

Note

# Metal fragment exchange from a molybdaborane to a tungstaborane

Malcolm L.H. Green <sup>a</sup>, John B. Leach <sup>b</sup>, Malcolm A. Kelland <sup>c,\*</sup>

<sup>a</sup> *Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK*

<sup>b</sup> *Department of Chemistry, Manchester Metropolitan University, John Dalton Building, Chester Street, Manchester M1 5GD, UK*

<sup>c</sup> *Department of Science and Technology, University of Stavanger, Kristine Bonnevie's vei 1, P.O. Box 8002, N-4036 Stavanger, Norway*

Received 10 May 2005; received in revised form 15 June 2005; accepted 20 June 2005

## Abstract

Reaction of the molybdaborane *arachno*-2-[Mo( $\eta$ -C<sub>5</sub>H<sub>5</sub>)( $\eta$ <sup>5</sup>: $\eta$ <sup>1</sup>-C<sub>5</sub>H<sub>4</sub>)B<sub>4</sub>H<sub>7</sub>] (I) with the electron-rich molecule [W(PMe<sub>3</sub>)<sub>3</sub>H<sub>6</sub>] at 60 °C for 12 h in toluene gives the novel tungstaborane *nido*-2-W(PMe<sub>3</sub>)<sub>3</sub>H<sub>2</sub>B<sub>4</sub>H<sub>7</sub>[Mo( $\eta$ -C<sub>5</sub>H<sub>5</sub>)( $\eta$ <sup>5</sup>: $\eta$ <sup>1</sup>-C<sub>5</sub>H<sub>4</sub>)H<sub>2</sub>] (II) in 60% yield. The reaction is almost quantitative when followed by NMR. This is a rare example of metal fragment exchange within a metallaborane cage. The molybdenum atom is retained in the molecule via a  $\sigma$ -bond between the substituted cyclopentadienyl ring and a basal boron atom in the metallaborane cluster.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Boron hydrides; Metallaboranes; Borane clusters; Molybdenum; Tungsten; NMR spectroscopy

The reaction of boranes with transition-metal compounds has led to a diverse range of structurally characterised metallaboranes with polyhedral cage structures [1–4]. However, there have been relatively few studies of the reactivity of metallaboranes. Some metallaboranes have been used as synthons in the stepwise synthesis of heterometallaboranes (or polymetallaboranes) by further reaction with metal complexes: these studies have been limited mainly to reactions of transition-metal halides and the larger, more stable metallaborane anions [5–15]. Some years ago we prepared the molybdaborane *arachno*-2-[Mo( $\eta$ -C<sub>5</sub>H<sub>5</sub>)( $\eta$ <sup>5</sup>: $\eta$ <sup>1</sup>-C<sub>5</sub>H<sub>4</sub>)B<sub>4</sub>H<sub>7</sub>] (I) in gram quantities permitting a study of its reactivity [16]. Here we report the novel reaction of (I) with the electron-rich compound [W(PMe<sub>3</sub>)<sub>3</sub>H<sub>6</sub>].

Stirring of a toluene solution of (I) with one equivalent of [W(PMe<sub>3</sub>)<sub>3</sub>H<sub>6</sub>] at 60 °C for 12 h gave a brown-orange solution, from which orange-yellow crystals of the tungstaborane *nido*-2-W(PMe<sub>3</sub>)<sub>3</sub>H<sub>2</sub>B<sub>4</sub>H<sub>7</sub>[Mo( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-

( $\eta$ <sup>5</sup>: $\eta$ <sup>1</sup>-C<sub>5</sub>H<sub>4</sub>)H<sub>2</sub>] (II) were isolated in 60% yield (Fig. 1). If the reaction is carried out in deuteriobenzene at 60 °C in a sealed NMR tube, <sup>11</sup>B and <sup>1</sup>H spectra indicate almost quantitative formation of (II). The compound has been characterised by <sup>1</sup>H, <sup>11</sup>B and <sup>31</sup>P NMR spectroscopy and elemental analysis.<sup>1</sup>

The metallaborane “MB<sub>4</sub>H<sub>8</sub>” cage in (II) is known for a number of transition metals including tantalum [17], molybdenum [18], tungsten [19], iron [20] and cobalt [21]. The metallaborane cage in (II) is also completely isostructural with that of the known cluster *nido*-2-[W(PMe<sub>3</sub>)<sub>3</sub>H<sub>2</sub>B<sub>4</sub>H<sub>8</sub>] except that the terminal

<sup>1</sup> Analytical data for compound (II). C<sub>19</sub>H<sub>47</sub>B<sub>4</sub>P<sub>3</sub>MoW Calc.: C, 33.1; H, 6.9. Found: C, 33.7; H, 7.0. Selected NMR data for compound (II) (solvent benzene-*d*<sub>6</sub>). <sup>1</sup>H NMR at 300 MHz, <sup>31</sup>P NMR at 121.49 MHz and <sup>11</sup>B NMR at 96.25 MHz. Compound (II): <sup>11</sup>B(*J*(<sup>11</sup>B–<sup>1</sup>H))  $\delta$  6.9 (br s, 1B, B<sub>4</sub>), –10.5 (s, 2B, B<sub>3,5</sub>), –27.4 (d, 1B, (150), B<sub>1</sub>); <sup>1</sup>H(<sup>11</sup>B)(*J*(<sup>31</sup>P–<sup>1</sup>H))  $\delta$  4.88 (t, 2H, *J*(<sup>1</sup>H–<sup>1</sup>H)) 1.5,  $\eta$ <sup>5</sup>: $\eta$ <sup>1</sup>-C<sub>5</sub>H<sub>4</sub>, 4.66 (d, 2H, *J*(<sup>1</sup>H–<sup>1</sup>H)) 1.5,  $\eta$ <sup>5</sup>: $\eta$ <sup>1</sup>-C<sub>5</sub>H<sub>4</sub>, 4.65 (s, 5H,  $\eta$ -C<sub>5</sub>H<sub>5</sub>) 3.23 (s, 2H, H<sub>3,5</sub>), 1.37 (d, 27H, (12), PMe<sub>3</sub>), 0.69 (s, 1H, H<sub>1</sub>), –1.35 (s, 2H, H<sub>34,45</sub>), –4.07 (br q, 2H, (40), W–H), –8.36 (s, 2H, Mo–H), –8.98 (s, 2H, H<sub>23,25</sub>); <sup>31</sup>P{<sup>1</sup>H}  $\delta$  –29.2 (s, PMe<sub>3</sub>).

\* Corresponding author. Tel.: +47 51831823; fax: +47 51831750.  
E-mail address: malcolm.kelland@uis.no (M.A. Kelland).

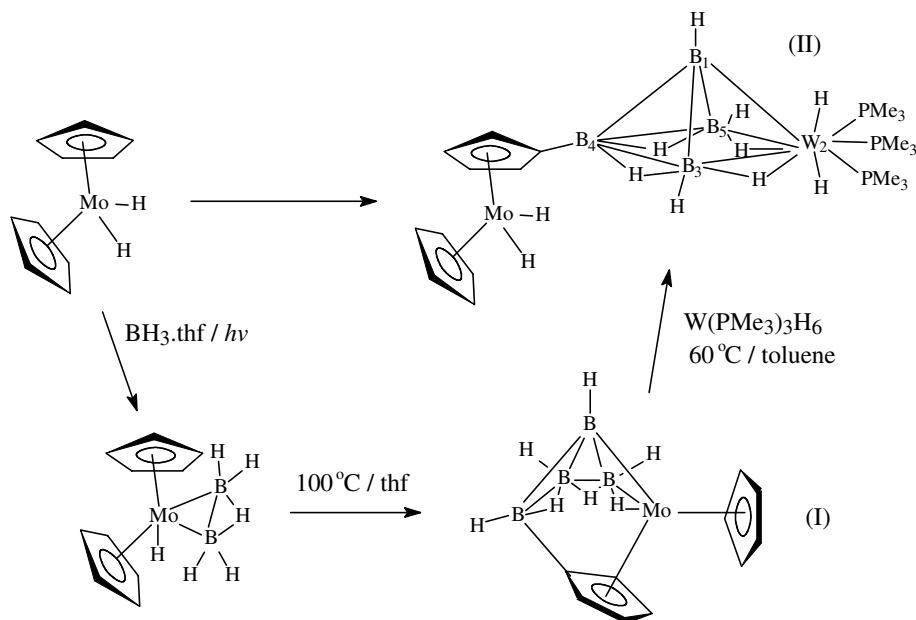


Fig. 1. Overall formation of *nido*-2- $W(PMe_3)_3H_2B_4H_7[Mo(\eta^5\text{-}C_5H_5)(\eta^5:\eta^1\text{-}C_5H_4)H_2]$  (II) in 3 steps from  $Mo(\eta\text{-}C_5H_5)_2H_2$ .

hydrogen on the basal atom furthest from the tungsten atom has been replaced by a  $\{Mo(\eta\text{-}C_5H_5)(\eta^5:\eta^1\text{-}C_5H_4)H_2\}$  fragment [22]. Consequently, the shielding patterns in both the  $^{11}B$  and  $^1H\{^{11}B\}$  NMR spectra of (II) closely resemble that of the unsubstituted cluster, except in the  $^{11}B$  NMR spectra for the boron atom attached to the  $\eta^5:\eta^1\text{-}C_5H_4$  ring. A comparison is given in Table 1 of the NMR data of the cluster fragment  $\{nido\text{-}2\text{-}W(PMe_3)_3H_2B_4H_7\}$  with the metallaborane *nido*-2- $[W(PMe_3)_3H_2B_4H_8]$ . Full NMR data for compound (II) is given elsewhere.<sup>1</sup>

The  $^{11}B$  NMR spectrum of (II) consists of 3 resonances in an integral ratio of 1:2:1. The broad singlet at  $\delta = 6.9$  ppm is assigned to  $B_4$  which does not have a terminal proton. In contrast to *nido*-2- $[W(PMe_3)_3H_2B_4H_8]$  the terminal B–H coupling on the two equivalent basal boron atoms ( $B_3$  and  $B_5$ ) is not resolved even

using line-narrowing techniques. The apical  $B_1$  atom however is a sharp doublet due to coupling to a terminal hydrogen atom ( $H_1$ ).

Compound (II) has a mirror plane through  $W_2$ ,  $B_4$  and the substituted cyclopentadienyl carbon atom. Thus, in the  $^1H$  NMR spectrum only two resonances are observed for the substituted cyclopentadienyl ring at  $\delta = 4.88$  ppm (t,  $I = 2$ ) and  $\delta = 4.66$  ppm (d,  $I = 2$ ). The resonance for a single unsubstituted cyclopentadienyl ring is at  $\delta = 4.65$  ppm (s,  $I = 5$ ). A sharp singlet at  $\delta = -8.36$  ppm ( $I = 2$ ) is assigned to two Mo–H protons. A broad quartet at  $\delta = -4.07$  ppm is assigned to two W–H protons coupled to three phosphorus atoms. No tungsten satellites were observed even in the  $^1H\{^{11}B\}$  spectrum. The  $^1H\{^{11}B\}$  NMR spectrum of (II) clearly sharpens four new resonances in a ratio 2:1:2:2 compared with the  $^1H$  NMR spectrum. These

Table 1

Comparison of NMR data for the  $\{nido\text{-}2\text{-}W(PMe_3)_3H_2B_4H_7\}$  fragment and *nido*-2- $[W(PMe_3)_3H_2B_4H_8]$

NMR/ppm	$\{nido\text{-}2\text{-}W(PMe_3)_3H_2B_4H_7\}$ fragment	<i>nido</i> -2- $[W(PMe_3)_3H_2B_4H_8]$
$^{11}B$ ( $J(^{11}B\text{-}^1H)$ )	6.9 [br s, 1B, $B_4$ ] –10.5 [br s, 2B, $B_{3,5}$ ] –27.4 [d, 1B, (150), $B_1$ ]	–3.7 [1B] –9.7 [2B] –29.7 [d, 1B, (150)]
$^1H\{^{11}B\}$ ( $J(^{31}P\text{-}^1H)$ )	3.23 [s, 2H, $H_{3,5}$ ] 1.37 [d, 27H, $PMe_3$ ] 0.69 [s, 1H, $H_1$ ] –1.35 [s, 2H, $H_{34,45}$ ] –4.07 [br q, 2H, (40), W–H] –8.98 [s, 2H, $H_{23,25}$ ]	5.36 [s, 1H] 3.50 [s, 2H] 1.40 [d, 27H, $PMe_3$ ] 1.05 [s, 1H] –2.10 [s, 2H] –4.05 [br q, 2H, (39), W–H] –8.75 [s, 2H]
$^{31}P\{^1H\}$	–29.2 [s, $PMe_3$ ]	–28.7 [s, $PMe_3$ ]

are assigned the terminal and bridging protons in the metallaborane cluster fragment  $\{\text{WB}_4\text{H}_7\}$ . Importantly, selective decoupling of  $\text{B}_4$  does not sharpen any resonances attributable to a terminal B–H proton, only the bridging protons  $\text{H}_{34,45}$  are sharpened.

The transfer of a borane cage from one metal atom to another is very rare. For example, the reaction of *nido*-2- $[\text{Fe}(\eta\text{-C}_5\text{H}_5)\text{B}_5\text{H}_{10}]$  with  $[\text{Re}(\text{PMe}_3)_5\text{H}]$  gives as one of the products the compound *nido*-2- $[\text{Re}(\text{PMe}_3)_3\text{B}_5\text{H}_{10}]$  via exchange of the  $\text{B}_5\text{H}_{10}$  borane fragment from the  $\text{Fe}(\eta\text{-C}_5\text{H}_5)$  group to  $\text{Re}(\text{PMe}_3)_3$  [23]. Interestingly, in the same paper, reaction of *nido*-2- $[\text{Fe}(\eta\text{-C}_5\text{H}_5)\text{B}_5\text{H}_{10}]$  with  $[\text{W}(\text{PMe}_3)_3\text{H}_6]$ , the same phosphine hydride molecule as in the present study, does not give borane fragment exchange but instead leads to capped-*closo*-1- $[\{\text{Fe}(\eta\text{-C}_5\text{H}_5)\}_2\text{-}\{\text{W}(\text{PMe}_3)_3\text{H}\}\text{B}_5\text{H}_7]$ . Other examples of borane fragment exchange usually involve salt-metathesis type reactions. For example, the thallium atom in  $[\text{TlR}_2\text{C}_2\text{B}_9\text{H}_9^-]$  ( $\text{R} = \text{H}$ , alkyl) is easily displaced by transition metals to give the corresponding metallacarboranes [24]. Gold to rhodium carborane cage transfer has been observed by Stone et al. [25].

The unique feature in the formation of (II) is that whilst the borane fragment has been completely removed from the molybdenum atom, the resulting tungstaborane is still attached to the compound by the B–C  $\sigma$ -bond between one of the cyclopentadienyl rings and a basal boron atom in the tungstaborane.

Compound (II) is formed in 3 steps from  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  (Fig. 1). Thus the overall reaction has been to substitute a proton on one of the cyclopentadienyl rings with the metallaborane cluster *nido*-2- $[\text{W}(\text{PMe}_3)_3\text{H}_2\text{B}_4\text{H}_8]$ . Attempts to form (II) by the thermolysis or photolysis of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  with *nido*-2- $[\text{W}(\text{PMe}_3)_3\text{H}_2\text{B}_4\text{H}_8]$  did not give the desired product.

Compound (I) was reacted with a variety of hydride- and carbonyl-containing molecules and analysed by multi-nuclear NMR to see if metal fragment exchange was more general. Samples of (I) thermolysed with  $[\text{Mo}(\text{PMe}_3)_4\text{H}_4]$ ,  $[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ ,  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{H}_3]$  or  $[\text{W}(\text{PMe}_3)_4\text{H}_2\text{Cl}_2]$  showed no evidence of metal fragment exchange rather  $[\text{BH}_3 \cdot \text{PMe}_3]$  and a new molybdacarborane [26] were identified as the only boron-containing products. Samples of (I) thermolysed or photolysed with  $[\text{Co}(\eta\text{-C}_5\text{Me}_5)_2(\text{CO})_2]$ ,  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Mo}(\text{CO})_6]$  and  $[\text{W}(\text{CO})_6]$  showed no evidence of metal fragment exchange either.

### Preparation of (II)

$[\text{W}(\text{PMe}_3)_3\text{H}_6]$  (0.15 g, 0.36 mmol) and (I) (0.10 g, 0.36 mmol) were dissolved in toluene (10 ml) and heated

in a sealed Young's ampoule at 60 °C for 12 h. Silica gel (1 g) was added to the resulting brown-orange solution and volatiles removed in vacuo. Chromatography of the resulting sand on silica, eluting with petroleum ether:THF 9:1, gave first a yellow band of the known compound  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  (1–2 mg) followed by a yellow-orange band. Elution with petroleum ether:THF 7:1 removed this band which was pumped down to an oil. The oil slowly crystallised on standing. Recrystallisation from petroleum ether: toluene 4:1 (5 ml) at –78 °C overnight gave orange yellow crystals of (II) which were filtered off, washed quickly with cold petroleum ether and pumped dry. Yield: 0.15 g, 60%.

### References

- [1] L. Barton, Comprehensive Organometallic Chemistry II, Pergamon Press, Oxford, 1995 (Chapter 8).
- [2] J.D. Kennedy, Progr. Inorg. Chem. 32 (1984) 519.
- [3] J.D. Kennedy, Progr. Inorg. Chem. 34 (1986) 211.
- [4] T.P. Fehlner, Organometallics 19 (2000) 2643.
- [5] R.N. Leyden, B.P. Sullivan, R.T. Baker, M.F. Hawthorne, J. Am. Chem. Soc. 100 (1978) 3578.
- [6] R. Weiss, J.R. Bowser, R. Grimes, Inorg. Chem. 17 (1978) 1522.
- [7] M. Mangion, J.D. Ragaini, T.A. Schmitkons, S.G. Shore, J. Am. Chem. Soc. 101 (1979) 754.
- [8] M. Elrington, N.N. Greenwood, J.D. Kennedy, M. Thornton-Pett, J. Chem. Soc., Chem. Commun. (1984) 1398.
- [9] L. Barton, D.K. Srivastava, Organometallics 10 (1991) 2983.
- [10] J. Bould, J.E. Crook, N.N. Greenwood, J.D. Kennedy, J. Chem. Soc., Dalton Trans. (1991) 185.
- [11] R.L. Thomas, L. Barton, Inorg. Chim. Acta 289 (1–2) (1999) 134.
- [12] J. Bould, N.P. Rath, H. Fang, L. Barton, Inorg. Chem. 35 (1996) 2062.
- [13] J. Bould, N.P. Rath, L. Barton, Inorg. Chem. 35 (1996) 35.
- [14] J. Bould, N.P. Rath, L. Barton, J. Chem. Soc., Chem. Commun. (1995) 1285.
- [15] J. Bould, M. Pasieka, J. Braddock-Wilking, N.P. Rath, L. Barton, C. Gloeckner, Organometallics 14 (1995) 5138.
- [16] P.D. Grebenik, M.L.H. Green, M.A. Kelland, J.B. Leach, P. Mountford, J. Chem. Soc., Chem. Commun. (1989) 1397.
- [17] S. Aldridge, H. Hashimoto, M. Shang, T.P. Fehlner, J. Chem. Soc., Chem. Commun. (1998) 207.
- [18] M.A. Kelland, D.Phil. Thesis, Oxford University, 1993.
- [19] A.S. Weller, M. Shang, T.P. Fehlner, Organometallics 18 (1999) 53.
- [20] P.D. Grebenik, M.L.H. Green, M.A. Kelland, J.B. Leach, in: IMEBORON, Torun, Poland, 1990.
- [21] L.G. Sneddon, D. Voet, J. Chem. Soc., Chem. Commun. (1976) 118.
- [22] M.L.H. Green, M.A. Kelland, L.L. Wong, P.D. Grebenik, J.B. Leach, in: IMEBORON, Bechyne, Czechoslovakia, 1987.
- [23] H.J. Bullick, P.D. Grebenik, M.L.H. Green, A.K. Hughes, J.B. Leach, P. Mountford, J. Chem. Soc., Dalton Trans. (1994) 3337.
- [24] J.L. Spencer, M. Green, F.G.A. Stone, J. Chem. Soc., Chem. Commun. (1972) 1178.
- [25] J.C. Jeffrey, P.A. Jelliss, F.G.A. Stone, J. Chem. Soc., Dalton Trans. (1993) 1073.
- [26] M.L.H. Green, M.A. Kelland, J.B. Leach (manuscript in preparation).