Reactions of an anionic chelate phosphane/borata-alkene ligand with [Rh(nbd)Cl]₂, [Rh(CO)₂Cl]₂ and [Ir(cod)Cl]₂†‡

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Borata-alkenes can serve as anionic olefin equivalent ligands in transition metal chemistry. A chelate ligand of this type is described and used for metal coordination. Deprotonation of the Mes₃P(CH₃)₂B(C₆F₅)₂ frustrated Lewis pair in the α-CH[B] position gave the methylene-bridged phosphate/borata-alkene anion. It reacted with the [Rh(nbd)Cl] or [Rh(CO)₂Cl] dimers to give the respective neutral chelate [P/C=B][Rh] complexes. The reaction of the [P/C=B]⁻ anion with [Ir(cod)Cl]₂ proceeded similarly, only that the complex underwent a subsequent oxidative addition reaction at the mesityl substituent. Both the resulting Ir(III)hydride complex 15 and the P/borata-alkene Rh system 12 were used as hydrogenation catalysts. The [P/C=B(C₆F₅)₂]Rh(nbd) complex 12 served as a catalyst for arylacetylene polymerization.

Introduction

Carbanions in the α-position to boryl groups show a conjugative interaction with the adjacent Lewis acid. Such systems can be described as borata-alkenes. Borata-alkenes derived from some alkylidylnoboranes had previously been prepared. Typically, short C–B bond lengths around 1.45 Å were found in these systems. In addition, a variety of related boryl-carbanion ↔ borata-alkene systems were in situ generated and employed as reagents e.g. in borata-Wittig olefination chemistry. These reactions are the formal boron analogues of the conventional phosphorus ylide derived Wittig olefination reaction of organic carbonyl compounds.

It was recently shown that the presence of the strongly electron-withdrawing –B(C₆F₅)₂ group resulted in a markedly increased α-CH acidity in the respective boranes. A DFT study had revealed that, e.g. H₃C–B(C₆F₅)₂ showed a pKₐ-value comparable to that of cyclopentadiene. According to this study the H₃C–B(C₆F₅)₂ borane must be considered >10 pKₐ values more C=H acidic than the related H₃C-BMes₂ borane.

Consequently, R–H₃C–B(C₆F₅)₂ systems were easily deprotonated to give the corresponding [R–HC=B(C₆F₅)₂]⁻ borata-alkene systems. Several of such systems were isolated as their Li⁺ salts. Some were used in borata-Wittig olefination reactions.

Neutral borata-alkene compounds had previously been used as ligands and there are reports about the use of borata-benzenes in organometallic chemistry. There are a few examples of η¹-borata-allyl metal complexes and related systems known. Piers et al. had prepared the borata-alkene tantalocene complex 4 (Scheme 1) and emphasized the relation of the anionic η¹-[H₂C=C(B(C₆F₅)₂)²]⁻ ligand with the neutral η¹-olefin analogues. The Piers group developed some follow-up chemistry of complex 4. C. Martin et al. have just recently described a conceptually related borata-phenanthrene gold complex.

Formal substitution of a hydrogen atom of the borata-alkene =CH₂⁻ terminus by a Mes₃P–CH₂-substituent now gave an anionic [P/C=B]⁻ system that served as a chelate ligand in Rh and Ir coordination chemistry. The preparation of first

Scheme 1 Formation of borata-alkene derivatives containing the =B(C₆F₅)₂ unit.
examples of this class of compounds and some uses are described in this account.

Results and discussion
Development of the chelate phosphane/borata-alkene ligand system

We started our phosphane/borata-alkene chelate ligand synthesis from the ethylene-bridged frustrated P/B Lewis pair (FLP) 7. This was obtained from the hydroboration reaction of Mes₂P-vinyl (5) with Piers’ borane [HB(C₆F₅)₂] (6) as we had previously reported.15

We first attempted deprotonation of 7 at the α-position to the boron atom by treatment with LDA (r.t., pentane, 16 h). Compound 7 is α-CH acidic, but it is also an active boron Lewis acid that is able to abstract hydride from amines in the α-position to nitrogen with iminium salt formation.16 We found that a variant of the latter reaction is favoured in this system. Hydride abstraction from an isopropyl substituent of the LDA reagent by the borane Lewis acid functional group of 7 generated the respective imine. This is found as a component in the product 8 that we isolated from the reaction mixture as a white solid in 67% yield (Scheme 2). Compound 8 was characterized by an X-ray crystal structure analysis (Fig. 1). It shows the intact phosphane/borata-alkene product by spectroscopy and by X-ray diffraction. The X-ray crystal structure analysis confirmed the formation of the borata-alkene functionality. It shows the typical short B1-C2 linkage of 1.441(3)Å, which is much shorter than the adjacent boron-aryl bonds (B1-C31: 1.607(3)Å, B1-C41: 1.602(3)Å). The boron coordination geometry in compound 9 is trigonal-planar (ΣBt 360.0°). The B1-C2-C1 angle amounts to 126.4(2)°. The lithium ion in 9 shows contacts to the borata-alkene unit as well as to the phosphorus atom and one ortho-C₆F₅ fluorine.

![Scheme 2 Reaction of the FLP 7 with LDA.](image1.png)

Fig. 1 Molecular structure of compound 8 (thermal ellipsoids at 15% probability). Selected bond lengths (Å) and angles (°): P1–Li1 2.536(6), F46–Li1 2.051(7), N1–C51 1.475(5), N1–C54 1.297(5), C2–B1–C31 115.8(3), C2–B1–C41 108.3(3), C31–B1–C41 109.1(3).

![Scheme 3 Formation and borylation reaction of the borata-alkene 9.](image2.png)

In order to avoid the unwanted N–CH hydride abstraction we reacted the FLP 7 with the LiTMP reagent, a base that has no CH groups α to nitrogen. The reaction was carried out with the in situ generated FLP 7. Treatment with LiTMP in pentane for 16 h at room temperature followed by workup gave the methylene-linked phosphane/borata-alkene product 9 (Scheme 3), that we isolated as a white solid in 78% yield.

Compound 9 was characterized by C,H,N elemental analysis, by spectroscopy and by X-ray diffraction. The X-ray crystal structure analysis confirmed the formation of the borata-alkene functionality. It shows the typical short B1-C2 linkage of 1.441(3)Å, which is much shorter than the adjacent boron-aryl bonds (B1-C31: 1.607(3)Å, B1-C41: 1.602(3)Å). The boron coordination geometry in compound 9 is trigonal-planar (ΣBt 360.0°). The B1-C2-C1 angle amounts to 126.4(2)°. The lithium ion in 9 shows contacts to the borata-alkene unit as well as to the phosphorus atom and one ortho-C₆F₅ fluorine.
atom. The lithium atom Li\(^+\) also has the HTMP amine ligand bonded to it that had been formed in the deprotonation process (Fig. 2).

In solution (THF-\(d_8\)) compound 9 features a typical borata-alkene \(^{11}B\) NMR signal at \(\delta = 18.6\). The \(^{31}P\) NMR signal is at \(\delta = -20.6\) and the -\(CH_2-CH=\) backbone shows \(^1H\) NMR resonances at \(\delta = 4.21\) (BCH; \(^{13}C:\ \delta = 106.7\) (br)) and \(\delta = 3.36\) (CH\(_2\); \(^{13}C:\ \delta = 33.5\), \(J_{PC} = 16.0\) Hz). The \(^{19}F\) NMR spectrum of compound 9 shows two equal-intensity sets of \(o/p/m\)-resonances of the \(C=B(C_6F_5)_2\) moiety (E and Z to the alkyl group at the adjacent sp\(^2\)-hybridized borata-alkene carbon atom C2).

We briefly investigated the nucleophilic property of the borata-alkene unit in compound 9. For that purpose, we reacted it with the ClB(C\(_6\)F\(_5\))\(_2\) reagent.\(^{14,17}\) The reaction (in toluene, r.t., \(16\) h) resulted in a substitution reaction at boron to give the P/B/B compound 10 (isolated as a yellow solid in 52\% yield). It was characterized by C, H-elemental analysis, by spectroscopy and by its reaction with dihydrogen (see below). Compound 10 is a typical intramolecular FLP, showing a P–B interaction with one boron atom and having the other one free. However, the temperature dependent \(^{19}F\) NMR spectrum showed exchange between the pair of \(B(C_6F_5)_2\) groups at e.g. 299 K. Only at low temperature (e.g. 203 K) we observed a set of three broad \(^{19}F\) NMR resonances of a free trigonal planar \(B(C_6F_5)_2\) unit and a set of ten separate signals [four ortho, two para and four meta] of the rotationally hindered P–\(\cdot\cdot\cdot\)B(\(C_6F_5)_2\) group. The \(^{31}P\) NMR (299 K) signal of compound 10 is at \(\delta = 16.3\) and the \(-CH_2-CH=\) backbone shows \(^1H\) NMR features at \(\delta = 3.55\) and \(\delta = 4.30\), respectively (\(^{13}C:\ \delta = 29.2\), 38.1 (br)).

Compound 10 reacted rapidly with dihydrogen under mild conditions (\(d_c\)-benzene, r.t., \(16\) h, 1 bar \(H_2\)) to give the phosphonium/hydridoborate dihydrogen splitting product 11 (isolated as a solid in 71\% yield). The X-ray crystal structure analysis (Fig. 3) showed the presence of the phosphonium unit (\(\Sigma P^1CC\) 339.7°) and the newly formed hydride-bridged bisborane moiety. In solution (CD\(_3\)Cl\(_2\)) the phosphonium [\(P^1\)-H] unit showed up at \(\delta = 7.58\) (\(^1H\) NMR) and \(\delta = -3.7\) (\(^{31}P, J_{PH} \sim 480\) Hz), respectively. We recorded a broadened \(^{11}B\) NMR signal at \(\delta = -18.1\) with a corresponding broad \(^1H\) NMR [\(\beta\)]\(\mu\)-H) feature at \(\delta = 5.45\). The \(^{19}F\) NMR spectrum of compound 11 shows two equal-intensity sets of \(o/p/m\)-C\(_6\)F\(_5\) signals of the pair of \(B(C_6F_5)_2\) groups and we observed the \(^1H/\(^{13}C\) NMR signals of the \(-CH_2-CH\) backbone at \(\delta = 2.84/27.8\) (PCH\(_2\)) and \(\delta = 1.80/7.6\) (br)(BCH), respectively.

**Synthesis and characterization of the P/C=B chelate metal complexes**

We used the methylene-bridged phosphane/borata-alkene anion of the lithium salt 9 as a chelate ligand in Rh chemistry. For that purpose, we treated the (norbornadiene)RhCl dimer with the prefabricated borata-alkene reagent 9 for 18 h in toluene solution at room temperature. Workup then gave the respective neutral chelate phosphane/borata-alkene(norbornadiene)Rh complex 12 in >60\% yield (Scheme 4). Suitable crystals for the X-ray crystal structure analysis were obtained from slow diffusion of pentane into a saturated solution in dichloromethane at -30 °C (Fig. 4). Compound 12 shows a distorted square-planar coordination geometry at rhodium. The P/C=B system serves as a chelate ligand. It is

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**Fig. 3** Molecular structure of the P/B/B dihydrogen splitting product 11 (thermal ellipsoids at 30\% probability). Selected bond lengths (Å) and angles (°): B1–C1 1.601(3), B2–C2 1.601(3), C1–C2 1.524(3), C1–P1–C11 107.3(1), C1–P1–C21 121.1(1), C11–P1–C21 111.3(1).

**Fig. 4** A view of the molecular structure of the chelate phosphane/borata-alkene Rh complex 12 (thermal ellipsoids at 30\% probability).
unsymmetrically $\eta^2$-coordinated through both backbone atoms of the borata-alkene moiety and k$^p$-bonded to the attached phosphanyl group. As the P/C=C=B ligand is mono-anionic, the resulting Rh complex is neutral. The C2–B1 bond is only marginally elongated, it is still within the typical C=B distance of borata-alkene examples\(^5\) (Table 1). The metal center has both olefinic $\pi$-systems of the norbornadiene ligand bonded through its endo-face. Both olefinic units are oriented perpendicular to the mean coordination plane of the transition metal center. In complex 12 the phosphane donor exhibits a stronger structural trans-effect\(^*\) than the borata-alkene ligand as judged from the respective Rh–C (olefin) bond lengths [trans: Rh1–C54: 2.214(2) \AA, Rh1–C55: 2.213(2) \AA; cis: Rh1–C51: 2.172(2) \AA, Rh1–C52: 2.162(2) \AA, see Fig. 4].

In solution, complex 12 shows a $^{31}$P NMR signal (CD$_2$Cl$_2$) at $\delta$ = 89.0 with a $^{1}J_{PB}$ $\approx$ 120 Hz coupling constant. This changed only marginally when the spectrum of 12 was recorded in d$_{6}$-THF solution. Compound 12 shows a $^{11}$B NMR signal at $\delta$ 24.3, a value that is similar to that of the uncomplexed borata-alkene anion 9 (see above).\(^5\) The $^{31}$P NMR spectrum of 12 shows two sets of $\alpha$, $\beta$, $\gamma$, $\delta$-C$_6$F$_5$ signals for the pair of pentafluorophenyl substituents at boron. We observed the $^1$H NMR signals of the chelate ligand backbone at $\delta$ 4.14/3.90 (PCH$_2$) and $\delta$ 3.68 (B–CH$_2$) respectively (corresponding $^{13}$C NMR signals at 59.8 [br]), and there are the $^1$H/$^{13}$C NMR signals of the coordinated norbornadiene ligand at rhodium (see the ESI\(^\dagger\) for details).

The reaction of the P/borata-alkene lithium salt 9 with the chloro(dicarbonyl)Rh dimer was carried out at r.t. (in dichloromethane, 2 h). Workup involving extraction with pentane and crystallization gave the neutral chelate P/borata-alkene Rh(CO)$_2$ complex 13 as a yellow crystalline solid in 46% yield. The X-ray crystal structure analysis (Fig. 5) showed a distorted square planar coordination geometry around Rh. The phosphane (P1–Rh1: 2.335(1) \AA) and the borata-alkene moiety of the chelate ligand are both bonded to rhodium (Rh1–C2: 2.251(4) \AA, Rh1–B1: 2.590(5) \AA). The B1–C2 linkage is found in the typical borata-alkene range at 1.476(7) \AA. Again, the phosphane exerts a stronger trans effect than the C=B unit [Rh1–C4 (CO trans to P1): 1.915(5) \AA, Rh1–C3 (CO cis to P1): 1.868(5) \AA]. Compound 13 shows strong IR CO bands at $\nu$ = 2069 and 1997 cm$^{-1}$.$^{19}$ In CD$_2$Cl$_2$ solution it shows a $^{11}$B NMR signal at $\delta$ 27.3, i.e. in the typical borata-alkene range. The $^{31}$P NMR resonance was located at $\delta$ = $-$105.0 with a $^{1}J_{PB}$ = 88.5 Hz coupling constant. The borata-alkene unit in complex 13 shows $^{19}$F NMR signals of a pair of inequivalent $\text{C}_6\text{F}_5$ substituents at boron.

The reaction between the borata-alkene reagent 9 and the iridium(cyclooctadiene)chloride dimer was carried out similarly (toluene, 24 h, r.t.). It gave a slightly different outcome. We assume that initially a (P/borata-alkene)Ir(cod) complex 14 was generated, analogous to the formation of the Rh system 12. However, it was apparently not persistent under the prevailing reaction conditions but underwent intramolecular C–H bond activation\(^28\) at an ortho-methyl group of a mesityl substituent at phosphorus to give the oxidative addition product 15 (Scheme 4). It was isolated in 44% yield. Complex 15 was characterized spectroscopically and by X-ray diffraction (single crystals were obtained by crystallization from pentane at $-$30 $^\circ$C).

The X-ray crystal structure analysis of complex 15 revealed that the iridium atom has undergone oxidative addition at a mesityl group at phosphorus, with formation of a new benzylic –CH$_2$–Ir–H moiety (Fig. 6). The resulting Ir-hydride shows a contact to the boron atom. We note that the C2–B1 linkage in 15, consequently, is much longer than in 9 or 12, it corresponds to a short boron-carbon $\sigma$-bond. The Ir–C2 linkage is rather short (Table 1). The hydride is bridging between Ir and B [independent molecule A: Ir1A–H01 1.64(4) \AA, H01–B1A 1.56(4) \AA; molecule B: Ir1B–H02 1.59(4) \AA, H02–B1B 1.50(4) \AA] (Fig. 6).

In solution (CD$_2$Cl$_2$) the iridium complex 15 shows four olefinic $^1$H NMR signals of the coordinated cyclooctadiene ligand. It also features four arene CH$^1$H NMR signals of the mesitylene and the CH-activated Mes substituents at phosphorus. Complex 15 shows a broadened $^{13}$B NMR resonance at $\delta$ = $-$17.5. The $^{31}$P NMR signal is observed at $\delta$ = $-$104.0. It shows coupling to the Ir–H moiety ($^{2}J_{PH}$ $\approx$ 70 Hz).$^{24}$ Consequently, the Ir-hydride signal shows up at $\delta$ = $-$10.4 with ca. 70 Hz coupling to phosphorus (for additional details see the ESI\(^\dagger\)).

### Catalytic reactions

Our study has shown that the methylene linked phosphane/borata-alkene anion of the salt 9 served well as a chelate ligand in Rh coordination chemistry. It is likely that the Ir(u)
complex 15 was actually formed by an oxidative addition reaction at a mesityl methyl group at the stage of the analogous intermediate 14. We carried out some preliminary investigation toward the use of the new chelate phosphane/borata-alkene complexes in catalysis. For this reason, we performed two sets of catalytic reactions using either of the complexes 12 and 15. We first turned to alkene and alkyne hydrogenation catalysis.

Exposure of complex 15 to dihydrogen (1.0 bar, r.t.) revealed the stoichiometric formation of cyclooctane, the reduction product of the cod ligand of the Ir complex 15. Consequently, we employed compound 15 as a catalyst in our hydrogenation experiments. The hydrogenation of styrene is a typical example. With both 1 or 0.5 mol% of 15 quantitative hydrogenation to ethylbenzene was achieved (Scheme 5); with 0.1 mol% catalyst still a ca. 50% conversion was obtained. The catalytic hydrogenation sequence starting from complex 15 may possibly involve the not directly observed equilibration with its likely synthetic precursor 14, the Ir(cod) analogue of the Rh complex 12 (see above).

Quantitative alkene hydrogenation was found at the 15 derived catalyst system with 1 mol% of vinylcyclohexene or cyclohexene, as well. The more sterically encumbered 1-methylcyclohexene substrate gave only a 39% conversion under these conditions and phenylacetylene eventually furnished a ca. 3:1 mixture of styrene and ethylbenzene with a combined conversion of 77% after 16 h.

Styrene was quantitatively hydrogenated to ethylbenzene with 0.5 mol% of the Rh catalyst 12 under our standard conditions (Scheme 6). With 0.1 mol% a ca. 50% conversion was obtained, similar as with the Wilkinson catalyst under these conditions. Cyclohexene was hydrogenated at the catalyst system 12 (0.1 mol%, 34% conversion). The bulkier 1-methylcyclohexene was not hydrogenated at the Rh catalyst system 12 under our typical conditions.

So far we assume a conventional pathway of dihydrogen activation at the metal centre in the complexes 12 or 15, but we presently cannot rule out an alternative “FLP-like” metal/borane dihydrogen splitting reaction.24

A variety of Rh catalysts are able to polymerize arylacetylenes and so does the phosphane/borata-alkene complex 12.25 The phenylacetylene polymerization reaction by the neutral system 12 was carried out in the non-polar solvent benzene or in ethereal solution (diethyl ether or tetrahydrofuran). We carried out the phenylacetylene polymerization at room temperature for a duration between 30 min (in ether) or 2 h (in benzene). With decreasing catalyst amounts (0.1 mol%, 0.05 mol%) an almost quantitative amount of polyphenylacetylene was isolated from the reaction in benzene. Even with 0.025 mol% as well as 0.01 mol% of the catalyst poly(phenylacetylene) was isolated, albeit in lower yields (45%, 28%). The obtained polymer was similar in appearance (yellow to orange solids) as the poly(phenylacetylene) obtained by Noyori et al. at the remotely related neutral [(Ph3P)n(hbd)Rh-CCPh] (n: 1 or 2) derived catalysts, so we assume it has a similar structure.25 A We also polymerized p-fluorophenylacetylene and p-
methoxynaphthalene at the catalyst system 12 (0.1 mol%) and isolated the respective polyacetylenes in close to quantitative yields (Scheme 7).26

Each of the arylacetylene polymers shows a single set of 1H NMR signals, which indicates its origin from a stereo- and regioselective polymerization process25a (see the ESI‡ for details). The poly(p-ansylacetylene) sample was characterized by MALDI-TOF mass spectrometry, which showed the regular sequence of signals separated by the mass of the respective monomer unit of 132 (depicted in the ESI‡). The molecular weights of the polyacetylene samples were determined by GPC. Under our typical conditions, the polymerization reactions in benzene or THF furnished polymers of somewhat lower molecular weight than in ether. The latter reaction produced a higher molecular weight polyacetylene.27 The samples contained varying amounts of insoluble material (potentially very high molecular weight polymer). For the sizable soluble fraction of the poly(p-ansylacetylene) sample obtained in ether with the Rh complex 12 derived catalyst we found a molecular weight of \( M_n \geq 100000 \). The respective poly(phenylacetylene) sample had an about twice as high \( M_n \), and the poly(p-fluoroacetylene) had the highest measured \( M_n \) in the series of \( >400000 \) (Table 2). In all cases rather large polydispersities of close to 3 were found (see the ESI‡ for further details).

### Conclusions

Our study has shown that the seminal study published by Piers et al. on the use of a borata-alkeene as a π-ligand equivalent to ethene at an early transition metal can be substantially extended. In the Piers’ system the \( \text{H}_2\text{C} \equiv \text{B} (\text{C}_6\text{F}_5) _2 \) ligand was generated by a typical organometallic reaction pathway within the coordination sphere of the metal (in that case at tantalum). Since we found about the vastly increased \( x\text{-CH} \) acidity of the \( \text{B}(\text{C}_6\text{F}_5) _3 \) boranes4 an improved and potentially more general pathway to \( \text{K}^+\text{C}_2\text{B} \)-borata-alkeene complexes has become evident: deprotonation of the respective substituted \( [\text{P}]^{-}\text{CH}_3\text{–CH}_2\text{–B}(\text{C}_6\text{F}_5) _3 \) borane gave the borata-alkeene in an independent initial step. Our syntheses of the methylene-bridged chelate phosphane/borata-alkeene Rh and Ir complexes serve as examples of this development. The complexes are readily prepared, although the Ir system undergoes a subsequent rearrangement reaction. This new approach will probably allow for some variation on the ligand side, and it may open pathways to choosing variations on the metal side. The P/C=–B ligands in the here reported complexes do not interfere with catalytic features in our examples. To us this indicates that the readily available borata-alkenes might see useful applications as polar alkene ligand analogues in organometallic and coordination chemistry as well as in catalysis.

### Conflicts of interest

There are no conflicts to declare.

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