This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Journal Name

COMMUNICATION

A bidentate boryl ligand: syntheses of platinum and iridium complexes

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

A methylenediphenylphosphine substituted diazaborole was obtained in a two step procedure in amounts around 4 g. This B-P ligand was coordinated at platinum and iridium and the structures of the boryl complexes were discussed. In the case of the iridium derivative an interesting boron-boron contact was found.

The chemistry of transition metal boryl complexes has been an active field of research for more than fifteen years.[1-4] Besides ligand design and reactivity studies of M–B units catalytic transformations, like Ir-catalyzed borylations, play an important role.[5-16] Boryl ligand coordination was realized by nucleophilic attack of the metal fragment at the electrophilic boron or by oxidative addition of B–H, B–X (X = halide) and B–B bonds.[9, 17-23] Furthermore, nucleophilic boron ligands were employed such as the diazaborole anion.[24, 25] Monodentate as well as tridentate PBP boryl ligands are so far present in the literature.[26-28] We are interested in the coordination chemistry of bidentate boryl ligands, as they lead to more flexible coordination spheres, which was mentioned recently in patent literature.[29] In this publication we are presenting a straightforward synthetic procedure of a diazaborole which provides a methylene-diphenylphosphine as a second donor unit (Scheme 1) and two examples for reactions of this molecule as a bidentate boryl phosphine ligand with platinum and iridium transition metal complex fragments (Scheme 2).

Following a slight modification of the work from Yamashita and Nozaki we synthesized the methyldiphenylphosphine substituted diazaborole via a two step procedure.[26, 27] Starting with *N*-phenyl-*o*-phenylenediamine the methylenediphenylsubstitutent was introduced in a condensation type reaction (Scheme 1). In the second step two equivalents of borane reagent have to be used to form the diazaborole cycle (Scheme 1). The second equivalent of borane reagent reacts to give a phosphine–borane adduct, which was destroyed by the reaction with dipropylamine. Purification by column chromatography yields the ligand in amounts of around 4 g (yield 56 %). This borane exhibits characteristic signals in the [11]B

NMR at 26 ppm and in the ^{31}P NMR spectrum at –22.5 ppm. The electronic properties of benzodiazaboroles were intensively investigated with respect to their electronic properties.[30, 31]
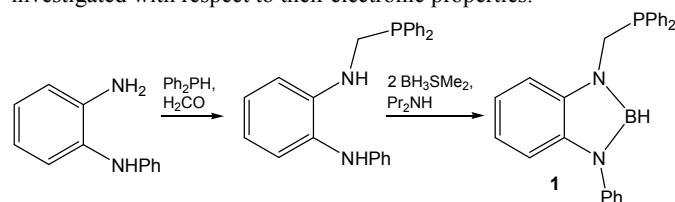
Scheme 1. Formation of the diphenylphosphine diazaborole **1**.

In order to form a platinum and an iridium complex two equivalents of the borane phosphine (B-P) **1** were reacted with [Pt(nbe)$_3$] and the iridium olefin complex [(coe)$_2$IrCl]$_2$ (nbe = norbornene, coe = cyclooctene) (Scheme 2). In both cases the boron coordination compound was isolated in high yield after crystallization.
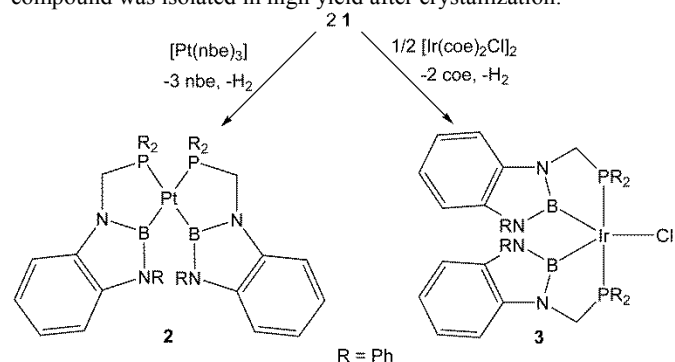
Scheme 2. Synthesis of Pt- and Ir-complexes. (nbe = norbornene, bicyclo[2.2.1]hept-2-en; coe = cyclooctene)

The new coordination compounds **2** and **3** were characterized by elemental analysis, NMR spectroscopy and single crystal X-ray diffraction (see ESI). Only one set of resonances was observed in the NMR spectra of both complexes and is compatible with C$_2$

symmetric coordination spheres as displayed in Scheme 2. In the case of the platinum boryl complex (**2**) the singlet in the ^{11}B NMR spectrum at 49 ppm can be compared with the ^{11}B NMR signal of the complex *cis*-[Pt(BCat)₂(PCy₃)₂] (Cat = 1,2-O₂C₆H₄²⁻) at 49.9 ppm. The [195]Pt NMR signal at –4970 ppm lies close to that of *trans*-[Pt(BCat´)Me(PCy₃)₂] (cat´ = Cat-4-*t*Bu, Cy = cyclohexyl) (–4784 ppm).[32] The resonance for the phosphorus atom shifts from –22.5 to 62.8 ppm and shows a $^1J_{31P-195Pt}$ coupling of 1248 Hz. This large downfield shift of the ^{31}P NMR resonance is characteristic for the formation of a five membered metallacycle.[33] The rather small $^1J_{31P-195Pt}$ coupling constant is indicative of a strong field ligand (stronger than *e.g.* methyl) *trans* to the phosphorus atoms and compares well with other *trans* substituted boryl-phosphorus-platinum complexes.[12, 20, 34-36] In the solid state structure of the bis(B-P) platinum complex **1**, which is depicted in Figure 1, the platinum is nearly square planar coordinated by two B-P-ligands. The B–Pt–P angles are 80.9° small and the P–Pt–P angle of 108.9° is large with respect to ideal square planar coordination. The deviations from the ideal square planar geometry are due to the steric requirements of the B-P-ligands. The Pt–B bond length of 2.072(2) Å is slightly longer than Pt–B bonds with monodentate boryl ligands.[17, 19, 32]
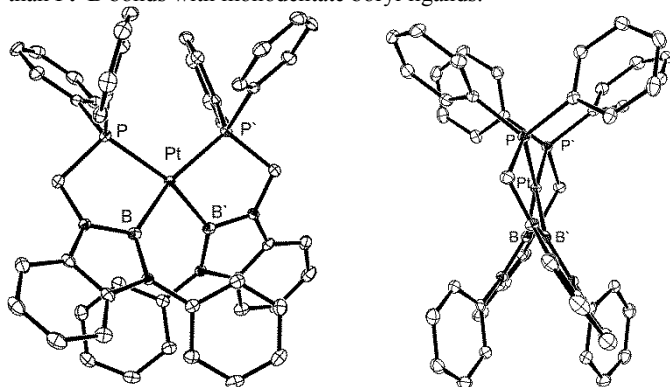

Fig. 1. Molecule structure of compound **2** (two projections). Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°]: Pt–B 2.072(2), Pt–P 2.3242(5), B–Pt–B`93.75(12) 2, B–Pt–P` 162.27(7) 2, B–Pt–P 80.92(6), P–Pt–P` 108.92(3).

Boryl complex **3** shows a resonance at 30 ppm in the ^{11}B NMR spectrum. This chemical shift can be compared with the ^{11}B NMR signal at 30.1 ppm of [IrCl(PEt₃)₂(Bcat)₂].[18] The resonance in the ^{31}P NMR spectrum of **2** at 47.7 ppm shows also a downfield shift in comparison to the ligand, which is indicative for the formation of a five membered metallacycle.[33] The molecular structure of the iridium complex **3** shows a distorted trigonal bipyramidal coordination at iridium by two B-P moieties and a chlorine atom with the phosphorus atoms in axial positions (Figure 2). The geometry and the position of the ligands can be compared with an iridium complex [IrCl(PEt₃)₂(Bcat)₂] published by Marder and Norman.[18] The length of the Ir–B bonds in **3** lie at the upper end of the range of reported Ir–B interatomic distances.[5, 7, 10, 18, 26, 37-39] The Ir–Cl bond is slightly longer than comparable values while the phosphorus atoms show coordination distances at iridium within the range of literature values. Interestingly the B–Ir–B angle of 64.7° as well as the B–B interatomic distance (2.221 Å) is significantly smaller in complex **3** in comparison to other bisboryl iridium complexes. Furthermore the relative orientations of the boryl ligands in complex **3** does allow for the possibility of 2p-2p interaction. This type of bonding between two boryl ligands was discussed in platinum and cobalt bisboryl complexes. Especially the cobalt complex exhibits also a small B–Co–B angle (67.9°) and a short B–B (2.185 Å) interaction.[40, 41] A comparable bonding situation [H–

Rh–B moiety] was studied by neutron diffraction and theoretical methods in the pentacoordinated rhodium complexes [(PR₃)₂RhHCl{B(OR´)₂}] (R = H, Me, [i]Pr, Ph; B(OR´)₂ = Bcat, Bpin, cat = 1,2-O₂C₆H₄, pin = OCMe₂CMe₂O).[23]
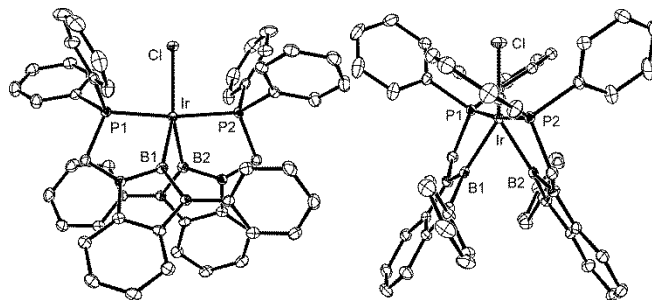

Fig. 2. Molecular structure of compound **3** (two projections). Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°]: Cl–Ir 2.3949(9), Ir–B2 2.067(4), Ir–B1 2.076(4), Ir–P2 2.3086(10), Ir–P1 2.3111(10), B2–Ir–B1 64.73(17), P2–Ir–P1 172.06(3), B2–Ir–Cl 147.28(13), B1–Ir–Cl 147.99(12), P2–Ir–Cl 86.11(3), P1–Ir–Cl 85.95(3).

In order to examine the bonding situation in the bis(diazaborole) iridium moiety the geometry was optimized and the resulting molecular orbitals (MOs) were analysed. The calculations were performed using KS-DFT with the meta-GGA-functional M06-L and the def2-TZVP basis set with a relativistic effective core potential at iridium as included in Orca 3.0.0.[42-48] The orbitals are obtained from a single point calculation with an all electron basis set of comparable quality and the zeroth-order regular approximation (ZORA) to consider relativistic effects (see supporting information for more details).[45, 46, 49-52] The structural parameters of the optimized geometry (Figure 3, left) are in good agreement with the structure from X-ray analysis. However the Ir–Cl and Ir–B bond lengths are around 6.8 and 3.9 pm longer while the B–Ir–B angle is 5.4° smaller than their counterparts from crystallography. Consequently, the B–B distance (2.095 Å) is 0.126 Å shorter in the optimized structure.
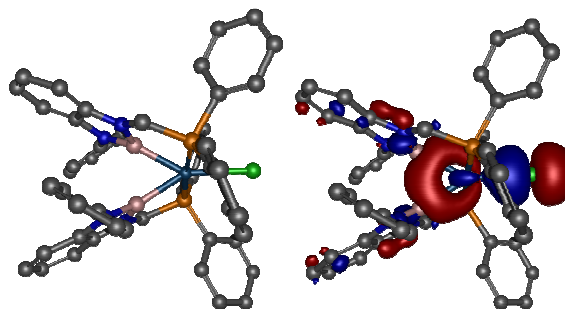

Fig. 3. Left: structure of **3** obtained from geometry optimization. Right: structure of **3** superimposed by its HOMO-21. Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] (atom numbering according to Fig. 2): Cl–Ir 2.463, Ir–B1,2 2.115, Ir–P1,2 2.329, B2–Ir–B1 59.37, P2–Ir–P1 176.25, B2–Ir–Cl 150.30, B1–Ir–Cl 150.33, P1,2–Ir–Cl 88.12.[53]

The inspection of the occupied molecular orbitals (MOs) reveals two interesting types of MOs. The first type of MOs shows electron density between the iridium centre and each of the boron atoms and the second type of MOs exhibits bonding overlaps between the boron atoms. The most distinctive and energetically highest B–B bonding MO (HOMO-21) is shown in Fig. 3 (right). This MO might

be attributed to a kind of three centre interaction which is basically in accordance with the bonding description in a Co boryl complex.[54] There are further MOs (see supporting information) with only a little (two centre) σ-interaction between the boron atoms which are either π-bonding orbitals of the diazaborole systems (HOMO-23, HOMO-27) or can be ascribed to three-centre B–Ir–B interactions (HOMO-5, HOMO-6, HOMO-35). The most distinctive Ir–B σ-bonding molecular orbitals (HOMO-7, HOMO-24) are accompanied by a few MOs containing less pronounced two-centre Ir–B interactions. Finally, there are no occupied molecular orbitals observed displaying a clear anti-bonding interaction between the boron atoms. Therefore, this structure might be described as an intermediate state (η^2-coordinated B–B bond) on a reductive elimination (or alternatively an oxidative addition) reaction coordinate leading finally to the B–B single bond.

Conclusions

We have presented a synthesis for the first bidentate B-P ligand, and coordination of this molecule at platinum and iridium. Although being cis-coordinated in the square planar platinum complex the structural constraints do not allow any B–B interactions of the two diazaborole ligands. In contrast to this the higher flexibility of the trigonal bipyramid and the arrangement of the boron donors at the equatorial positions support a B–B interaction.

Notes and references

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

† Electronic Supplementary Information (ESI) available: Synthetic details, characterization data, crystal structure analysis data and details of quantum chemical calculations. See DOI: 10.1039/c000000x/

1. H. Braunschweig, *Angew. Chem., Int. Ed.*, 1998, **37**, 1786-1801.
2. G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell and L. J. Wright, *Chem. Rev.*, 1998, **98**, 2685-2722.
3. H. Braunschweig and M. Colling, *Coord. Chem. Rev.*, 2001, **223**, 1-51.
4. S. Aldridge and D. L. Coombs, *Coord. Chem. Rev.*, 2004, **248**, 535-559.
5. T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi and J. F. Hartwig, *J. Am. Chem. Soc.*, 2001, **124**, 390-391.
6. B. A. Vanchura II, S. M. Preshlock, P. C. Roosen, V. A. Kallepalli, R. J. Staples, J. R. E. Maleczka, D. A. Singleton and M. R. Smith III, *Chem. Commun.*, 2010, **46**, 7724-7726.
7. C. W. Liskey, C. S. Wei, D. R. Pahls and J. F. Hartwig, *Chem. Commun.*, 2009, 5603-5605.
8. S. A. Westcott, N. J. Taylor, T. B. Marder, R. T. Baker, N. J. Jones and J. C. Calabrese, *Chem. Commun.*, 1991, 304-305.
9. R. T. Baker, D. W. Ovenall, J. C. Calabrese, S. A. Westcott, N. J. Taylor, I. D. Williams and T. B. Marder, *J. Am. Chem. Soc.*, 1990, **112**, 9399-9400.
10. G. A. Chotana, I. I. B. A. Vanchura, M. K. Tse, R. J. Staples, J. R. E. Maleczka and M. R. Smith III, *Chem. Commun.*, 2009, 5731-5733.
11. H. Tamura, H. Yamazaki, H. Sato and S. Sakaki, *J. Am. Chem. Soc.*, 2003, **125**, 16114-16126.
12. G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg and N. C. Norman, *Organometallics*, 1996, **15**, 5137-5154.
13. H. Chen and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 1999, **38**, 3391-3393.
14. C. N. Iverson and M. R. Smith III, *J. Am. Chem. Soc.*, 1999, **121**, 7696-7697.
15. S. Shimada, A. S. Batsanov, J. A. K. Howard and T. B. Marder, *Angew. Chem., Int. Ed.*, 2001, **40**, 2168-2171.
16. I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2009, **110**, 890-931.
17. W. Clegg, F. J. Lawlor, G. Lesley, T. B. Marder, N. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, A. J. Scott and F. E. S. Souza, *J. Organomet. Chem.*, 1998, **550**, 183-192.
18. W. Clegg, F. J. Lawlor, T. B. Marder, P. Nguyen, N. C. Norman, A. Guy Orpen, M. J. Quayle, C. R. Rice, E. G. Robins, A. J. Scott, F. E. S. Souza, G. Stringer and G. R. Whittell, *Dalton Trans.*, 1998, 301-310.
19. H. Braunschweig and A. Damme, *Chem. Commun.*, 2013, **49**, 5216-5218.
20. H. Braunschweig, P. Brenner, A. Müller, K. Radacki, D. Rais and K. Uttinger, *Chem.-Eur. J.*, 2007, **13**, 7171-7176.
21. H. Braunschweig, C. Kollann and D. Rais, *Angew. Chem., Int. Ed.*, 2006, **45**, 5254-5274.
22. H. Braunschweig, R. D. Dewhurst and A. Schneider, *Chem. Rev.*, 2010, **110**, 3924-3957.
23. W. H. Lam, S. Shimada, A. S. Batsanov, Z. Lin, T. B. Marder, J. A. Cowan, J. A. K. Howard, S. A. Mason and G. J. McIntyre, *Organometallics*, 2003, **22**, 4557-4568.
24. Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113-115.
25. T. Kajiwara, T. Terabayashi, M. Yamashita and K. Nozaki, *Angew. Chem., Int. Ed.*, 2008, **47**, 6606-6610.
26. Y. Segawa, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 9201-9203.
27. M. Hasegawa, Y. Segawa, M. Yamashita and K. Nozaki, *Angew. Chem., Int. Ed.*, 2012, **51**, 6956-6960.
28. A. F. Hill, S. B. Lee, J. Park, R. Shang and A. C. Willis, *Organometallics*, 2010, **29**, 5661-5669.
29. P. Stoessel, H. Heil, D. Joosten, C. Pflumm and A. Gerhard, *(Merck KGaA)*, WO2010099852A1 (2012).
30. L. Weber, D. Eickhoff, T. B. Marder, M. A. Fox, P. J. Low, A. D. Dwyer, D. J. Tozer, S. Schwedler, A. Brockhinke, H.-G. Stammler and B. Neumann, *Chem.-Eur. J.*, 2012, **18**, 1369-1382.
31. L. Weber, V. Werner, M. A. Fox, T. B. Marder, S. Schwedler, A. Brockhinke, H.-G. Stammler and B. Neumann, *Dalton Trans.*, 2009, 2823-2831.
32. H. Braunschweig, R. Bertermann, P. Brenner, M. Burzler, R. D. Dewhurst, K. Radacki and F. Seeler, *Chem.-Eur. J.*, 2011, **17**, 11828-11837.

Chemical Communications Accepted Manuscript

33. P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229-266.

34. J. Zhu, Z. Lin and T. B. Marder, *Inorg. Chem.*, 2005, **44**, 9384-9390.

35. F. H. Allen and A. Pidcock, *J. Chem. Soc. (A)*, 1968, 2700-2704.

36. T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335-422.

37. P. Nguyen, H. P. Blom, S. A. Westcott, N. J. Taylor and T. B. Marder, *J. Am. Chem. Soc.*, 1993, **115**, 9329-9330.

38. S. A. Westcott, T. B. Marder, R. T. Baker and J. C. Calabrese, *Can. J. Chem.*, 1993, **71**, 930-936.

39. C. Dai, G. Stringer, T. B. Marder, R. T. Baker, A. J. Scott, W. Clegg and N. C. Norman, *Can. J. Chem.*, 1996, **74**, 2026-2031.

40. C. Dai, G. Stringer, J. F. Corrigan, N. J. Taylor, T. B. Marder and N. C. Norman, *J. Organomet. Chem.*, 1996, **513**, 273-275.

41. K. C. Lam, W. H. Lam, Z. Lin, T. B. Marder and N. C. Norman, *Inorg. Chem.*, 2004, **43**, 2541-2547.

42. Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 224105.

43. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theoret. Chim. Acta*, 1990, **77**, 123-141.

44. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.

45. K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283-290.

46. K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor Chem Acta*, 1997, **97**, 119-124.

47. F. Neese, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2012, **2**, 73-78.

48. F. Neese, *J. Comput. Chem.*, 2003, **24**, 1740-1747.

49. D. A. Pantazis, X.-Y. Chen, C. R. Landis and F. Neese, *J. Chem. Theo. Comp.*, 2008, **4**, 908-919.

50. C. Chang, M. Pelissier and P. Durand, *Physica Scripta*, 1986, **34**, 394.

51. E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597-4610.

52. C. van Wüllen, *J. Chem. Phys.*, 1998, **109**, 392-399.

53. A.-R. Allouche, *J. Comput. Chem.*, 2011, **32**, 174-182.

54. C. J. Adams, R. A. Baber, A. S. Batsanov, G. Bramham, J. P. H. Charmant, M. F. Haddow, J. A. K. Howard, W. H. Lam, Z. Lin, T. B. Marder, N. C. Norman and A. G. Orpen, *Dalton Trans.*, 2006, 1370-1373.