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# Synthesis and structure of the first heterodinuclear bis(borylene) complexes†

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**We report a facile synthesis of the first heterodinuclear bis(borylene) complex by reaction of an iron bis(borylene) complex with [Pt(PCy<sub>3</sub>)<sub>2</sub>], and its fully-reversible CO uptake and liberation reaction.**

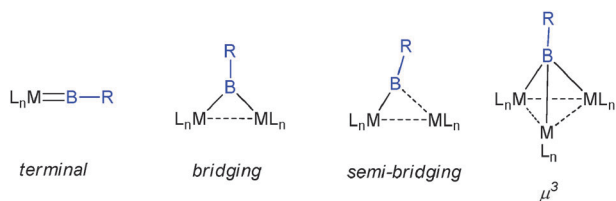
Hypovalent free borylenes “:BR”, unlike their isoelectronic counterpart CO, are highly reactive and can only be generated as transient species under drastic conditions<sup>1</sup> or stabilised to a certain extent upon coordination by carbenes.<sup>2</sup> However, numerous computational studies have revealed a close relationship of borylenes with the ubiquitous CO ligand in terms of coordination modes, and moreover, higher thermodynamic stability of the M=B linkage due to better  $\sigma$ -donor and  $\pi$ -acceptor properties of borylene ligands in comparison to CO.<sup>3</sup> Since the synthesis of the first bridged borylene complexes,<sup>4</sup> the common coordination modes of CO (*i.e.* terminal,<sup>5</sup> bridging,<sup>4,5i,6</sup> semi-bridging,<sup>7</sup> and triply bridging<sup>8</sup>) have thus been mimicked by borylene ligands (Scheme 1). In addition to the fundamental aspects of metal borylene bonding, significant interest in this class of compounds stems from an increasing number of applications in organometallic and organic synthesis, such as borylene transfer and borylene-based metathesis.<sup>9</sup>

Nonetheless, whilst homoleptic carbonyl complexes are well known, incorporation of more than one borylene moiety into the

coordination sphere of transition metals remains a major challenge. To date, only three fully characterised examples have been reported (1–3 in Scheme 2), which were exclusively obtained by transferring the :BN(SiMe<sub>3</sub>)<sub>2</sub> moiety from reliable borylene sources [(OC)<sub>5</sub>M=BN(SiMe<sub>3</sub>)<sub>2</sub>] (M = Cr, Mo, W) to the corresponding transition-metal substrates.<sup>5*kr,h*,10</sup> While severely limited in numbers, bis(borylenes) have disclosed unique reactivity patterns far beyond the scope of their well-established mono(boryl) congeners, including tandem borylene transfer to yield unprecedented boron heterocycles<sup>11</sup> and most notably borylene coupling<sup>10,12</sup> and catenation.<sup>10</sup> In particular, the latter, which was achieved by incorporation of four borylene units into the coordination sphere of one iron nucleus, represents a novel and potentially useful protocol for the generation of electron-precise B–B bonds (5 in Scheme 2).<sup>10,13</sup>

Herein, we present a facile synthesis of the first heterodinuclear bis(borylene) complexes and their intriguing CO absorption and desorption properties.

Addition of an equimolar amount of [Pt(PCy<sub>3</sub>)<sub>2</sub>] (6) to a C<sub>6</sub>D<sub>6</sub> solution of [(OC)<sub>3</sub>Fe(BDur){BN(SiMe<sub>3</sub>)<sub>2</sub>}] (3) led to formation of the heterodinuclear bis(borylene) complex [(OC)<sub>3</sub>Fe{ $\mu$ -BN(SiMe<sub>3</sub>)<sub>2</sub>}-( $\mu$ -BDur)Pt(PCy<sub>3</sub>)] (7) almost quantitatively (Scheme 3). The <sup>11</sup>B NMR spectrum of 7 displayed two broad resonances at  $\delta_B$  = 122 and 98 and the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum revealed a signal at  $\delta_P$  = 74.4 (Pt–PCy<sub>3</sub>, <sup>1</sup>J<sub>Pt–P</sub> = 4123.4). The concomitant formation of free PCy<sub>3</sub> was indicated by a <sup>31</sup>P NMR resonance at  $\delta_P$  = 9.8.



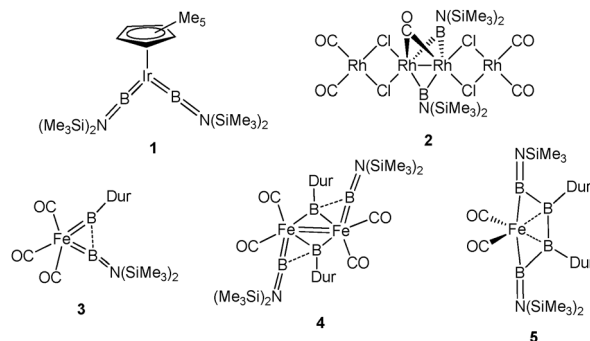
**Scheme 1** Coordination modes of borylenes.

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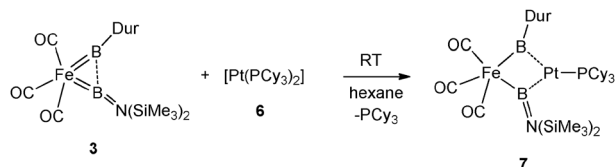
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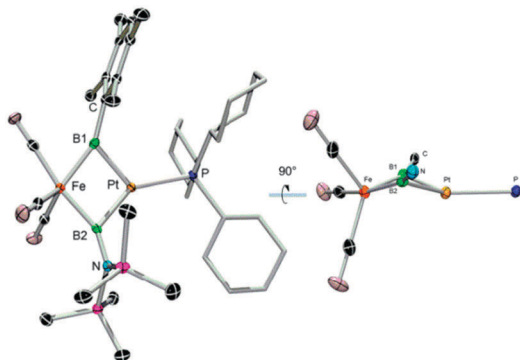
† Electronic supplementary information (ESI) available: Experimental details including synthesis and X-ray crystallographic data of 7 and 8. CCDC 940839 and 940840. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc43877e



**Scheme 2** Published bis(borylene) and tetra(borylene) complexes.



**Scheme 3** Preparation of compound 7.



**Fig. 1** Molecular structure of  $[(OC)_3Fe(\mu-BN(SiMe_3)_2)(\mu-BDur)Pt(PCy_3)]$  (**7**) in the solid state. Thermal ellipsoids are depicted at the 50% probability level. For clarity, ellipsoids of the cyclohexyl groups and hydrogen atoms have been removed. Selected bond lengths (Å) and angles ( $^\circ$ ): Fe–B1 1.934(4), Fe–B2 1.945(3), Pt–B1 2.004(3), Pt–B2 2.063(4), B2–N 1.393(4); B1–Fe–B2 96.88(15), Fe–B2–N 153.7(3), Fe–B1–C 155.0(2), Fe–B2–Pt 80.06(13), N–B2–Pt 126.2(2), Fe–B1–C 155.0(2), Pt–B1–C 123.2(2), Fe–B1–Pt 81.80(14).

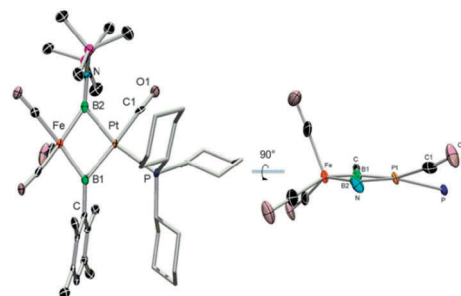
Complex **7** was isolated as red crystals upon storage of the concentrated reaction solution at  $-35\text{ }^\circ\text{C}$  overnight, in the monoclinic space group  $P2_1/c$ . The atom connectivity was clarified by X-ray diffraction analysis (Fig. 1). In comparison to the previously reported heterodinuclear monoborylene species  $[(OC)_2(Me_3P)Fe(\mu-CO)(\mu-BDur)Pt(PCy_3)]$  (**9**),<sup>5n</sup> in which the borylene moiety  $[BDur]$  adopts a symmetric bridging coordination mode with almost identical M–B bond distances (M = Fe, 1.970(4) Å; Pt, 1.976(4) Å), the borylenes in **7** both adopt a semi-bridging coordination mode. The Pt–B separations are 7–12 pm longer than the corresponding Fe–B bonds. The angles of Fe–B1–C ( $155.0(2)^\circ$ ) and Fe–B2–N ( $153.7(3)^\circ$ ) are similar to the corresponding angles of the semi-bridged  $[BN(SiMe_3)_2]$  moiety in  $[(OC)_4M(\mu-CO)(\mu-BN(SiMe_3)_2)Pd(PCy_3)]$  (M = Cr, Mo, W).<sup>7b,c</sup> Furthermore, the overall geometry of the central Fe–B1–Pt–B2 fragment adopts a slightly bent ring structure (Fig. 1, right). The almost orthogonal orientation of the boron-bound duryl and bis(trimethylsilyl)amino substituents with respect to the  $BR_3$  plane is presumably due to steric reasons. Although the orthogonal disposition of the amino substituent might preclude effective  $\pi$  donation from N to the formally  $sp^2$ -hybridised boron atom, the B–N separation of 1.393(4) Å is comparable with that (1.400(19) Å) of the boracumulene complex  $[CpRh(PCy_3)-\{\eta^2-B,C\}-(SiMe_3)_2N=B=C=CH_2]]$ ,<sup>15</sup> thus indicating significant B–N double bond character. In fact, this intriguing structural feature is consistent with our previously reported semi-bridging aminoborylene complexes.<sup>7b,c</sup>

As previous studies have proved that heterodinuclear bridging borylene complexes act as key intermediates for intermetal borylene transfer,<sup>5i,10</sup> we addressed the question of whether the double

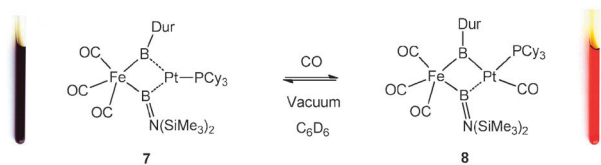
borylene transfer process could be accomplished by removing the iron fragment under a CO atmosphere in the form of  $[Fe(CO)_5]$ . Hence, a solution of **7** in  $C_6D_6$  was exposed to CO (1.2 bar) in a sealed Young NMR tube, which resulted in a dramatic colour change from dark brown to orange. Multinuclear NMR spectroscopy revealed quantitative formation of a new boron- and phosphorus-containing species, displaying  $^{11}B$  NMR resonances at  $\delta_B = 134$  and 98, which lie in the expected range for borylene complexes. Nevertheless, there was no sign for the formation of  $[Fe(CO)_5]$  according to the  $^{13}C$  NMR spectrum. Moreover, the  $^{31}P$  NMR spectrum showed a new, broad signal at  $\delta_P = 31.4$ . Interestingly, when all volatiles were removed under vacuum, a colour change from orange back to dark brown was observed, thus suggesting a reversible reaction. Indeed, multinuclear NMR spectroscopy of the residue dissolved in  $C_6D_6$  confirmed the regeneration of compound **7**. These findings suggest that CO might ligate to the Pt center. In fact, facile loss of CO is known for dicarbonyl platinum complexes.<sup>14</sup>

In order to clarify the atom connectivity of the unknown orange species, single crystals suitable for X-ray diffraction analysis were obtained after exposing a suspension of **7** in hexane to CO with stirring. The reaction mixture became homogenous within several minutes. The obtained orange hexane solution was kept under a CO atmosphere overnight at ambient temperature, yielding orange crystals (Fig. 2).

The molecular structure of **8** confirmed our proposal of a bis(borylene)-based platinum carbonyl complex (Scheme 4). Bearing a carbonyl ligand, the Pt centre features a distorted tetragonal planar geometry with an angular sum of  $363.1^\circ$ . The increased steric congestion caused by introduction of an extra ligand on platinum led to slight displacement of the boron-bound substituents towards iron. As a result, the  $[BDur]$  moiety adopts a symmetric bridging coordination mode with almost identical M–B1–C angles (M = Fe,  $140.5(4)^\circ$ ; Pt,  $139.9(4)^\circ$ ), while the  $BN(SiMe_3)_2$  ligand retains its semi-bridging character as indicated by the bond angles of M–B2–N (M = Fe,  $148.3(4)^\circ$ ; Pt,  $133.7(4)^\circ$ ). In addition, the Pt–B separations are correspondingly elongated by ca. 10 pm, while the Fe–B distances are slightly elongated by 1–5 pm. Remarkably, the central B–Fe–B–Pt ring becomes planar (Fig. 2, right), as indicated by the sum



**Fig. 2** Molecular structure of  $[(OC)_3Fe(\mu-BN(SiMe_3)_2)(\mu-BDur)Pt(PCy_3)(CO)]$  (**8**) in the solid state. Thermal ellipsoids are at the 50% probability level. For clarity, ellipsoids of the phosphine ligand and hydrogen atoms have been removed. Selected bond lengths (Å) and angles ( $^\circ$ ): Fe–B1 1.973(6), Fe–B2 1.944(6), Pt–B1 2.096(6), Pt–B2 2.144(6), Pt–C1 1.920(6), C1–O1 1.148(6), B2–N 1.415(7); B1–Fe–B2 107.3(2), Fe–B2–N 148.3(4), Fe–B1–C 140.5(4), Fe–B2–Pt 78.0(2), N–B2–Pt 133.7(4), Pt–B1–C 139.9(4), Fe–B1–Pt 78.5(2), B2–Pt–C1 78.9(2), C1–Pt–P 90.67(15), P–Pt–B1 97.41(17), B2–Pt–B1 96.1(2).



**Scheme 4** Reversible CO incorporation in, and loss from, a bis(borylene) platinum center.

(359.9°) of angles within the four-membered ring. Although the heterodinuclear borylene complexes 7–9 feature almost identical Fe–Pt distances (*ca.* 2.57 Å) that are indeed less than the sum of the covalent radii, previous computational studies on this class of compounds exclude a distinct interatomic interaction.<sup>16</sup>

The NMR spectroscopic features of complex **8** are in full agreement with the solid state formulation. The aforementioned broadening of the <sup>31</sup>P resonance is due to the mutual *trans* disposition of the phosphorus and boron atoms that leads to unresolved coupling between phosphorus and the quadrupolar boron nuclei. The mutual *trans* disposition of the C-bound boron and the CO ligand results in a slight downfield shift (12 ppm) of the <sup>11</sup>B resonance, while the <sup>11</sup>B signal for the N-bound boron that is mutually *trans* to PCy<sub>3</sub> remains unchanged. This can be explained by the stronger π-acidity of carbonyl in comparison to a phosphine ligand.

In conclusion, the reaction of [(OC)<sub>3</sub>Fe(BDur){BN(SiMe<sub>3</sub>)<sub>2</sub>}] (**3**) with Pt(0) complex [Pt(PCy<sub>3</sub>)<sub>2</sub>] (**6**) has provided facile access to the first heterodinuclear bis(borylene) complex [(OC)<sub>3</sub>Fe{μ-BN(SiMe<sub>3</sub>)<sub>2</sub>}(μ-BDur)Pt(PCy<sub>3</sub>)] (**7**). Preliminary investigations into the reactivity of **7** revealed a fully reversible CO binding and liberation reaction in solution. The chemical environment switch (CO or CO-free) on platinum can be easily controlled by changing the reaction atmosphere and is indicated by a diagnostic colour change.

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