# H-D Exchange Reaction of Borane-Lewis Base Adducts by Rhenium Polyhydride Complexes

Taeko Kakizawa, Yasuro Kawano,* and Mamoru Shimoi*
*Department of Basic Science, Graduate School of Arts and Sciences, Univesity of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902*

(Received May 13, 1999; CL-990379)

Heating of a benzene-$d_6$ solution of $BH_3{\cdot}L$ (L = $PMe_3$, $NMe_3$) and $[ReH_7(PPh_3)_2]$ resulted in the formation of the deuterated boranes, $BH_{3-n}D_n{\cdot}L$ ($n$ = 0–3). Deuteration of $BH_3{\cdot}L$ with $[ReH_5(PR_3)_3]$ ($PR_3$ = $PPh_3$, $PPhMe_2$) required photo-irradiation. The mechanism of the H-D exchange is discussed.

---

Transition metal polyhydride complexes have attracted much interest in recent studies.[1] They are known to liberate $H_2$ giving coordinatively unsaturated species under mild conditions. The resulting intermediates are highly reactive and interact with various substrates to produce new complexes. In many cases, polyhydride complexes are fluxional, where the hydrogen atoms in the coordination sphere rapidly exchange their positions.

Borane-Lewis base adducts, $BH_3{\cdot}L$ are isoelectronic and isostructural with alkanes. We previously reported complexes of $BH_3{\cdot}L$, $[M(CO)_5(\eta^1\text{-}BH_3{\cdot}L)]$ (M = Cr, W; L = $PMe_3$, $PPh_3$, $NMe_3$), in which the borane coordinates to the central metal through a M–H–B single bridge.[2] These complexes show fluxional behavior due to rapid scrambling between the bridging and terminal hydrogen atoms. In an attempt to synthesize highly fluxional polyhydride(borane) complexes, we examined the reactions of borane-Lewis base adducts with rhenium polyhydride complexes. However, treatment of several boranes with the rhenium complexes in deuterated solvents resulted in an unexpected reaction, H-D exchange between the boranes and solvents. This is the first example of H-D exchange between $sp^2$ carbon and $sp^3$ boron, and closely associated with metal-catalyzed deuteration of alkanes.[3]

A benzene-$d_6$ solution of $BH_3{\cdot}PMe_3$ and $ReH_7(PPh_3)_2$ (**1**) in 1 : 2 ratio was heated at 47 °C, and the progress of the reaction was monitored by NMR spectroscopy. The $^{11}B\{^1H\}$ NMR spectral change during the reaction is shown in Figure 1. Before heating, $BH_3{\cdot}PMe_3$ displays a doublet coupled with a $^{31}P$ nuclei at –37.0 ppm. This signal changed to the overlapping multiplets upon heating. The spectrum after 40 min of heating essentially consists of a doublet of triplets. This is attributed to the coupling with a $^{31}P$ ($I$ = 1/2) and a $^2H$ ($I$ = 1) nuclei, and assigned to the mono-dueterated isotopomer, $BH_2D{\cdot}PMe_3$. This signal is shifted to the slightly higher field relative to that of starting $BH_3{\cdot}PMe_3$ due to an isotope effect. Owing to the overlap with the doublet of $BH_3{\cdot}PMe_3$, two peaks in the signal are observed strongly. At the base of the signal, toward the higher field, the weak peaks of the di- and tri-deuterated isotopomers, $BHD_2{\cdot}PMe_3$ and $BD_3{\cdot}PMe_3$ are also found. Apparent change of the $^{11}B$ NMR spectra ceased after 24 h of heating. The final spectrum was consistent with that of independently prepared $BD_3{\cdot}PMe_3$ in the chemical shift, and the splitting pattern was similar to that. The ratio of deuteration of $BH_3{\cdot}PMe_3$ was ca. 80% as estimated by $^{11}B$ NMR.[4] At this stage, the signal of **1** completely disappeared in the $^{31}P$ NMR. Thus, the H-D exchange in $BH_3{\cdot}PMe_3$ is terminated with the decomposition of complex **1**. Similarly, $BH_3{\cdot}NMe_3$ underwent H-D exchange in the reaction with **1** in benzene-$d_6$. The final percentage of the deuteration was also ca. 80%. On the other hand, no reaction was observed when $BH_3{\cdot}PMe_3$ was treated with **1** in cyclohexane-$d_{12}$.

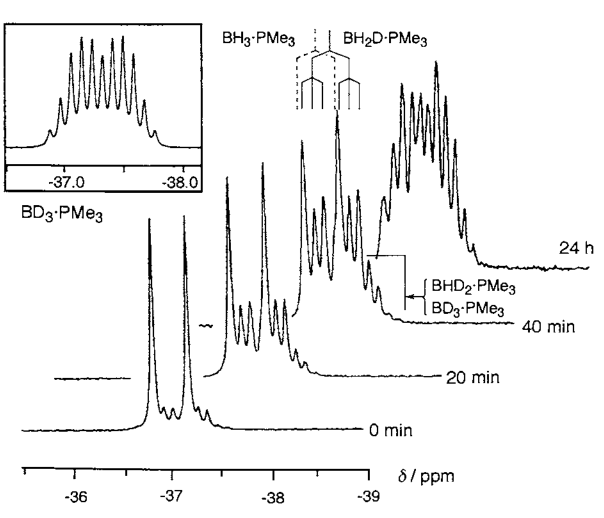
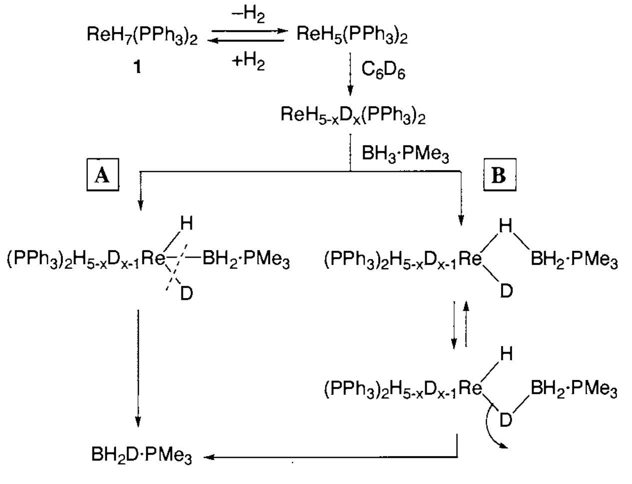


**Figure 1.** $^{11}B$ NMR spectral change (160.4 MHz, reference: $BF_3{\cdot}OEt_2$) during the reaction of $BH_3{\cdot}PMe_3$ with **1**. The spectrum of $BD_3{\cdot}PMe_3$ is shown in the frame.

Possible mechanisms for the H-D exchange of $BH_3{\cdot}L$ are shown in Scheme 1. First, a polydeuteride intermediate $[ReH_{5-x}D_x(PPh_3)_2]$ is formed by repeated oxidative addition / reductive elimination of $C_6D_6$ to the coordinatively unsaturated rhenium center, which was generated by elimination of $H_2$.[5] In pathway **A**, oxidative addition of $BH_3{\cdot}L$ to the polydeuteride intermediate gives a boryl complex. Reductive elimination of the boryl group with a deuterido ligand affords the deuterated boranes. In path **B**, $BH_3{\cdot}L$ coordinates to the polydeuteride intermediate through a 3c2e bond as found in $[M(CO)_5(\eta^1\text{-}BH_3{\cdot}L)]$.[2] The H-D exchange of the boranes is achieved by rapid scrambling of hydrido or deuterido ligands on rhenium, the



**Scheme 1.**

**Table 1.** Reaction of borane–Lewis base adducts with rhenium polyhydride complexes

| Re complex | Borane | B : Re | Solvent | Conditions | Product (percentage of deuteration) |
|---|---|---|---|---|---|
| $ReH_7(PPh_3)_2$ (**1**) | $BH_3{\cdot}PMe_3$ | 1 : 1 | $C_6D_6$ | 40 °C (24 h) | $BH_{3\text{-}n}D_n{\cdot}PMe_3$ (~90%) |
| | $BH_3{\cdot}PMe_3$ | 1 : 1 | $C_6D_{12}$ | 40 °C (2 h) | no reaction |
| | $BH_3{\cdot}NMe_3$ | 2 : 1 | $C_6D_6$ | 40 °C (24 h) | $BH_{3\text{-}n}D_n{\cdot}NMe_3$ (80%) |
| | $BH_2Cl{\cdot}PMe_3$ | 1 : 1 | $C_6D_6$ | 40 °C (7 h) | $BH_{2\text{-}n}D_nCl{\cdot}PMe_3 : BH_{3\text{-}n}D_n{\cdot}PMe_3 = 3 : 1$[a] |
| | $B_2H_4{\cdot}2PMe_3$ | 1 : 1 | $C_6D_6$ | 40 °C (24 h) | $B_2H_{4\text{-}n}D_n{\cdot}2PMe_3$[b] |
| | $B_2H_4{\cdot}2PMe_3$ | 1 : 1 | $C_6D_6$ | 80 °C (24 h) | $B_2H_{4\text{-}n}D_n{\cdot}2PMe_3 : BH_{3\text{-}n}D_n{\cdot}PMe_3 = 4 : 1$[a,b] |
| $ReH_5(PPh_3)_3$ (**2**) | $BH_3{\cdot}PMe_3$ | 1 : 1 | $C_6D_6$ | hv (24 h)[c] | $BH_{3\text{-}n}D_n{\cdot}PMe_3$ (80%) |
| | $BH_3{\cdot}PMe_3$ | 1 : 1 | $C_6D_5CD_3$ | hv (1 h) | $BH_{3\text{-}n}D_n{\cdot}PMe_3$ (40%) |
| | $BH_3{\cdot}PMe_3$ | 1 : 1 | $C_6D_{12}$ | hv (2 h) | no reaction |
| | $BH_3{\cdot}NMe_3$ | 2 : 1 | $C_6D_6$ | hv (24 h) | $BH_{3\text{-}n}D_n{\cdot}NMe_3$ (80%) |
| | $BH_2Cl{\cdot}PMe_3$ | 1 : 1 | $C_6D_6$ | hv (17 h) | $BH_2Cl{\cdot}PMe_3 : BH_{3\text{-}n}D_n{\cdot}PMe_3 = 1 : 3$[a,b] |
| $ReH_5(PMe_2Ph)_3$ (**3**) | $BH_3{\cdot}PMe_3$ | 1 : 1 | $C_6D_6$ | hv (24 h) | $BH_{3\text{-}n}D_n{\cdot}PMe_3 : BH_{3\text{-}n}D_n{\cdot}PMe_2Ph = 2 : 1$[a] |
| | $BH_3{\cdot}PMe_3$ | 1 : 2 | $C_6D_5CD_3$ | hv (-64 °C, 1.5 h) | $BH_{3\text{-}n}D_n{\cdot}PMe_3$ (50%) |
| | $BH_3{\cdot}NMe_3$ | 2 : 1 | $C_6D_6$ | hv (24 h) | $BH_{3\text{-}n}D_n{\cdot}NMe_3$ (90%) |
| | $BH_2Cl{\cdot}PMe_3$ | 1 : 1 | $C_6D_6$ | hv (12 h) | $BH_{2\text{-}n}D_nCl{\cdot}PMe_3 : BH_{3\text{-}n}D_n{\cdot}PMe_3 = 1 : 1$[a] |
| $CpReH_2(PPh_3)_2$ (**4**) | $BH_3{\cdot}PMe_3$ | 2 : 1 | $C_6D_6$ | hv (2 h) | $BH_{3\text{-}n}D_n{\cdot}PMe_3$ (trace) |
| | $BH_3{\cdot}NMe_3$ | 1 : 1 | $C_6D_6$ | hv (2 h) | $BH_{3\text{-}n}D_n{\cdot}NMe_3$ (trace) |

[a] The ratio of deuteration could not be estimated due to the overlap of the signals. [b] The signal was so broad that the percentage of deuteration was not clear.
[c] Photolysis was carried out at 7 °C unless stated.

hydrogen atom bridging rhenium and boron, and terminal hydrogen on boron[6] followed by the elimination of the borane. Although no intermediates have been detected spectroscopically, we prefer path **B** as the mechanism of deuteration of the boranes since the following reasons. An MO calculation for $BH_3{\cdot}PH_3$ indicates that the antibonding orbitals of BH are energetically so high that oxidative addition of the BH bond would be quite difficult.[2] Moreover, rapid interchange between terminal and bridging BH's is observed in many polyboranes.[7] For zirconium and osmium tetrahydroborate complexes $[Cp_2ZrH(\eta^2\text{-}BH_4)]$[8] and $[OsH_3(\eta^2\text{-}BH_4)(PR_3)_2]$,[9] scrambling of the terminal and bridging BH atoms as well as the hydrido ligands on metal has been found. The fact that the H-D exchange does not occur in cyclohexane-$d_{12}$ indicates that $C_6D_{12}$ is not activated by **1**. This contrasts with the report of Baudry et al., where cyclohexane undergoes dehydrogenation by **1** in the presence of a hydrogen acceptor neohexene, to give cyclohexene.[10]

The results of this work are summarized in Table 1. Deuteration of boranes by the use of pentahydride complexes $[ReH_5L_3]$ (**2**: L = $PPh_3$, **3**: L = $PPhMe_2$) required photo-irradiation using a medium-pressure Hg lamp. Photochemical liberation of a phosphine ligand rather than $H_2$ from $[ReH_5L_3]$ has been reported.[11,12] Thus, thermolysis of **1** and photolysis of **2** give the identical intermediate, and it mediates the H-D exchange of boranes. In the **3**–$BH_3{\cdot}PMe_3$ system, formation of $BH_{3\text{-}n}D_n{\cdot}PPhMe_2$ by ligand exchange on borane was also observed. The photolysis and following measurement of $^{11}B$ NMR of a toluene-$d_8$ solution of $BH_3{\cdot}PMe_3$ and **3** at -64 °C was carried out for the purpose of direct observation of the intermediate. Even under such a condition, however, no complex with a borane–rhenium interaction was detected. The table also includes the results of the reactions with use of $BH_2Cl{\cdot}PMe_3$ and $B_2H_4{\cdot}2PMe_3$, which lead to B–Cl and B–B bond cleavage to produce $BH_{3\text{-}n}D_n{\cdot}PMe_3$. Treatment of boranes with $CpReH_2(PPh_3)_2$ (**4**) under photo-irradiation yielded only a trace amount of $BH_2D{\cdot}PMe_3$. This indicates that the boranes scarcely interact with the intermediate derived from **4**, as opposed to the alkane–$C_6D_6$ H-D exchange catalyzed by **4**.[3]

This work was supported by a grant (no. 960288) to Y. K. from The Sumitomo Foundation.

## References and Notes

1 a) R. H. Crabtree, *Angew. Chem., Int. Ed. Engl.*, **32**, 789 (1993). b) G. J. Kubas, *Acc. Chem. Res.*, **21**, 120 (1988). c) D. M. Heinekey and W. J. Oldham, Jr., *Chem. Rev.*, **93**, 913 (1993).

2 M. Shimoi, S. Nagai, M. Ichikawa, Y. Kawano, K. Katoh, M. Uruichi, and H. Ogino, submitted for publication.

3 For example, W. D. Jones, G. P. Rosini, and J. A. Maguire, *Organometallics*, **18**, 1754 (1999), and references cited therein.

4 In $^1H$ NMR, decrease of the phenyl signals was also observed, indicating deuteration of the phenyl groups of the phosphine ligands.

5 Progressive decrease of the hydrido signal of **1** in $CD_2Cl_2$ has been reported, suggesting the incorporation of deuteron onto the rhenium: D. Baudry, M. Ephritikhine, and H. Felkin, *J. Organomet. Chem.*, **224**, 363 (1982).

6 This process can also be regarded as a migration of a boryl cation $[BH_2{\cdot}L]^+$ from a hydrido onto a deuterido ligand in an anionic complex $[ReH_{6\text{-}n}D_n(PPh_3)_2]^-$. Several boryl cations with the formula $[BX_2{\cdot}L]^+$ are known.[a] The anion $[ReH_6(PPh_3)_2]^-$ has also been isolated.[b] a) P. Kölle and H. Nöth, *Chem. Rev.*, **85**, 399 (1985). b) D. Alvarez, Jr., E. G. Lundquist, J. W. Ziller, W. J. Evans, and K. G. Caulton, *J. Am. Chem. Soc.*, **111**, 8392 (1989).

7 H. Beall and C. H. Bushweller, *Chem. Rev.*, **73**, 465 (1973).

8 T. J. Marks and J. R. Kolb, *J. Am. Chem. Soc.*, **97**, 3397 (1975).

9 a) P. W. Frost, J. A. K. Howard, and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, **1984**, 1362. b) I. Dewachy, M. A. Esteruelas, Y. Jean, A. Lledós, F. Maseras, L. A. Oro, C. Valero, and F. Volatron, *J. Am. Chem. Soc.*, **118**, 8388 (1996).

10 a) D. Baudry, M. Ephritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, **1982**, 606. b) D. Baudry, M. Ephritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, **1980**, 1243. c) D. Baudry and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, **1980**, 249.

11 M. A. Green, J. C. Huffman, K. G. Caulton, W. K. Rybak, and J. Ziolkowski, *J. Organomet. Chem.*, **218**, C39 (1981).

12 Free $PPh_3$ was actually observed in $^{31}P$ NMR during the reaction.