

# Synthesis and Reactivity of Diborane(4)yl Complexes

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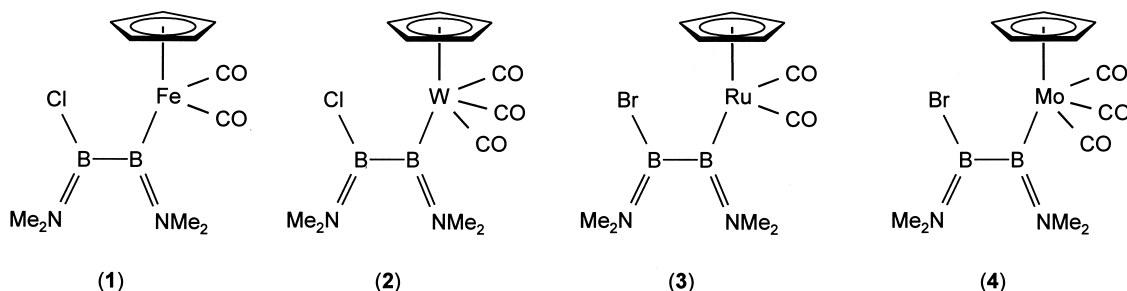
Boranes, Diboranes(4), Boryl Complexes

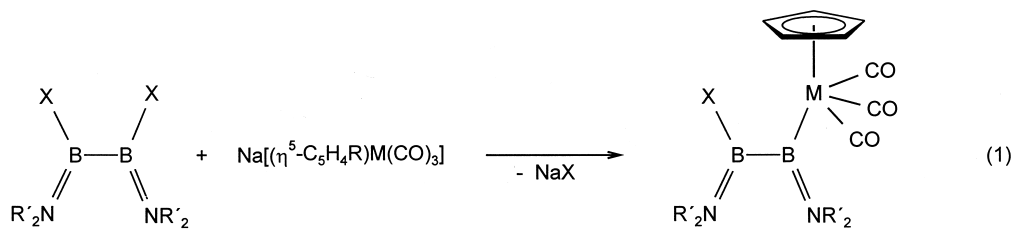
Reaction of various 1,2-dihalodiboranes(4) with  $\text{Na}[\{\eta^5\text{-C}_5\text{H}_4\text{R}\}\text{M}(\text{CO})_3]$  yielded the diborane(4)yl complexes  $[\text{X}(\text{Me}_2\text{N})\text{B}-\text{B}(\text{NMe}_2)\{\eta^5\text{-}(\text{C}_5\text{H}_4\text{R})\text{M}(\text{CO})_3\}]$  (**5**, X = Cl, R = H, M = Mo; **6**, X = Br, R = Me, M = Mo; **7**, X = Br, R = H, M = W; **8**, X = Br, R = Me, M = W) and  $[\text{Cl}(\text{C}_4\text{H}_8\text{N})\text{B}-\text{B}(\text{NC}_4\text{H}_8)\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3\}]$  (**9**). The reactivity of diborane(4)yl complexes of the type  $[\text{X}(\text{Me}_2\text{N})\text{B}-\text{B}(\text{NMe}_2)\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{M}(\text{CO})_n\}]$  (X = Cl, Br;  $\text{M}(\text{CO})_n = \text{Fe}(\text{CO})_2, \text{Mo}(\text{CO})_3$ ) with respect to substitution of X and CO, respectively, was investigated. The novel derivatives  $[\text{MeO}(\text{Me}_2\text{N})\text{B}-\text{B}(\text{NMe}_2)\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3\}]$  (**10**),  $[\text{MeO}(\text{Me}_2\text{N})\text{B}-\text{B}(\text{NMe}_2)\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\}]$  (**11**), and  $[\text{Br}(\text{Me}_2\text{N})\text{B}-\text{B}(\text{NMe}_2)\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PMe}_3)\}]$  (**12**) were obtained. All compounds were fully characterised in solution by NMR spectroscopy and by elemental analysis.

## Introduction

Over the past decade transition metal complexes of boron have become established as the fourth class of compounds made up by direct metal-boron interactions. In contrast to the other three major groups in this area i. e. borides, metallaboranes, and  $\pi$ -complexes with boron-containing ligands, transition metal complexes of boron are characterised by electron-precise two-centre two-electron bonds between boron and the metal centre [1]. Most of these compounds are derived from monoboranes, but diboranes(4) also play an important role in the chemistry of these complexes. With strongly electronegative groups RO<sup>-</sup> [2] and F<sup>-</sup> [3] as substituents to both boron atoms the corresponding diboranes(4) generally react with cleavage

of the boron-boron bond and oxidative addition to suitable metal centres, thus forming products with one to three borylligands. The use of 1,2-diaminodihalodiboranes(4) and anionic transition metal complexes, however, has led to the first diborane(4)yl complexes  $[\text{Cl}(\text{Me}_2\text{N})\text{B}-\text{B}(\text{NMe}_2)\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{M}(\text{CO})_n\}]$  (**1**,  $\text{M}(\text{CO})_n = \text{Fe}(\text{CO})_2$ ; **2**,  $\text{M}(\text{CO})_n = \text{W}(\text{CO})_3$ ) [4], and  $[\text{Br}(\text{Me}_2\text{N})\text{B}-\text{B}(\text{NMe}_2)\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{M}(\text{CO})_n\}]$  (**3**,  $\text{M}(\text{CO})_n = \text{Ru}(\text{CO})_2$ ; **4**,  $\text{M}(\text{CO})_n = \text{Mo}(\text{CO})_3$ ) [5], which were obtained via salt elimination reactions (Fig. 1). Complexes of this type are still rare and are restricted to **1** - **4** and two further examples  $[\text{Cl}(\text{R}_2\text{N})\text{B}-\text{B}(\text{NR}_2)\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\}]$  ( $\text{NR}_2 = \text{NC}_4\text{H}_8, \text{NC}_5\text{H}_{10}$ ) [6]. Although the reactivity of related boryl complexes  $\text{L}_x\text{M}-\text{BR}_2$  is well established [1], there is no informa-






5: X = Cl, M = Mo, R = H, R<sub>2</sub>'N = Me<sub>2</sub>N

6: X = Br, M = Mo, R = Me, R<sub>2</sub>'N = Me<sub>2</sub>N

7: X = Br, M = W, R = H, R<sub>2</sub>'N = Me<sub>2</sub>N

8: X = Br, M = W, R = Me, R<sub>2</sub>'N = Me<sub>2</sub>N

9: X = Cl, M = W, R = H, R<sub>2</sub>'N = 

tion as yet about reactions of diborane(4)yl complexes.

In the present paper we report on the synthesis and spectroscopic characterisation of further diborane(4)yl complexes of group VI metals and on the first reactivity studies leading to new derivatives of such compounds.

## Results and Discussion

### Synthesis and Characterisation of Diborane(4)yl Complexes

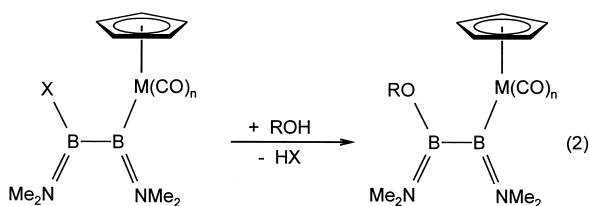
According to eq. (1) the complexes [X(Me<sub>2</sub>N)B-B(NMe<sub>2</sub>){η<sup>5</sup>-(C<sub>5</sub>H<sub>4</sub>R)M(CO)<sub>3</sub>}] (**5**, X = Cl, R = H, M = Mo; **6**, X = Br, R = Me, M = Mo; **7**, X = Br, R = H, M = W; **8**, X = Br, R = Me, M = W) and [Cl(C<sub>4</sub>H<sub>8</sub>N)B-B(NC<sub>4</sub>H<sub>8</sub>){η<sup>5</sup>-(C<sub>5</sub>H<sub>5</sub>)W(CO)<sub>3</sub>}] (**9**) were obtained from the corresponding 1,2-dihalodiboranes(4) and anionic transition metal complexes via salt elimination reactions.

All complexes were isolated as yellow or red crystalline solids, which are soluble in common aliphatic and aromatic solvents. The corresponding solutions can be stored for prolonged periods without significant signs of degradation. The yields of **5**–**9** range from 8% (**9**) to 52% (**6**) and obviously correspond to the reactivity of the starting diborane, i. e. 1,2-dibromodiboranes(4) give considerably better results than 1,2-dichlorodiboranes(4). The formation of (boryloxy)carbyne rather than diborane(4)yl complexes has been observed before, and accounts for the potentially nucleophilic character of the CO oxygen atom in [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)M(CO)<sub>3</sub>]<sup>−</sup> (M = Mo, W) [7]. However, even in the case of lower yields

the inspection of the reaction mixtures provided no evidence for the formation of boryloxy compounds as possible side products. All new complexes were characterised in solution by IR and multinuclear NMR spectroscopy. They show characteristically deshielded <sup>11</sup>B NMR resonances (δ <sup>11</sup>B = 65.4 (**5**), 65.9 (**6**), 62.7 (**7**), 63.2 (**8**), 60.2 (**9**)) for the metal coordinated boron atoms with respect to those of the starting materials, while the resonances for the halide substituted boron atoms range from δ <sup>11</sup>B = 38.0 to 40.0, thus matching those of the non-coordinated diboranes(4). The complexes **5**–**8** show four signals for the dimethylamino ligands in the <sup>1</sup>H and <sup>13</sup>C NMR spectra, thus giving clear evidence for a restricted rotation with respect to both boron-nitrogen double bonds [4, 5]. Corresponding <sup>1</sup>H NMR signals for the more complex pyrrolidino groups in **9** could not be resolved. The presence of eight signals in the <sup>13</sup>C NMR spectrum ranging from δ = 25.46 to 55.76, however, indicates the same situation with respect to the two boron-nitrogen bonds. All five compounds show three very similar CO-stretching frequencies in the IR spectra ranging from ν = 1883 to 1989 cm<sup>−1</sup>, which match those of the structurally characterised tungsten diborane(4)yl complex **2** (ν = 1892, 1908, and 1988 cm<sup>−1</sup>), thus giving no evidence for a metal-boron π-backbonding [4, 5].

### Reactivity Studies

In order to investigate some reactions of diborane(4)yl complexes [Cl(Me<sub>2</sub>N)B-B(NMe<sub>2</sub>){η<sup>5</sup>-(C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>}] (**1**) [4] and [Br(Me<sub>2</sub>N)B-B(NMe<sub>2</sub>){η<sup>5</sup>-(C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>}] (**4**) [5] were cho-



1: X = Cl, M(CO)<sub>n</sub> = Fe(CO)<sub>2</sub>

4: X = Br, M(CO)<sub>n</sub> = Mo(CO)<sub>3</sub>

10: M(CO)<sub>n</sub> = Fe(CO)<sub>2</sub>, R = Me

11: M(CO)<sub>n</sub> = Mo(CO)<sub>3</sub>, R = Me

12: M(CO)<sub>n</sub> = Fe(CO)<sub>2</sub>, R = Et

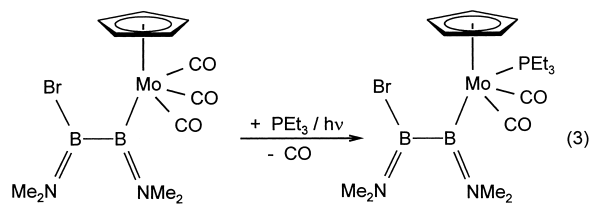
13: M(CO)<sub>n</sub> = Mo(CO)<sub>3</sub>, R = Et

sen as the most convenient starting materials as they were obtained with the highest yields.

The substitution of the boron bound halides by methoxy groups according to eq. (2) was achieved by simply dissolving **1** and **4**, respectively, in methanol. The new diborane(4)yl complexes **10** and **11** were obtained in good yields of 74% and 68%, respectively, as yellow, amorphous solids.

The compounds were characterised in solution by IR and multinuclear NMR spectroscopy. As expected, the substitution of halide by methoxide results in a significant high field shift of the <sup>11</sup>B NMR signals for the corresponding boron atoms ( $\delta^{11}\text{B} = 39.0$  (**1**), 34.4 (**10**), 38.2 (**4**), 33.7 (**11**)), while all other NMR shifts and the carbonyl stretching frequencies are not affected. Alcoholysis in ethanol yielded the complexes **12** and **13**, which are characterised by a similar shielding of the corresponding boron atoms with respect to the halide substituted precursors ( $\delta^{11}\text{B} = 34.0$  (**12**), 33.4 (**13**)). Isolation of the pure compounds, however, was hampered by the formation of considerable amounts of [ $\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{-Fe}(\text{CO})_2\}_2$ ] and [ $\eta^5\text{-}(\text{C}_5\text{H}_5)\text{MoH}(\text{CO})_3$ ], respectively, which were identified by NMR spectroscopy. The formation of such complexes is well known from the corresponding reactions of boryl complexes with protic reagents and is due to the facile cleavage of the labile metal-boron bond [1, 8].

In addition to substitution reactions at the diborane(4)yl moiety the exchange of transition metal coordinated ligands was investigated in one case. Irradiation of **4** in the presence of PEt<sub>3</sub> afforded the phosphane complex **14** according to eq. (3) in 75% yield as an amorphous, bright yellow solid. The compound shows two signals in the <sup>11</sup>B NMR spectrum ( $\delta^{11}\text{B} = 40.7$  and 68.8) and a single resonance in the <sup>31</sup>P NMR spectrum at  $\delta^{31}\text{P} = 52.8$ .



4

14

In the IR spectrum the CO stretching frequencies range between 1932 and 1812 cm<sup>-1</sup>, thus displaying the expected red shift due to substitution of one carbonyl group by triethylphosphane.

### Experimental Section

NMR: Varian Unity 500 (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>31</sup>P) in C<sub>6</sub>D<sub>6</sub> with usual standards. IR: Perkin-Elmer FT-IR 1720. Elemental analyses (C, H, N): Carlo-Erba elemental analyzer, model 1106.

**5**: 0.50 g (1.76 mmol) of K[ $\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3\}$ ] [9] suspended in 10 ml of benzene is treated with 0.32 g (1.76 mmol) of B<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub> [10] and the mixture is stirred for 6 d at ambient temperature. All volatiles are removed under high vacuum, and the residue is treated with 35 ml of hexane. After filtration 0.35 g (51.0%) of **5** is obtained at -30 °C as a yellow solid. – IR (toluene):  $\nu = 1982, 1900, 1887$  (CO) cm<sup>-1</sup>. – <sup>1</sup>H NMR (499.843 MHz):  $\delta = 2.41, 2.53, 2.64, 2.84$  (4s, 12 H, NMe<sub>2</sub>), 4.98 (s, 5 H, C<sub>5</sub>H<sub>5</sub>). – <sup>11</sup>B NMR (160.34 MHz):  $\delta = 38.0$  (BCl), 65.4 (BMo). – <sup>13</sup>C{<sup>1</sup>H} NMR (125.697 MHz):  $\delta = 36.90, 41.16, 42.39, 47.72$  (NMe<sub>2</sub>), 93.64 (C<sub>5</sub>H<sub>5</sub>), 224.63, 227.68, 233.63 (CO). – C<sub>12</sub>H<sub>17</sub>B<sub>2</sub>ClMoN<sub>2</sub>O<sub>3</sub> (390.29): calcd. C 36.93, H 4.39, N 7.18; found C 36.68, H 4.47, N 7.19.

**6**: As described for **5**, 0.99 g (3.32 mmol) of K[ $\{\eta^5\text{-}(\text{C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_3\}$ ] [9] is treated with 0.90 g (3.34 mmol) of B<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>Br<sub>2</sub> [11] to give 0.78 g (52.0%) **6** as a red solid. – IR (hexane):  $\nu = 1979, 1898, 1883$  (CO) cm<sup>-1</sup>. – <sup>1</sup>H NMR:  $\delta = 1.74$  (s, 3H, C<sub>5</sub>H<sub>4</sub>Me), 2.48, 2.64, 2.66, 2.84 (4s, 12 H, NMe<sub>2</sub>), 4.97 (m, 4 H, C<sub>5</sub>H<sub>4</sub>Me). – <sup>11</sup>B NMR:  $\delta = 38.2$  (BBr), 65.9 (BMo). – <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta = 14.06$  (C<sub>5</sub>H<sub>4</sub>Me), 39.46, 41.98, 42.44, 47.76 (NMe<sub>2</sub>), 92.83, 92.84, 94.19, 94.68, 111.94 (C<sub>5</sub>H<sub>4</sub>Me), 224.97, 228.32, 234.11 (CO). – C<sub>13</sub>H<sub>19</sub>B<sub>2</sub>BrMoN<sub>2</sub>O<sub>3</sub> (448.77): calcd. C 34.79, H 4.27, N 6.24; found C 34.57, H 4.18, N 5.67.

**7**: As described for **5**, 0.86 g (2.31 mmol) of K[ $\{\eta^5\text{-}(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3\}$ ] [9] is treated with 0.61 g (2.31 mmol) of B<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>Br<sub>2</sub> [11] to give 0.51 g (42.4%) of **7** as a yellow solid. – IR (hexane):  $\nu = 1989, 1909, 1892$  (CO) cm<sup>-1</sup>. – <sup>1</sup>H NMR:  $\delta = 2.42, 2.62, 2.68, 2.87$  (4s, 12 H, NMe<sub>2</sub>), 4.96 (s, 5 H, C<sub>5</sub>H<sub>5</sub>). – <sup>11</sup>B NMR:  $\delta = 40.0$

(BBr), 62.7 (BW). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.697 MHz):  $\delta$  = 39.32, 41.30, 41.93, 43.08 (NMe<sub>2</sub>), 92.40 (C<sub>5</sub>H<sub>5</sub>), 216.17, 219.23, 222.77 (CO). – C<sub>12</sub>H<sub>17</sub>B<sub>2</sub>BrWN<sub>2</sub>O<sub>3</sub> (522.65): calcd. C 27.58, H 3.28, N 5.36; found C 27.12, H 3.24, N 4.87.

**8:** As described for **5**, 2.13 g (5.53 mmol) of K[ $\{\eta^5\text{-(C}_5\text{H}_4\text{Me)W(CO)}_3\}$ ] [9] is treated with 1.49 g (5.53 mmol) of B<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>Br<sub>2</sub> [11] to give 0.37 g (12.5%) of **8** as a yellow solid. – IR (hexane):  $\nu$  = 1987, 1907, 1889 (CO) cm<sup>-1</sup>. –  $^1\text{H}$  NMR:  $\delta$  = 1.77 (s, 3H, C<sub>5</sub>H<sub>4</sub>Me), 2.47, 2.61, 2.66, 2.89 (4s, 12 H, NMe<sub>2</sub>), 5.00 (m, 4 H, C<sub>5</sub>H<sub>4</sub>Me). –  $^{11}\text{B}$  NMR:  $\delta$  = 40.0 (BBr), 63.2 (BW). –  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  = 13.88 (C<sub>5</sub>H<sub>4</sub>Me), 39.38, 41.99, 43.10, 48.08 (NMe<sub>2</sub>), 90.80, 91.12, 93.30, 93.57, 110.93 (C<sub>5</sub>H<sub>4</sub>Me), 216.81, 219.95, 233.73 (CO). – C<sub>13</sub>H<sub>19</sub>B<sub>2</sub>BrWN<sub>2</sub>O<sub>3</sub> (536.68): calcd. C 29.09, H 3.57, N 5.22; found C 28.62, H 3.61, N 5.03.

**9:** As described for **5**, 1.97 g (5.30 mmol) of K[ $\{\eta^5\text{-(C}_5\text{H}_5\text{)W(CO)}_3\}$ ] [9] is treated with 1.23 g (5.30 mmol) of B<sub>2</sub>(NC<sub>4</sub>H<sub>8</sub>)<sub>2</sub>Cl<sub>2</sub> [6, 12] to give 0.23 g (8.1%) of **9** as a yellow solid. – IR (toluene):  $\nu$  = 1985, 1900, 1884 (CO) cm<sup>-1</sup>. –  $^1\text{H}$  NMR:  $\delta$  = 1.79 (m, 8 H, NCH<sub>2</sub>CH<sub>2</sub>), 3.28 (m, 8 H, NCH<sub>2</sub>CH<sub>2</sub>), 5.02 (s, 5 H, C<sub>5</sub>H<sub>5</sub>). –  $^{11}\text{B}$  NMR:  $\delta$  = 39.6 (BCl), 60.2 (BW). –  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  = 25.46, 25.76, 26.36, 26.75 (NCH<sub>2</sub>CH<sub>2</sub>), 47.15, 49.84, 51.63, 55.76 (NCH<sub>2</sub>CH<sub>2</sub>), 92.37 (C<sub>5</sub>H<sub>5</sub>), 216.71, 218.77, 222.90 (CO). – C<sub>16</sub>H<sub>21</sub>B<sub>2</sub>ClN<sub>2</sub>O<sub>3</sub>W (530.28): calcd. C 36.24, H 3.99, N 5.28; found C 35.89, H 4.18, N 5.01.

**10:** 0.30 g (0.93 mmol) of **1** [4] is dissolved in 20 ml of methanol and stirred for 1 h at ambient temperature. All volatiles are removed under high vacuum, and the residue is treated with 40 ml of hexane. After filtration 0.22 g (74.4%) of **10** is obtained at –30 °C as a yellow solid. – IR (hexane):  $\nu$  = 1980, 1921 (CO) cm<sup>-1</sup>. –  $^1\text{H}$  NMR:  $\delta$  = 2.45, 2.68, 2.87, 2.92 (4s, 12 H, NMe<sub>2</sub>), 3.46 (s, 3 H, OMe) 4.41 (s, 5 H, C<sub>5</sub>H<sub>5</sub>). –  $^{11}\text{B}$  NMR:  $\delta$  = 34.4 (BO), 69.0 (BFe). –  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  = 34.17, 38.94, 44.52, 48.41 (NMe<sub>2</sub>), 53.65 (OMe), 85.14 (C<sub>5</sub>H<sub>5</sub>), 218.06, 218.15 (CO). – C<sub>12</sub>H<sub>20</sub>B<sub>2</sub>FeN<sub>2</sub>O<sub>3</sub> (317.77): calcd. C 45.36, H 6.34, N 8.82; found C 44.98, H 6.24, N 8.37.

**11:** As described for **10**, 0.38 g (0.87 mmol) of **4** [5] is dissolved in 20 ml of methanol to give 0.23 g (68.0%) of **11** at –30 °C as a yellow solid. – IR (hexane):  $\nu$  = 1981, 1898, 1882 (CO) cm<sup>-1</sup>. –  $^1\text{H}$  NMR:  $\delta$  = 2.50, 2.60, 2.70, 2.87 (4s, 12 H, NMe<sub>2</sub>), 3.52 (s, 3 H, OMe) 5.01 (s, 5 H, C<sub>5</sub>H<sub>5</sub>). –  $^{11}\text{B}$  NMR:  $\delta$  = 33.7 (BO), 67.1 (BMo). –

$^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  = 34.36, 39.01, 42.63, 47.97 (NMe<sub>2</sub>), 54.09 (OMe), 92.64 (C<sub>5</sub>H<sub>5</sub>), 226.07, 226.71, 234.14 (CO). – C<sub>13</sub>H<sub>20</sub>B<sub>2</sub>MoN<sub>2</sub>O<sub>4</sub> (385.87): calcd. C 40.46, H 5.22, N 7.26; found C 40.51, H 5.01, N 7.18.

**12:** As described for **10**, 0.54 g (1.68 mmol) of **1** [4] is dissolved in 20 ml of ethanol to give an inseparable, solid mixture of **12** and [ $\{\eta^5\text{-(C}_5\text{H}_5\text{)Fe(CO)}_2\}_2$ ]. –  $^1\text{H}$  NMR:  $\delta$  = 1.19 (t,  $^3J$  = 6.71 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 2.46, 2.70, 2.89, 2.92 (4s, 12 H, NMe<sub>2</sub>), 3.73 (q,  $^3J$  = 6.71 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>) 4.43 (s, 5 H, C<sub>5</sub>H<sub>5</sub>). –  $^{11}\text{B}$  NMR:  $\delta$  = 34.0 (BO), 69.1 (BFe). –  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  = 18.48 (OCH<sub>2</sub>CH<sub>3</sub>), 34.28, 38.93, 44.68, 48.60 (NMe<sub>2</sub>), 61.52 (OCH<sub>2</sub>CH<sub>3</sub>), 85.14 (C<sub>5</sub>H<sub>5</sub>), 218.13, 218.24 (CO).

**13:** As described for **10**, 0.50 g (1.15 mmol) of **4** [5] is dissolved in 20 ml of ethanol to give an inseparable, solid mixture of **12** and [ $\eta^5\text{-(C}_5\text{H}_5\text{)MoH(CO)}_3$ ]. –  $^1\text{H}$ -NMR:  $\delta$  = 1.20 (t,  $^3J$  = 6.86 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 2.51, 2.62, 2.71, 2.88 (4s, 12 H, NMe<sub>2</sub>), 3.82 (q,  $^3J$  = 6.86 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>) 5.68 (s, 5 H, C<sub>5</sub>H<sub>5</sub>). –  $^{11}\text{B}$  NMR:  $\delta$  = 33.4 (BO), 67.3 (BMo). –  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  = 18.33 (OCH<sub>2</sub>CH<sub>3</sub>), 34.46, 39.00, 42.66, 48.13 (NMe<sub>2</sub>), 61.88 (OCH<sub>2</sub>CH<sub>3</sub>), 93.93 (C<sub>5</sub>H<sub>5</sub>), 226.04, 226.87, 234.18 (CO).

**14:** 0.64 g (1.48 mmol) of **4** is dissolved in 90 ml of hexane and 0.52 g (4.44 mmol) of PEt<sub>3</sub> is added. The resulting mixture is irradiated for 15 h at –20 °C with a Heraeus TQ 150 high pressure mercury lamp. The solution is filtered, concentrated to 10 ml in high vacuum and stored at –30 °C. 0.58 g (74.7%) of **14** is obtained as a yellow solid. – IR (toluene):  $\nu$  = 1932, 1885, 1853, 1812 (CO) cm<sup>-1</sup>. –  $^1\text{H}$  NMR:  $\delta$  = 0.82 (dt,  $^3J_{\text{HH}} = 7.60$  Hz,  $^3J_{\text{PH}} = 15.30$  Hz, 9 H, PCH<sub>2</sub>CH<sub>3</sub>), 1.41 (dq,  $^3J_{\text{HH}} = 7.60$  Hz,  $^2J_{\text{PH}} = 7.60$  Hz, 6 H, PCH<sub>2</sub>CH<sub>3</sub>), 2.70, 2.81, 2.97, 3.08 (4s, 12 H, NMe<sub>2</sub>), 5.10 (s (broad), 5 H, C<sub>5</sub>H<sub>5</sub>). –  $^{11}\text{B}$  NMR:  $\delta$  = 40.7 (BBr), 68.8 (BMo). –  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  = 7.94 (d,  $^2J = 2.20$  Hz, PCH<sub>2</sub>CH<sub>3</sub>), 22.12 (d,  $^3J = 26.30$  Hz, PCH<sub>2</sub>CH<sub>3</sub>), 39.32, 42.25, 42.96, 48.46 (NMe<sub>2</sub>), 92.32 (C<sub>5</sub>H<sub>5</sub>), 231.70 (d,  $^2J = 21.40$  Hz, CO), 224.30 (d,  $^2J = 21.90$  Hz, CO). –  $^{31}\text{P}\{^1\text{H}\}$  (202.34 MHz):  $\delta$  = 52.8 (s). – C<sub>17</sub>H<sub>32</sub>B<sub>2</sub>BrMoN<sub>2</sub>O<sub>2</sub>P (524.89): calcd. C 38.90, H 6.14, N 5.34; found C 38.56, H 6.20, N 5.06.

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