT.<sup>2</sup> An Intel Core i5-3470 (quad-core) PC including 8 GB random access memory and the openSuSE 12.3 (64bit) operating system serves as hardware platform. The structural input for the geometry optimization was obtained from the crystal structure and the optimization is done without symmetry or geometry restrictions using the meta-GGA functional M06-L with the valence triple zeta basis set def2-TZVP.<sup>3,4</sup> At the iridium atom the innermost 60 electrons were substituted by a relativistic effective core potential (ECP60MWB) while the remaining "valence" electrons were

handled quantum mechanically.<sup>5</sup> Furthermore the program makes use of the resolution of identity (RI) approximation (also known as coulomb/density fitting) and therefore the auxiliary (fitting) basis set TVZ/J was applied to all atoms.<sup>6,7</sup> Additionally a vibrational frequency calculation was done to verify the absence of imaginary frequencies and hence the energy minimum of the optimized structure. In order to gain accurate molecular orbitals, for the final geometry from the optimization, a separate single point calculation was performed using all electrons at the iridium atom. Due to the zeroth-order regular approximation (ZORA) relativistic effects were taken into account in the Hamiltonian.<sup>8</sup> Therefore relativistically recontracted versions of the def2-TZVP basis set were used for all main group atoms as included in Orca.<sup>9</sup> At the iridium atom a segmented all electron relativistically contracted (SARC) basis set was applied with valence triple zeta (TZV) quality. As auxiliary basis set again TZV/J was used for all atoms to benefit from the RI approximation.<sup>7,9</sup> The optimized structures as well as the molecular orbitals were visualized and transformed into pictures with the open-source program Gabedit.<sup>10</sup>







Figure: HOMO and LUMO (top line) of 3 beside a selection of molecular orbitals presenting significant contributions to bonding interactions between B-B or B-Ir. All hydrogen atoms were omitted for clarity.

### References

- 1) R, J. Angelici, (ed.), *Reagents for Transition Metal Complex and Organometallic Syntheses, Inorganic Syntheses*, 1990, **28**, 127-128.
- 2) F. Neese, Wiley Interdisciplinary Reviews: Computational Molecular Science, 2012, 2, 73–78.
- 3) Y. Zhao and D. G. Truhlar, J. Chem. Phys., 2006, 125, 194101.
- 4) F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297-3305.
- 5) D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, Theoret. Chim. Acta, 1990, 77, 123-141.
- 6) F. Neese, J. Comp. Chem., 2003, 24, 1740–1747.
- 7a) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, and R. Ahlrichs, Chem. Phys. Lett., 1995, 240, 283–290.
- b) K. Eichkorn, F. Weigend, O. Treutler, and R. Ahlrichs, Theor. Chem. Acta, 1997, 97, 119–124.
- 8a) C. Chang, M. Pelissier, and P. Durand, Phys. Scr., 1986, 34, 394.
- b) E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys., 1993, 99, 4597-4610.
- 9a) D. A. Pantazis, X.-Y. Chen, C. R. Landis, and F. Neese, J. Chem. Theory Comput., 2008, 4, 908-919.
- b) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, and R. Ahlrichs, Chem. Phys. Lett., 1995, 240, 283–290.

c) K. Eichkorn, F. Weigend, O. Treutler, and R. Ahlrichs, Theor. Chem. Acta, 1997, 97, 119–124.

10) A.-R. Allouche, J. Comp. Chem., 2011, 32, 174–182.