Exploring unsymmetrical diboranes(4) as boryl ligand precursors: platinum(II) bis-boryl complexes†

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A series of five unsymmetrical platinum(II) bis-boryl complexes, bearing two distinct boryl ligands, are obtained by the oxidative addition reaction of unsymmetrical diborane(4) derivatives, bearing either two different dialkoxy or one dialkoxy and one diamino boryl moiety, with [Pt3P]2Pt(C2H4)2. All five complexes were structurally and spectroscopically characterised. The bis-boryl platinum(II) complexes exhibit slightly distorted square-planar cis-boryl structures with acute B–Pt–B angles, short B–B distances of 2.44–2.55 Å and relatively long trans-boryl P–Pt distances around 2.34 Å. The 31P–195Pt NMR coupling constants are indicative for the strongly donating/trans-influencing boryl ligands. Despite the structural and spectroscopic data at hand no finally conclusive order of the donor properties/trans-influence of the boryl ligands can be deduced on the basis of these data. This may be explained by an (residual) interaction of two boryl ligands.

Introduction

Boryl complexes of transition metals have received considerable attention in the last few years, either due to their role as reactive intermediates in various catalytic processes or due to their unique coordination properties and reactivity of their complexes.1,2 In particular a substantial number of boryl platinum(II) complexes have been reported over the last years, amongst these complexes those of the type (R3P)2Pt(boryl)2 are especially well studied.3–6 The latter type of complexes are typically straightforwardly prepared by the oxidative addition reaction of a diborane(4) derivative (1) with a suitable platinum(0) precursor (e.g. [Pt(R3P)2(C2H4)]2 (2)) and, most importantly, more than 35 complexes of this type are structurally and spectroscopically characterised.3,4 About half of these complexes are symmetrical complexes of the specific type [[(R3P)2Pt(boryl)]2] (3) with both identical boryl ligands ranging from dialkoxy and diaryloxy boryl ligands but also including ligands such as BCl(NMe2) or BF2 (Scheme 1). Moreover, we have reported the first unsymmetrical congeners with one dialkoxy and one diamino boryl ligand ([[R3P]2Pt(Bpin)[B(NR)2C6H4]] with R = Me (3ad) and R = Bn).3 Hence, complexes of the type [[(R3P)2Pt(boryl)]2] (3) suggest themselves as well suited to comparatively study the coordination properties of different boryl ligands due to their abundant data available and their facile synthesis. In particular, complexes of the type cis-[[(R3P)2PtXY] [X, Y: anionic ligands] have been especially useful to study the cis and the trans influence of different anionic ligands X, Y.7

We have recently reported the synthesis of a number of unsymmetrical diborane(4) bearing different dialkoxy as well as one diaryloxy boryl ligand.8

Scheme 1 Synthesis of 3aa and examples of complexes [[(R3P)2Pt(boryl)]2].3,4
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as one dialkoxy and one dianinoboryl moieties (1) as potential precursors for boryl complexes. In this work we endeavour to the study reactivity of these diborane(4) derivatives towards 2 and the coordination properties of the resulting unsymmetrical platinum boryl complexes of the type \([\text{[Ph}_3\text{P}]_2\text{Pt(boryl)(boryl)}^\prime]\).
The facile availability of this series of unsymmetrical complexes \([\text{[Ph}_3\text{P}]_2\text{Pt(boryl)(boryl)}^\prime]\) renders a comparative study of sterically and electronically different boryl moieties within one complex fragment for the first time possible.

### Experimental

#### General considerations

The unsymmetrical diboranes(4) 1ab, 1ac, 1ae-ag, 1bd and 1be were prepared according to literature procedures. The synthesis and analytical data of 1hh are described in the ESL. All other compounds were commercially available and were used as received; their purity and identity was checked by appropriate methods. All solvents were dried using MBraun solvent purification systems, deoxygenated using the freeze–pump–thaw method and stored under purified nitrogen. All manipulations were performed using standard Schlenk techniques under an atmosphere of purified nitrogen or in a nitrogen filled glove box (MBraun). NMR spectra were recorded on Brucker Avance II 300, Avance III HD 300, Avance III 500 or Avance 600 spectrometers. For air sensitive samples NMR tubes equipped with screw caps (WILMAD) were used and the solvents were dried over potassium/benzophenone and tubes equipped with screw caps (WILMAD) were used and the solvents were dried over potassium/benzophenone and degassed. Chemical shifts (δ) are given in ppm, using the (residual) resonance signal of the solvents for calibration (C6D6: 1H NMR: 7.16 ppm, 13C NMR: 128.06 ppm).\(^{10,11}\) B[1H] and 1P[1H] NMR chemical shifts are reported relative to external BF3·Et2O and 85% aqueous H3PO4, respectively. 13C[1H], 1B[1H] and 31P[1H] NMR spectra were recorded employing composite pulse 1H decoupling. If necessary 2D NMR techniques were employed to assign the individual signals (1H–1H NOESY (1 s mixing time), 1H–1H COSY, 1H–13C HSQC, 1H–13C HMBC and 1H–31P HMBC). Melting points were determined in flame sealed capillaries under nitrogen using a Büchi 535 apparatus and are not corrected. Elemental analyses were performed at the Institut für Anorganische und Analytische Chemie of the Technische Universität Carolo-Wilhelmina zu Braunschweig using an Elementar vario MICRO cube instrument. GC/MS measurements were performed using a Shimadzu GCMS-QP2010SE instrument operating in positive EI mode (70 eV, 60–700 m/z) with the following conditions: injection temperature 250 °C; interface temperature 280 °C; temperature program: start temperature 50 °C for 3 min, heating rate 10 °C min \(^{-1}\), end temperature 310 °C for 3 min; column type: ZB-5MS, 30 m × 0.25 mm, 0.25 μm film thickness; He carrier gas (1.0 mL min \(^{-1}\)).

**X-ray diffraction studies.** The crystals were, inside a nitrogen-filled glovebox, transferred into inert perfluoroether oil and, outside of the glovebox, rapidly mounted on top of a human hair or a MITEGEN mount and placed in the cold nitrogen gas stream on the diffractometer.\(^{14e}\) The data were either collected on an Oxford Diffraction Xcalibur Eos instrument using graphite monochromated MoKα radiation (conventional sealed X-ray tube), an Oxford Diffraction Nova Atlas instrument using mirror-focused CuKα radiation (micro focus source) or an Rigaku Oxford Diffraction XtaLAB Synergy HyPix instrument using mirror-focused MoKα radiation (micro focus source). The reflections were indexed, integrated and absorption corrections applied as implemented in the CrystAlisPro software.\(^{14e}\) The structures were solved employing the programs SHELXT or SHELXS and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on all F\(^2\) using SHELXL software.\(^{14e}\) Generally hydrogen atoms were refined employing a riding model; methyl groups were treated as rigid bodies and were allowed to rotate about the C–CH\(_3\) bond. During refinement and analysis of the crystallographic data the programs WinGX, PLATON, DSR, Mercury and Diamond were used.\(^{14f}\) Unless noted otherwise the shown ellipsoids represent the 50% probability level and the hydrogen atoms are omitted for clarity; adapted numbering schemes may be used to facilitate readability.

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\text{[Pt(PPh}_3\text{)\text{]}_2(Bpin)(Bcat)] (3ab)}.
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\text{[Pt(PPh}_3\text{)\text{]}_2(C}_2\text{H}_4\text{)\text{] (2) (50 mg, 67 μmol, 1.0 eq.) and pinB–Bcat (1ab) (16.4 mg, 67 μmol, 1.0 eq.) were mixed in toluene (5 mL). The red solution was stirred at room temperature for 5 h whilst flask was evacuated for a few seconds every 60 min. The solvent was removed under reduced pressure to give a brownish solid, from which after recrystallization by vapour diffusion of n-pentane in a benzene solution at room temperature colourless (single) crystals of 3ab(C\(_6\text{H}_6\))\(_{1/2}\) (39 mg, 39 μmol, 58%) were obtained after drying in vacuo. Mp 189 °C (decomposition, from n-pentane/C\(_6\text{H}_6\)). Found: C, 60.95; H, 5.2. Calc. for C\(_{54}\text{H}_{32}\text{B}_2\text{O}_4\text{P}_2\text{Pt} (3ab(C}_6\text{H}_6\))\(_{1/2}\): C, 61.0; H, 4.9)
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eq.) were mixed in toluene (5 mL). The orange-red solution was stirred at room temperature for 3 h whilst flask was evacuated for a few seconds every 30 min. The solvent was removed under reduced pressure to give an orange-red solid. The latter was recrystallised by vapour diffusion of n-pentane into a THF solution at room temperature. The product was obtained as a colourless single crystalline solid (21 mg, 22%, mp 165 °C). The mother liquor was layered with additional n-pentane to give additional slightly less pure product as a pale orange solid (12 mg, 13 mil), 19%). Mp 149 °C (decomposition, from n-pentane/THF). Found: C, 59.05; H, 5.4%. Calc. for C\textsubscript{52}H\textsubscript{63}B\textsubscript{2}O\textsubscript{2}P\textsubscript{2}Pt (3ac): C, 58.8; H, 5.5%. \(\delta_{\text{H}}\) (500 MHz, C\textsubscript{6}D\textsubscript{6}, rt): 0.79 (6H, s, OC(CH\textsubscript{3})\textsubscript{3}), 1.04 (12H, s, OC(CH\textsubscript{3})\textsubscript{3}), 3.04 (4H, s, OC(CH\textsubscript{3})\textsubscript{2}), 6.86–6.96 (18H, m, CH\textsubscript{N}H\textsubscript{2}), 7.57–7.66 (6H, m, 2-CH\textsubscript{2}PPh\textsubscript{3}(trans-Bnep)). 0\textsubscript{1}B\textsubscript{1}H\textsubscript{1} (125 MHz, C\textsubscript{6}D\textsubscript{6}, rt): 23.1 (OC(CH\textsubscript{3})\textsubscript{3}), 25.6 ((OC(CH\textsubscript{3})\textsubscript{2})C(CH\textsubscript{3})\textsubscript{3}), 31.9 ((OC(CH\textsubscript{3})\textsubscript{2})C(CH\textsubscript{3})\textsubscript{2}), 72.0 (d, \textit{J}_{CP} = 4 Hz, J\textsubscript{CP} = 44 Hz (satellites) (OC(CH\textsubscript{3})\textsubscript{2})C(CH\textsubscript{3})\textsubscript{2}), 80.9 (d, \textit{J}_{CP} = 3 Hz, J\textsubscript{CP} = 38 Hz (satellites), OC(CH\textsubscript{3})\textsubscript{2}), 127.7 (d, \textit{J}_{CP} = 10 Hz, 3-CH\textsubscript{3}PPh\textsubscript{3}), 127.9 (d, \textit{J}_{CP} = 10 Hz, 3-CH\textsubscript{3}PPh\textsubscript{3}), 129.0 (br, \textit{J}_{CP} = 1.2 Hz, 4-CH\textsubscript{3}PPh\textsubscript{3}), 129.1 (br, s, 4-CH\textsubscript{3}PPh\textsubscript{3}), 134.7 (d, \textit{J}_{CP} = 13 Hz, J\textsubscript{CP} = 13 Hz (satellites), 2-CH\textsubscript{2}PPh\textsubscript{3}(trans-Bnep)), 135.1 (d, \textit{J}_{CP} = 13 Hz, J\textsubscript{CP} = 13 Hz (satellites), 2-CH\textsubscript{2}PPh\textsubscript{3}(trans-Bnep)), 137.0–137.8 (m, 1-CH\textsubscript{2}PPh\textsubscript{3}), 1455 Hz (satellites), PPh\textsubscript{3}(trans-Bnep)), 33.7 (\textit{J}_{CP} = 1585 Hz (satellites), PPh\textsubscript{3}(trans-Bnep)). 0\textsubscript{1}B\textsubscript{1}H\textsubscript{1} (161 MHz, C\textsubscript{6}D\textsubscript{6}, rt): 25.0 Hz), \(\delta_{\text{H}}\) (500 MHz, C\textsubscript{6}D\textsubscript{6}, rt): 27.5 (\textit{J}_{CP} = 1455 Hz (satellites), PPh\textsubscript{3}(trans-Bnep)). 33.7 (\textit{J}_{CP} = 1585 Hz (satellites), PPh\textsubscript{3}(trans-Bnep)). 0\textsubscript{1}B\textsubscript{1}H\textsubscript{1} (161 MHz, C\textsubscript{6}D\textsubscript{6}, rt): 25.0 Hz), \(\delta_{\text{H}}\) (500 MHz, C\textsubscript{6}D\textsubscript{6}, rt): 27.5 (\textit{J}_{CP} = 1455 Hz (satellites), PPh\textsubscript{3}(trans-Bnep)). 33.7 (\textit{J}_{CP} = 1585 Hz (satellites), PPh\textsubscript{3}(trans-Bnep)). 0\textsubscript{1}B\textsubscript{1}H\textsubscript{1} (161 MHz, C\textsubscript{6}D\textsubscript{6}, rt): 25.0 Hz), \(\delta_{\text{H}}\) (500 MHz, C\textsubscript{6}D\textsubscript{6}, rt): 27.5 (\textit{J}_{CP} = 1455 Hz (satellites), PPh\textsubscript{3}(trans-Bnep)). 33.7 (\textit{J}_{CP} = 1585 Hz (satellites), PPh\textsubscript{3}(trans-Bnep)). 0\textsubscript{1}B\textsubscript{1}H\textsubscript{1} (161 MHz, C\textsubscript{6}D\textsubscript{6}, rt): 25.0 Hz).
| Compound | 3ab(C₆H₆) | 3ac | 3ae(C₄H₈O)₁.₅ | 3bd | 3be(C₆H₆) | 3cc(C₄H₈O) | 3hh(C₄H₈O) |
|----------|----------|-----|----------------|-----|----------|----------|-----------|
| Formula  | C₄H₁₂B₂O₄P₂Pt | C₄H₁₂B₂O₄P₂Pt | C₄H₁₂B₂O₄P₂Pt | C₃H₅₀B₂N₂O₄P₂Pt | C₃H₅₀B₂N₂O₄P₂Pt | C₃H₅₀B₂N₂O₄P₂Pt |
| M_r/(g mol⁻¹) | 1043.60 | 959.53 | 1051.70 | 982.52 | 1013.59 | 1017.61 |
| Crystal shape | Rod | Irregular block | Rhombohedron | Block | Prism | Block |
| Crystal colour | Clear colourless | Clear colourless | Clear colourless | Clear pale yellow | Clear light orange | Clear colourless |
| Crystal dim./mm³ | 0.49 × 0.13 × 0.06 | 0.40 × 0.33 × 0.21 | 0.32 × 0.17 × 0.16 | 0.55 × 0.36 × 0.28 | 0.53 × 0.25 × 0.25 | 0.41 × 0.23 × 0.11 |
| Crystal system | Triclinic | Orthorhombic | Monoclinic | Triclinic | Triclinic | Monoclinic |
| Space group (no.) | P̅1 (2) | P̅ba (61) | P̅ba (61) | P̅1 (2) | P̅1 (2) | P̅1 (2) |
| a/Å | 13.1742(5) | 18.1453(3) | 13.1260(3) | 13.4322(3) | 11.8505(3) | 12.6116(6) |
| b/Å | 15.3010(5) | 14.2463(3) | 12.8989(3) | 13.6477(4) | 11.8550(5) | 14.3974(7) |
| c/Å | 24.3714(13) | 33.2215(7) | 29.1381(6) | 14.5369(4) | 21.5121(9) | 14.9326(7) |
| α | 73.469(4) | 90° | 73.469(4) | 90° | 70.017(2) | 94.470(3) |
| β | 89.111(4) | 90° | 89.111(4) | 90° | 70.017(2) | 94.470(3) |
| γ | 87.082(3) | 90° | 87.082(3) | 90° | 70.017(2) | 94.470(3) |
| V/˚A³ | 4703.6(4) | 8588.0(3) | 4849.0(2) | 2186.9(1) | 2257.8(2) | 2289.4(2) |
| Z, Z' | 8, 1 | 2, 1 | 2, 1 | 2, 1 | 2, 1 | 2, 1 |
| D_α/kcal/(g cm⁻³) | 1.474 | 1.484 | 1.484 | 1.441 | 1.494 | 1.476 |
| μ/mm⁻¹ (λ/Å) | 3.097 (0.7103) | 3.384 (0.7103) | 3.005 (0.7103) | 3.321 (0.7103) | 3.211 (0.71073) | 3.180 (0.71073) |
| Absorption corr. | Analytical | Gaussian | Gaussian | Analytical | Analytical | Gaussian |
| 2θ range (compl.) | 4.7–54.2° (99.4%) | 4.4–56.0° (100%) | 4.5–60.0° (99.9%) | 4.5–68.0° (99.7%) | 4.5–68.0° (99.7%) | 4.4–68.0° (99.4%) |
| Refl. Measured | 195.947 | 144.260 | 29.899 | 275.463 | 65.840 | 18.989 |
| Unique (R_int) | 20.759 (0.0195) | 10.365 (0.0465) | 29.899 | 18.533 (0.0426) | 13.137 (0.0315) | 18.989 |
| observed<sup>a</sup> | 13.218 | 9040 | 117184 | 16987 | 12617 | 1657 |
| Param./restr. | 11.430 | 511/0 | 593/0 | 534/0 | 552/0 | 547/0 |
| R₁ (obs. rfdns)<sup>b</sup> | 0.0093 | 0.0046 | 0.0089 | 0.0056 | 0.0056 | 0.0046 |
| wR<sub>2</sub> (all rfdns)<sup>c</sup> | 0.0083 | 0.0056 | 0.0056 | 0.0044 | 0.0035 | 0.0035 |
| Goof on F² | 0.019 | 0.1234 | 0.786 | 1.120 | 1.095 | 1.004 |
| max/min. ½ρ/ε (Å⁻³) | 1.646/−0.947 | 1.009/−0.724 | 2.305/−0.982 | 1.877/−1.095 | 0.518/−1.035 | 1.814/−1.177 |
| CCDC no. | 1881540 | 1881536 | 1881534 | 1881538 | 1881541 | 1881537 |

<sup>a</sup> Obs. criterion: I > 2σ(I).<sup>b</sup> The crystal is non-merohedrally twinned and contains disordered solvent. <sup>c</sup> The crystal is a non-merohedrally three-component twin.
13.2 Hz, J_{C-Pt} = 13 Hz (satellites), {CH}_{pph}), 136.6 (vitr. t, J_{C-Pt} = 3.5 Hz, J_{C-Pt} = 11 Hz (satellites), C_{pph}), 136.7-137.0 (m, C_{pph}), 151.1, (d, J_{C-Pt} = 2.9 Hz, C_{cat}, J_{\delta(CH2)} = 202 MHz, C_{ds}, rt): 30.9 (J_{P-Pt} = 1520 Hz (satellites), P_{pph}, 35.6 (J_{P-Pt} = 1745 Hz (satellites), P_{pph}, \delta(CH2) = 161 MHz, C_{ds}, rt): 46 (br. s, \Delta \nu_{1/2} = 2135 Hz).

\textbf{[Pt(PPH)]=([Bneop])]} (3c). \textbf{[Pt(PPH)=([C2H4])]}} (2) \text{(50 mg, 67 \mu mol, 1.0 eq.)} and \text{Bz2neop} (1eq) (15.1 mg, 67 \mu mol, 1.0 eq.) were mixed in toluene (5 mL). The pale-yellow solution was stirred at room temperature for 6 h whilst flask was evacuated for a few seconds every 30 min. The solvent was removed under reduced pressure to give an off-white solid. The residue was recrystallised from THF/n-pentane at -40 \degree C to give analytically pure 3c (36 mg, 38 \mu mol, 57\%). Single crystals suitable for X-ray diffraction analysis were obtained by vapour diffusion of n-pentane into a THF solution at room temperature. Mp 154 \degree C (decomposition). Found: C, 58.6; H, 5.5. Calc. for C_{36}H_{50}B_{2}O_{2}P_{2}Pt (3c): C, 58.4; H, 5.3. \delta(CH2) = 500 MHz, C_{ds}, rt): 0.70 (12H, s, OC(CH2)2CH2), 3.20 (8H, br. s, J_{C-Pt} = 7 Hz (satellites), OC(CH2)2CH2), 6.88-6.95 (18H, m, CH_{pph}), 7.64-7.72 (12H, m, 2-CH_{map}), \delta(CH2) = 125 MHz, C_{ds}, rt): 22.7 ((O(CH2))2C(CH3)2), 6.88 (2H, t, J_{C-Pt} = 7.6 Hz, 5-CH_{map}), 6.82 (2H, t, J_{C-Pt} = 7.6 Hz, 6-CH_{map}), 6.81 (2H, m, 2-CH_{map}), \delta(CH2) = 150 MHz, C_{ds}, rt): 20.7 (\approx (C(Bdbm)CH2), 24.5 (OC(CH2)2), 29.5 (NCH2), 83.0 (OC(CH2)2), 108.1 (C(CH2)2), 119.0 (CH_{ds}, 126.2 (C(CH2)2), 128.4 (C(CH2)2), 129.4 (C(CH2)2), 139.0 (C(CH2)2), 142.3 (C(CH2)2), 144 (br, BC=CB), 148 (br, BC=CB), m/z \approx (EI, 70 eV, GC/MS) 388.25114 [(M+)], calc. for C_{32}H_{32}B_{2}N_{2}O_{2}: 388.24934 (1.80 mmu). \text{(pinb)Pt}=([C(Bdbm)]=([Ph])]} (major component), \delta(CH2) = 600 MHz, C_{ds}, rt): 0.74 (12H, s, OC(CH2)2), 1.90 (3H, s, \approx (C(Bdbm)CH2), 3.16 (6H, s, NCH3), 7.00-7.02 (2H, m, C_{ds}, rt), 7.10-7.15 (1H, m, 4-CH_{ds}), 7.18-7.21 (2H, m, CH_{ds}, 7.28-7.32 (2H, m, CH_{ds}), 7.41-7.44 (2H, m, 2-CH_{ds}), \delta(CH2) = 150 MHz, C_{ds}, rt): 20.7 (\approx (C(Bdbm)CH2), 24.5 (OC(CH2)2), 29.5 (NCH2), 83.0 (OC(CH2)2), 108.1 (C(CH2)2), 119.0 (CH_{ds}, 126.2 (C(CH2)2), 128.4 (C(CH2)2), 129.4 (C(CH2)2), 139.0 (C(CH2)2), 142.3 (C(CH2)2), 144 (br, BC=CB), 148 (br, BC=CB), m/z \approx (HR-El, 70 eV, GC/MS) 388.25114 [(M+)], calc. for C_{32}H_{32}B_{2}N_{2}O_{2}: 388.24934 (1.80 mmu). \text{(pinb)Pt}=([C(Bdbm)]=([Bn])]} (minor component) \delta(CH2) = 600 MHz, C_{ds}, rt): 1.13 (12H, s, OC(CH2)2), 2.21 (3H, s, \approx (C(Bdbm)CH2), 3.52 (6H, s, NCH3), 6.94-6.97 (2H, m, C_{ds}, rt), 7.14-7.17 (2H, m, CH_{ds}, 7.44-7.49 (2H, m, 2-CH_{ds}), not all signals could be unambiguously identified. \delta(CH2) = 150 MHz, C_{ds}, rt): 18.5 (\approx (C(Bpin)CH2), 25.5 (OC(CH2)2), 30.9 (NCH2), 82.7 (OC(CH2)2), 108.1 (C(CH2)2), 118.9 (CH_{ds}, 129.3 (C(CH2)2), not all signals could be unambiguously identified. m/z \approx (EI, 70 eV, GC/MS) 388 (80) [(M+)], 331 (74), 305 (40), 288 (100), 245 (18), 185 (15), 162 (31), 145 (27), 117 (30), 69 (10), m/z \approx (HR-El, 70 eV, GC/MS) 388.25046 [(M+)], calc. for C_{32}H_{32}B_{2}N_{2}O_{2}: 388.24934 (1.12 mmu). \delta(CH2) = 96 MHz, C_{ds}, rt): 29.8 (s, \Delta \nu_{1/2} = 348 Hz), isomers not resolved. \text{(pinb)Pt}=([C(Bpin)]=([Bcat])]} (major component) \delta(CH2) = 100 mg, 407 \mu mol), Me-C-C=Me (56 mg, 529 \mu mol), 2 \text{(8.3 mg, 11.0 \mu mol, 3\%)}), toluene (10 mL), reaction time 122 h, brownish oil (133 mg, 343 \mu mol, 93\%). \text{(dmba}(B)Pt}=([C(Bpin)]=([Ph])]} (pinb) \text{(Me-C=C-Ph} (56 mg, 482 \mu mol), 2 \text{(8.3 mg, 11.0 \mu mol, 3\%)}), toluene (10 mL), reaction time 122 h, brownish oil (133 mg, 343 \mu mol, 93\%). \text{(dmba}(B)Pt}=([C(Bpin)]=([Ph])]} (pinb) \text{(Me-C=C-Ph} (56 mg, 482 \mu mol), 2 \text{(8.3 mg, 11.0 \mu mol, 3\%)}), toluene (10 mL), reaction time 122 h, brownish oil (133 mg, 343 \mu mol, 93\%). \text{(dmba}(B)Pt}=([C(Bpin)]=([Ph])]} (pinb) \text{(Me-C=C-Ph} (56 mg, 482 \mu mol), 2 \text{(8.3 mg, 11.0 \mu mol, 3\%)}), toluene (10 mL), reaction time 122 h, brownish oil (133 mg, 343 \mu mol, 93\%). \text{(dmba}(B)Pt}=([C(Bpin)]=([Ph])]} (pinb) \text{(Me-C=C-Ph} (56 mg, 482 \mu mol), 2 \text{(8.3 mg, 11.0 \mu mol, 3\%)}), toluene (10 mL), reaction time 122 h, brownish oil (133 mg, 343 \mu mol, 93\%).
Results and discussion

Synthesis

The unsymmetrical platinum bis-boryl complexes 3ab, 3ac, 3ae, 3bd and 3be were obtained by oxidative addition of the respective unsymmetrical diborane(4) derivatives 1 to the platinum(0) complex 2 (Scheme 2). The procedure involved...
The unsymmetrical diboranes 1 employed comprise dialkoxy/arylxy substituents such as Bpin (pin = (OCMe2)phenyl) and Bneop (neop = (OCH2)2(C6H4)), Bcat (cat = 1,2-O2C6H4) as well as diamino substituents such as BMeEn (MeEn = (NMe)2C6H4), Bdmab (dmab = 1,2-(NMe)2C6H4) but also the sterically more demanding congeners BiPrEn (iPrEn = (NMe)2C6H4) and BrBuEn (BuEn = (NtBu)2C6H4) (Scheme 2).

For the five unsymmetrical diboranes 1a, 1b, 1c, 1d and 1e the respective unsymmetrical platinum(II) complexes 3a, 3b, 3c, 3d and 3e were obtained as colourless or pale solids in good yields. In contrast, with the sterically more demanding congeners of 1a, 1b and 1c the complexes of 1a, 1b and 1c could be isolated. However, for the reaction of Pt(Bmap)2 with 1d, 1e and 1f the complexes could not be isolated. Instead, for the reaction of 1f with 2 in situ NMR spectroscopy indicates that an oxidative addition to the complex [(Ph3P)2Pt(Bpin)] (3af) takes place (Fig. 1). According to 1H NMR signals ratios a 1af: 3af ratio of 26:100 is obtained after repeated evacuation cycles. The 31P(1H) NMR spectrum indicates also incomplete reaction, as besides the signals assigned to the complex 3af unreacted 2 is observed (Fig. 1).⁹ In our hands all attempts to isolate 3af resulted in mixtures of 1af, 3af and variable amounts of unidentified decomposition products (Fig. 1).⁹

With the more demanding 1ag, however, no reaction is observed by in situ NMR spectroscopy (Fig. 1), as also reported for the related sterically demanding unsymmetrical diborane(4) pinB–Bdtab (tab = 1,2-(N(SiMe3))2C6H4).³,⁷

In addition to those unsymmetrical complexes the symmetrical complexes [(Ph3P)2Pt(Bpin)3] (3cc) and [(Ph3P)2–Pt(Bmap)3] (3hh, map = 1,2-(O)(NMe)C6H4) were analogously obtained from the respective symmetric diborane(4) derivatives BpinB–Bneop (1cc) and B2map2 (1hh) in yields of 57% and 39%, respectively (Scheme 3).

Crystallography

All five isolated unsymmetrical platinum(II) bis-boryle complexes 3ab, 3ac, 3ae, 3bd and 3be as well as the two symmetrical complexes 3cc and 3hh were structurally characterized by single-crystal X-ray diffraction (Table 1). Well-developed single-crystals suitable for X-ray diffraction studies were typically obtained by vapour diffusion of n-pentane at room temperature into solutions of the complexes in benzene or THF typically within 16–30 h. This technique gave repeatedly well-developed, relatively large crystals, whilst crystallisation from the same or related solvents combinations (toluene instead of benzene) at −40 °C results frequently microcrystalline powders or intergrown crystals. However, as the platinum(II) bis-boryle complexes appear not indefinitely stable in solutions at room temperature (vide infra) comparably fast crystallization at room temperature appears favourable. The complexes 3ab, 3ac, 3be, 3cc and 3hh crystallize as the solvates 3ab(C6H5), 3ae(C6H6)1.5, 3be(C6H5), 3cc(C6H6) and 3hh(C6H5)O whereas 3ac and 3bd crystallize without co-crystallization of solvent. 3ab(C6H5), 3bd, 3be(C6H6) and 3cc(C6H6)O crystallize in the triclinic system in the space group type P1, whilst 3ae(C6H6)1.5 and 3hh(C6H6)O were found to crystallise in the monoclinic system (P21/c), whereas 3ac crystallises in the orthorhombic system (Pbca). Common to the solid state structures of all seven complexes is the absence of any molecular symmetry; all complexes are situated on general positions. For the complexes 3ac, 3ae, 3bd, 3be, 3cc and 3hh the asymmetric unit of the respective structures contain one independent complex molecule (Z′ = 1), whereas for 3ab(C6H6) two independent molecules of 3ab as well as C6H5 are found in the asymmetric unit (Z′ = 2). Contrary to the platinum complexes
the solvent in 3ae(C4H8O)1.5 and 3be(C6H6) exhibits addition symmetry and resides (partially) on centres of inversion. In 3ae(C4H8O)1.5, two distinct THF moieties are found, one on a centre of inversion and one on a general position, whereas in 3be(C6H6) the two independent molecules of benzene are located on the two distinct types of centres of inversion in P1. None of the structures exhibits disorder within the platinum bis-boryl complex, however, positional disorder is observed for one of the co-crystallized solvent molecules in 3ae(C4H8O)1.5.

All described platinum(ii) bis-boryl complexes exhibit, as to be expected, a slightly distorted square-planar coordination environment at the platinum(ii) (d8) ion with cis-arrangement of the boryl ligands. The sum of angles in the coordination sphere lies in a very narrow range of 360–362°, except for 3bd where a value of 364.5(1)° is found (Fig. 2–5). The distortion from planarity towards a tetrahedron is, as indicated by the angle \( \tau_{(B,B/P,P)} \) included by the [B, Pt, B] and [P, Pt, P] planes, small but significant (Table 2).

All P–Pt distances are in a quite narrow range of 2.326–2.355 Å. These comparably long P–Pt distances are evidence for the generally strong trans-influence of boryl ligands, e.g. \([\text{Ph}_3\text{P}]_2\text{PtCl}_2\) 2.26 Å, \([\text{Ph}_3\text{P}]_2\text{Pt}(n\text{Bu})_2\) 2.30 Å, \([\text{Ph}_3\text{P}]_2\text{Pt}([\text{SiR}_3\text{H}]_2)\) (R = Me, Ph) 2.34–2.37 Å.³

It has been proposed that the P–Pt distances are a suitable measure for the donor properties of a ligand in a complex \([\text{Ph}_3\text{P}]_2\text{PtXY}\) (X, Y: anionic ligand), following the reasoning that a shortening of a trans-boryl P–Pt bond in dependence of a particular ligand indicates a relatively lower trans-influence of this ligand compared to a reference ligand, and analogously for the cis-influence of this ligand.³ However, the differences in P–Pt distances between the individual boryl ligands are quite small and appear not especially indicative for a comparison of the trans- and cis-influences of the individual boryl ligands given in Table 2. If at all, it may be stated that, taking 3aa as a reference compound, all other boryl ligands have a relatively lower trans- and cis-influence.³ However, this contradicts experimental and computational studies suggesting a significantly stronger trans-influence of diamino boryl than dialkoxy boryl ligands.¹²

The Pt–B distances vary significantly and apparently systematically with the type of the individual boryl ligand (Table 2). Within the set of structures discussed here (Table 2) three types of boryl ligands may be defined: (i) alkyloxy-B, such as Bpin and Bnep, (ii) aryloxylboryl ligands, here Bcat, (iii) and diamino boryl ligands, such as Bdmab and BMeEn. The first class

| Table 2 | Selected geometrical parameters of the complexes 3ab, 3ac, 3ad, 3ae, 3bd, 3be, 3aa, 3bb, 3cc and 3hh |
|---------|---------------------------------------------------------------------------------------------|
| 3yz     | B–B [Å]                                      | \( \tau_{(B,B/P,P)} \) ° | P(γ)–Pt [Å] | P(α)–Pt [Å] | B(γ)–Pt [Å] | B(α)–Pt [Å] |
| 3aa     | 2.54(1)                                      | 3.6(2)         | 2.351(2)    | 2.353(1)    | 2.076(8)    | 2.077(6)    |
| 3ab     | 2.443(8)                                     | 6.3(2)         | 2.340(1)    | 2.344(1)    | 2.041(6)    | 2.044(1)    |
| 3ac     | 2.457(8)                                     | 2.3(2)         | 2.340(1)    | 2.349(1)    | 2.079(6)    | 2.076(6)    |
| 3ad     | 2.532(5)                                     | 14.6(8)        | 2.330(7)    | 2.337(6)    | 2.073(3)    | 2.084(3)    |
| 3ae     | 2.448(5)                                     | 13.09(9)       | 2.339(8)    | 2.332(7)    | 2.078(3)    | 2.067(3)    |
| 3bb     | 2.430(6)                                     | 6.5(1)         | 2.325(9)    | 2.332(8)    | 2.062(4)    | 2.088(4)    |
| 3bc     | 2.554(9)                                     | 9.3(2)         | 2.354(1)    | 2.347(1)    | 2.040(5)    | 2.058(6)    |
| 3bd     | 2.443(2)                                     | 13.21(6)       | 2.335(3)    | 2.346(3)    | 2.041(2)    | 2.089(2)    |
| 3be     | 2.484(2)                                     | 2.09(5)        | 2.332(4)    | 2.357(4)    | 2.052(7)    | 2.093(2)    |
| 3cc     | 2.566(8)                                     | 11.4(1)        | 2.348(1)    | 2.345(1)    | 2.085(5)    | 2.075(4)    |
| 3hh     | 2.485(2)                                     | 6.25(4)        | 2.336(3)    | 2.340(3)    | 2.073(1)    | 2.065(2)    |

\[ \text{Angle included by the planes } [B, Pt, B] \text{ and } [P, Pt, P]. \]

* \( \tau_{(B,B/P,P)} \) \text{ included by the planes } [B, Pt, B] \text{ and } [P, Pt, P].
* \( \Sigma_{(Pt1)} 359.9(4). \)
* Two independent molecules in the asymmetric unit.
* \( \Sigma_{(Pt1)} 361.3(2). \)
* \( \Sigma_{(Pt1)} 360.2(3). \)
of ligands exhibits comparably long Pt–B distances in a range of 2.062–2.085 Å (0.003–0.008 Å esd) with an arithmetic mean of 2.076 Å (Table 2). Although slightly shorter values were found for individual B–Pt distances in the (alkyl)2B complexes \([\text{[Ph}_3\text{P}]_2\text{Pt}(\text{B(OCH}_2\text{COO})_2\text{Me})_2]\) and \([\text{[Ph}_3\text{P}]_2\text{Pt}(\text{B(OCH}_2\text{CH}(\text{H})\text{PhO})_2]\) (<2.06 Å) this range appears typical for this class of ligands. In contrast the aryloxy substituted Bcat ligand leads to significantly shorter B–Pt distances in a range of 2.040–2.058 Å (0.002–0.006 Å esd) with an arithmetic mean of 2.047 Å. This agrees also with the Pt–B distances found for the catechol derived boryl ligands in \([\text{[Ph}_3\text{P}]_2\text{Pt}(\text{B(O}_2\text{C}_6\text{H}_4\text{Cl})_2]\) (2.03(2), 2.04(2) Å) and \([\text{[Ph}_3\text{P}]_2\text{Pt}(\text{B(O}_2\text{C}_6\text{H}_4\text{H}_2+t\text{-Bu})_2]\) (2.046(13), 2.047(10) Å). Finally, dianinoboryl ligands result in B–Pt distances comparable to those in dialkoxy boryl complexes but on the long side of those in aryloxy boryl complexes, as evidenced by the complexes 3ad, 3ae, 3be and 3bb exhibiting B–Pt distances in a range of 2.067–2.093 Å (0.002–0.003 Å esd) with an arithmetic mean of 2.084 Å. The latter agrees also with the distances reported for \([\text{[Ph}_3\text{P}]_2\text{Pt}(\text{BNBn})_2\text{C}_6\text{H}_4\text{Cl})_2]\) (2.092(2), 2.080(2) Å).

The B–B distances are for all bis-boryl platinum(n) complexes of the type \([\text{[Ph}_3\text{P}]_2\text{Pt}(\text{boryl})_2]\) reported in this work (Table 2) or in the literature, much shorter, <2.62 Å, than the doubled van-der-Waals radius of boron (3.84 Å). However, those B–B distances are still much longer than those in the parent diborane(4) derivatives (averaged 1.7 Å, double covalent radii 1.68 Å). These B–B distances are also longer than those found in bis-boryl cobalt complexes (2.19–2.27 Å) and a bis-boryl iridium complex (2.22 Å) where the presence of a three-centre metal–boron–boron interaction is supported by DFT computations. Nonetheless, the short B–B distances still suggest an residual B–B interaction and, hence, the non-independence of the two boryl ligands within this series of complexes (vide infra).

**NMR spectroscopy**

The \(^{11}\text{B}\)\(^{1}\text{H}\) spectra of 3ac, 3ae, 3af (in situ NMR data, vide supra), 3be, 3ce and 3hh exhibit very broad signals (1200–2500 MHz FWHM) around 47 ppm in agreement with the chemical shifts reported for related complexes. However, for none of the unsymmetrical complexes 3ac, 3ae, 3af and 3be (and also 3ad and \([\text{[Ph}_3\text{P}]_2\text{Pt}(\text{NBn})_2\text{C}_6\text{H}_4\text{Cl})_2]\) (45 ppm, 3200 Hz) two discernible signals for the two individual boryl ligands were observed.\(^3\)\(^d\)\(^b\) For the complexes 3ab and 3bd, however, no \(^{11}\text{B}\)\(^{1}\text{H}\) NMR signal could be detected, presumably due to the very broad line shape of the quadrupolar \(^{11}\text{B}\) nucleus in a low-symmetry environment and overlapping of the signals of the two three coordinate boron nucleus in the unsymmetrical boryl complexes. The narrow range and the averaged nature of these signals render an assignment of individual chemical shifts to specific boryl ligands impossible.

All new complexes 3ab, 3ac, 3ae, 3af, 3bd, 3be, 3cc and 3hh were also characterised in solution by \(^{1}\text{H}\), \(^{13}\text{C}\)\(^{1}\text{H}\), and \(^{31}\text{P}\)\(^{1}\text{H}\) NMR spectroscopy. Beyond this, the complexes 3ab, 3ac and 3ae allowed a more detailed characterisation by \(^{1}\text{H}\)–\(^{1}\text{H}\) NOESY and \(^{1}\text{H}\)–\(^{31}\text{P}\) HMBC NMR spectroscopy allowing the assignment of the \(^{31}\text{P}\)\(^{1}\text{H}\) NMR signals to a specific boryl ligand (Table 3).\(^3\)\(^d\) For the other new unsymmetrical complexes 3bd and 3be this was not unambiguously possible for a lack of indicative \(^{1}\text{H}\)–\(^{1}\text{H}\) NOESY contacts,\(^3\) whilst 3af was not isolated in pure form and was characterised only in situ in the reaction mixture by NMR spectroscopy (vide supra).

The \(^{31}\text{P}\)\(^{1}\text{H}\) NMR chemical shifts of the phosphorous atom \(^{3}\text{trans}\) to a particular boryl ligand shows no systematic trend and varies e.g. for Bpin in a range of 4 ppm around 33.5 ppm (Table 3). However, for the \(^{3}\text{j}_{\text{P–B}}\) coupling constants a certain system-atic is discernible. The \(^{3}\text{j}_{\text{P–B}}\) coupling \(^{3}\text{trans}\) to a Bpin ligand varies in a range of 100 Hz between 1515 Hz and 1615 Hz (this includes also \([\text{[Ph}_3\text{P}]_2\text{Pt}(\text{NBn})_2\text{C}_6\text{H}_4\text{Cl})_2\)\(^\text{Bpin}\)): \(^{3}\text{j}_{\text{P–B}}\) varies between 1530 Hz, \(^{3}\text{j}_{\text{P–B}}\)\(^\text{trans}\)\(^B\text{pin}\) (1590 Hz), whereas for the closely related dialkyloxy boryl ligand Bneop lower values of 1440 Hz (3cc) and 1455 Hz (3ac) are observed.\(^3\)\(^b\)\(^c\)\(^f\) For the dialkyloxy ligand Bcat larger values above 1600 Hz are found, however, the restricted data set and the not unambiguously assigned data for 3bd and 3be renders this assignment tentative. Moreover, it should be noted that for the symmetrical 3bb two distinct \(^{3}\text{j}_{\text{P–B}}\) coupling constants are reported.\(^3\)\(^f\) From the data available it is clear that the \(^{3}\text{j}_{\text{P–B}}\) coupling constant is not a viable measure of the \(^{3}\text{trans}\)-influence of the trans-boryl

| Table 3 | NMR spectroscopic data of 3ab, 3ac, 3ad, 3ae, 3af, 3bd, 3be, 3cc and 3hh (161 MHz (\(^{11}\text{B}\)\(^{1}\text{H}\)) and 202 MHz (\(^{31}\text{P}\)\(^{1}\text{H}\)), rt in \(\text{C}_6\text{D}_6\)) |
|---------|---------------------------------------------------------------|
| 3aa     | 46.0                                                         |
| 3ab     | 35.5                                                         |
| 3ace    | 51.26                                                        |
| 3ad     | 47.5                                                         |
| 3ae     | 47.16                                                        |
| 3af     | 45.12                                                        |
| 3bb     | 47.01                                                        |
| 3be     | 45.15                                                        |
| 3cc     | 47.17                                                        |
| 3hh     | 47.17                                                        |
| \(\delta_\beta\) ppm | \(\delta_\beta\) ppm | \(\delta_\beta\) ppm |
| 27.8    | 33.7                                                         |
| 34.5    | 36.1                                                         |
| 28.7/32.4 | 30.2/28.7 (ref. 4c)                                         |
| 30.9/35.6 | 31.1                                                         |
| 32.8    | 1515                                                        |
| 1565    | 28.7                                                         |
| 1585    | 27.5                                                         |
| 1590    | 31.8                                                         |
| 1615    | 1690                                                        |
| 1455    | 1715                                                        |
| 1440    | 1590                                                        |

\(^a\) \(\Delta_\text{FWHM}\) (FWHM) [Hz] in parentheses. \(^b\) Measured at 96 MHz (\(^{11}\text{B}\)\(^{1}\text{H}\)) and 162 MHz (\(^{31}\text{P}\)\(^{1}\text{H}\)). \(^c\) Not isolated, in situ NMR data. Measured at 96 MHz (\(^{11}\text{B}\)\(^{1}\text{H}\)) and 122 MHz (\(^{31}\text{P}\)\(^{1}\text{H}\)). \(^d\) No assignment to individual ligands conducted.
ligand.\textsuperscript{7–18} It is clear, as suggested earlier, that the ligand in cis position has an appreciable influence on the trans \( ^1\text{J}_{\text{Pt-P}} \) coupling constants (cis influence).\textsuperscript{3}

**Stability and decomposition**

It has been earlier reported for 3ad and [(PCy\textsubscript{3})\textsubscript{2}Pt(B(OMe)\textsubscript{2})\textsubscript{2}] that bis-boryl platinum(n) complexes exist in solution in equilibria with their reductive elimination products, the parent diborane(4) and a platinum(0) complex \([\text{R}_2\text{nP}]=\text{Pt}].\textsuperscript{3,6} This appears to hold also for the complexes 3ac, 3ae and 3bd, as in the \(^1\text{H}\) NMR spectra of freshly prepared samples of these complexes signals indicative for the respective parent diborane(4) derivatives (Fig. S2a, S3b and S4a) were observed in minute amounts (3ac : 1ac 25 : 1, 3ae : 1ae 30 : 1, 3bd : 1bd 100 : 1). However, only for 3bd unambiguous exchange signals were detected by \(^1\text{H}-\text{H} NOESY spectroscopy (Fig. S4a).\textsuperscript{9} Nonetheless, it must be emphasised that these complexes are not indefinitely stable in solution at room temperature and one of the decomposition products is the parent diborane(4) derivative itself.

Freshly prepared C\textsubscript{6}D\textsubscript{6} solutions of the bis-boryl platinum(n) complexes are virtually colourless but over time an intense reddish or orange colouration is observed.\textsuperscript{19} Exemplarily the decomposition of 3ce was monitored by NMR spectroscopy over 38 h at ambient temperature in C\textsubscript{6}D\textsubscript{6} and indicates the reductive elimination of the diborane(4), \(\text{B}_2\text{neoP}_2\) (1ce), along with the formation of so far unidentified phosphine complexes (Fig. S7).\textsuperscript{9}

From solutions of the bis-boryl platinum(n) complexes 3 repeatedly intense orange crystals of \([\text{[Ph}]=\text{Pt}]=\mu=\text{Pt}]=\text{Ph}]\) [as their THF solvates] were obtained upon crystallisation at room temperatures after several days (vide supra) and were characterised crystallographically (Fig. S8 and S9).\textsuperscript{9} These two complexes have been described previously as thermal decomposition products of 2.\textsuperscript{20}

It should be noted that we could not observe any evidence for scrambling of the boryl ligands, hence the formation of symmetrical bis-boryl platinum(n) complexes or symmetrical diborane(4) derivatives. Considering that this could proceed e.g. via a bimolecular ligand exchange between two unsymmetrical bis-boryl platinum(n) complexes, a reaction of a bis-boryl platinum(n) complexes and a free boryl ligand (e.g. from dissociation from a bis-boryl platinum(n) complexes) or via an oxidative addition/reductive elimination pathway of a boryl platinum(n) complex and a diborane(4) derivative. All these reactions are apparently not favourable for the square-planar bis-boryl platinum(n) complexes considered here.

**Catalysis**

Since its introduction by Suzuki and co-worker in 1993 the platinum catalysed bis-borylation of alkenes with diborane(4) derivatives has been established as a facile and widely used access to 1,2-bis-borylated alkenes.\textsuperscript{5} For these borylation reactions bis-boryl platinum complexes are established reactive intermediates.\textsuperscript{5,4} More recently Sugino and co-worker have shown that the unsymmetrical diborane(4) pinB–Bdan (dan = naphthalene-1,8-diaminato) may be used as reagent in the regioselective bis-borylation of unsymmetrical alkenes.\textsuperscript{21}

The unsymmetrical diborane(4) derivatives 1ab, 1ac and 1ad were exemplarily used to borylate the unsymmetrical alkene Ph–C≡C–Me (Scheme 4) in the presence of 2 as pre-catalyst. The bis-borylation proceeds smoothly with all three diboranes, yielding the respective unsymmetrically borylated alkenes 5 in excellent yields (Scheme 4). However, the dialkoxy diamino diboran reagent 1ad reacts significantly slower than the unsymmetrical tetra alkoxy diboranes(4) 1ac and 1ad (Scheme 4). The sluggish reaction of 1ad is also apparent in the bis-borylation of symmetrical diphenyl acetylene to give 4ad (Scheme 4).

In the case of unsymmetrically substituted acetylene as substrates the bis-borylation gives mixtures of the regioisomers of the unsymmetrical bis-borylated alkenes (Scheme 4). The different regioisomeric bis-borylation products were assigned by \(^1\text{H}-\text{H} NOESY NMR spectroscopy and the isomeric ratio were determined on the basis of the ratio of the characteristic methyl group signals. The alkene 4ad was also characterised by single crystal X-ray diffraction (Fig. S11).\textsuperscript{7}

The bis-borylation of Ph–C≡C–Me proceeds for all diboranes 1ab, 1ac and 1ad with some degree of selectivity (Scheme 4). For the dialkoxy diamino borane(4) 1ad a selectivity of 1 : 10 in favour of the isomer 5ad was observed, notably, the same preference, the Bpin moiety adjacent to the phenyl ring, was also reported for pinB–Bdan as borylating reagent.\textsuperscript{21} In contrast to that the selectivity with 1ab and 1ac is significantly lower, and for 1ab even reversed. Hence, the isomer 5ab with the Bpin moiety located at the carbon atom remote from the phenyl ring becomes predominant. It may be speculated that the selectivity origins for steric reasons – the sterically less demanding boryl moiety favours the more encumbered position adjacent to the phenyl ring. However, more data are certainly needed to derive final conclusions.
Conclusions

The facile access to unsymmetrical diborane(4) derivatives enables the first time the synthesis of a series of unsymmetrical platinum(ii) bis-boryl complexes (\(\text{Ph}_3\text{P})_2\text{Pt}(\text{boryl})(\text{boryl})\)). The diborane(4) compounds used comprises seven combinations of dialkoxo boryl (Bpin, Bcat, Bneo) and diamino boryl (Bdmab, BMeEn, BiPrEn, BtBuEn) moieties. From these diborane(4) precursors five bis-boryl complexes (\(\text{Ph}_3\text{P})_2\text{Pt}(\text{boryl})(\text{boryl})\)) were obtained; the sterically demanding ligands BiPrEn and BtBuEn did not allow the isolation of the corresponding boryl complexes.

This series of complexes obtained was characterised spectroscopically as well as structurally. The most prominent feature of the distorted square-planar cis-bis-boryl platinum complexes is the short B-B distance of 2.44–2.55 Å, >1.2 Å shorter than the doubled van-der-Waals radius of boron. The trans-boryl P-Pt distances are comparably long but in a narrow range around 2.34 Å, as expected for the strongly trans-influencing boryl ligands. However, no distinct variations in the P-Pt distances within this series of boryl ligands is observed that allow to draw conclusions on the relative donor strength of the different boryl ligands. Similar is true for the \(^{31}\text{P}-\text{H}^1\text{Pt}\) NMR coupling constants, that are indicative for the strongly donating/trans-influencing boryl ligands, but exhibit no systematic variations to allow conclusions on the coordination properties. These findings may be rationalised by the interaction of the two boryl ligands: whilst the complexes may well be described as platnum(ii) bis-boryl complexes there is (residual) interaction between the two boryl ligands. In other words, the boryl ligands exhibit not only a significant trans-influence, but also a significant cis-influence. Hence, a specific pair of boryl ligands may be best considered as entity and not as two individual boryl ligands.

Conflicts of interest

There are no conflicts to declare.

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18 An attempt to differentiate between trans and cis influence implying an additive relation as suggested by Pasini and co-workers was not fruitful.⁷

19 It should be mentioned that even analytically pure samples of complexes 3 are often slightly coloured, presumably due to decomposition during preparation. However, a deepening of the reddish/orange colour of their solutions is clearly observed nonetheless.

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