COMMUNICATION

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

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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 are 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 catalytic transformations of M–B units, 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 have been reported 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 the patent literature.[29] In this communication we are presenting a straightforward synthetic procedure for a diazaborole which provides methylenediphenyl-phosphine as a second donor unit (Scheme 1) and two examples of reactions of this molecule as a bidentate boryl phosphine

Scheme 1 Formation of the diphenylphosphine diazaborole **1**.

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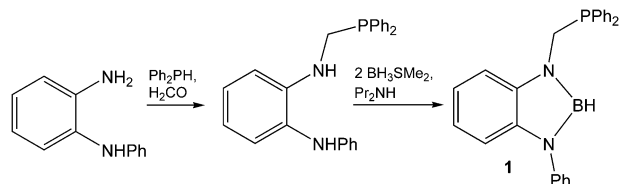
Scheme 2 Synthesis of Pt- and Ir-complexes (nbe = norbornene, bicyclo[2.2.1]hept-2-en; coe = cyclooctene).

ligand with platinum and iridium transition metal complex fragments (Scheme 2).

Following a slight modification of the work of Yamashita and Nozaki we synthesized the methyldiphenylphosphine sub-stituted diazaborole *via* a two-step procedure.[26,27] Starting with *N*-phenyl-*o*-phenylenediamine the methylenediphenyl substitu-ent was introduced in a condensation type reaction (Scheme 1). In the second step two equivalents of borane reagent were 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. Pur-ification by column chromatography yields the ligand in amounts around 4 g (yield 56%). This borane exhibits character-istic signals in the ^{11}B NMR spectrum at 26 ppm and in the ^{31}P NMR spectrum at −22.5 ppm. The electronic properties of benzodiazaboroles were intensively investigated.[30,31]

In order to form a platinum and an iridium complex two equiva-lents of the borane phosphine (B–P) **1** were reacted with [Pt(nbe)₃] and the iridium olefin complex [(coe)₂IrCl]₂ (nbe = norbornene, coe = cyclooctene) (Scheme 2). In both cases the boron coordination com-pound was isolated in high yield after crystallization.

The new coordination compounds **2** and **3** were character-ized by elemental analysis, NMR spectroscopy and single crystal X-ray diffraction (see ESI†). Only one set of resonances was

Fig. 1 Molecular 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).
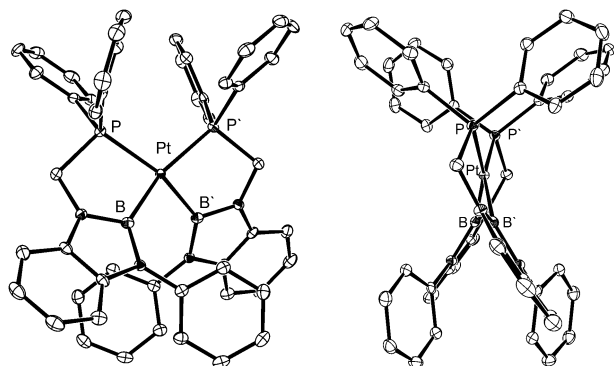

Fig. 2 Molecular structure of compound **3** (two projections). Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°]: Cl–Ir 2.3949(9), Ir–B2 2.067(4), Ir–B1 2.076(4), Ir–P2 2.3086(10), Ir–P1 2.3111(10), B2–Ir–B1 64.73(17), P2–Ir–P1 172.06(3), B2–Ir–Cl 147.28(13), B1–Ir–Cl 147.99(12),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

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)$_2$(PCy$_3$)$_2$] (Cat = 1,2-O$_2$C$_6$H$_4$$^{2-}$) at 49.9 ppm. The ^{195}Pt NMR signal at −4970 ppm lies close to that of *trans*-[Pt(BCat′)Me(PCy$_3$)$_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 of 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 Fig. 1, the platinum is nearly square planar coordinated by two B–P-ligands. The B–Pt–P angles of 80.9° are 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 that of Pt–B bonds with monodentate boryl ligands.[17,19,32]

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(PEt$_3$)$_2$(Bcat)$_2$].[18] The resonance in the ^{31}P NMR spectrum of **2** at 47.7 ppm also shows a downfield shift in comparison to the ligand, which is indicative of 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 (Fig. 2). The geometry and the position of the ligands can be compared with an iridium complex [IrCl(PEt$_3$)$_2$(Bcat)$_2$] reported by Marder and Norman.[18] The length of the Ir–B bonds in **3** lies 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
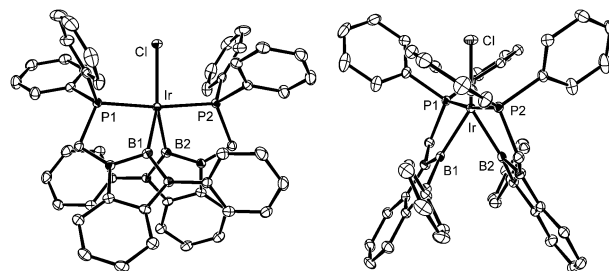
the range of literature values. Interestingly the B–Ir–B angle of 64.7° as well as the B–B interatomic distance (2.221 Å) are significantly smaller in complex **3** in comparison to other bisboryl iridium complexes. Furthermore, the relative orientations of the boryl ligands in complex **3** do allow 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 also exhibits 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 [(PR$_3$)$_2$RhHCl{B(OR′)$_2$}] (R = H, Me, ^{i}Pr, Ph; B(OR′)$_2$ = Bcat, Bpin, cat = 1,2-O$_2$C$_6$H$_4$, pin = OCMe$_2$CMe$_2$O).[23]

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 using 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 ESI† for more details).[45,46,49–52] The structural parameters of the optimized geometry (Fig. 3, left) are in good agreement with the structure determined by X-ray analysis. However the
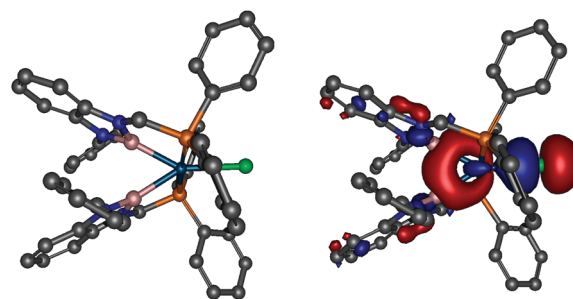

Fig. 3 Left: structure of **3** obtained from geometry optimization. Right: structure of **3** superimposed by its HOMO − 21. Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] (atom numbering according to Fig. 2): Cl–Ir 2.463, Ir–B1,2 2.115, Ir–P1,2 2.329, B2–Ir–B1 59.37, P2–Ir–P1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

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 those of their counterparts, as determined by crystallography. Consequently, the B–B distance (2.095 Å) is 0.126 Å shorter in the optimized structure.

The inspection of the occupied molecular orbitals (MOs) reveals two interesting types of MOs. The first type of MO shows electron density between the iridium centre and each of the boron atoms and the second type of MO 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 ESI†) with only a little (two-centre) σ-interaction between the boron atoms which are either π-bonding orbitals of the diazaborole systems (HOMO − 23 and HOMO − 27) or can be ascribed to three-centre B–Ir–B interactions (HOMO − 5, HOMO − 6 and HOMO − 35). The most distinctive Ir–B σ-bonding molecular orbitals (HOMO − 7 and 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) upon reductive elimination (or alternatively an oxidative addition) reaction coordinate leading finally to the B–B single bond.

We have presented a synthesis procedure 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.

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