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# Fluxional behavior of chromium and tungsten complexes of monodentate bis(trimethylphosphine)diborane(4), $[M(CO)_5(\eta^1\text{-}B_2H_4\cdot 2PMe_3)]$ ($M = Cr, W$): A model case for alkane–metal complexes

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## Abstract

Group 6 metal complexes of monodentate bis(trimethylphosphine)diborane(4), $[M(CO)_5(\eta^1\text{-}B_2H_4\cdot 2PMe_3)]$ ($M = Cr, W$) show two fluxional processes in solution: one is the very rapid exchange of the coordinated B*H* atom with the geminal hydrogen atom, and the other one is rather slow exchange with the vicinal hydrogens. This behavior embodies the fluxionality predicted for the tungsten ethane complex, $[W(CO)_5(\eta^1\text{-}C_2H_6)]$. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Borane complexes; Alkane complexes; Chromium; Tungsten; Fluxional behavior

## 1. Introduction

Much attention has been focused on transition metal alkane complexes [1]. In particular, ever since the photochemical formation of octahedral Group 6 metal complexes $[M(CO)_5(\text{alkane})]$ was discovered [2], significant efforts have been made to study the chemistry of these complexes. Nevertheless, the details of structures and solution behaviors of these compounds are not clear due to their extreme instability. In 1997, Zaric and Hall proposed a C–H–W bent linkage for the coordination mode of methane in the tungsten methane complex, $[W(CO)_5(\eta^1\text{-}CH_4)]$ [3]. They also predicted a fluxional character of the coordinated methane due to the rapid exchange of hydrogen atoms between the bridging and terminal positions.

We recently reported the photochemical syntheses of isolable metal complexes of monoborane-Lewis base adducts, $[M(CO)_5(\eta^1\text{-}BH_3\cdot L)]$ (**1**; $M = Cr, W$; $L = NMe_3, PMe_3, PPh_3$). Note that the ligand $BH_3\cdot L$ is isoelectronic with methane. In these complexes, the borane ligand is bound to the metal center through a *bent B–H–M single bridge*, and the *bridging and terminal hydrogen atoms are exchanging* very rapidly (Scheme 1) [4]. Thus, these properties of the borane adduct complexes manifest the predicted behavior of the methane complex.

Earlier, we reported the syntheses of isolable complexes of a diborane(4) derivative, $[M(CO)_5(\eta^1\text{-}B_2H_4\cdot 2PMe_3)]$ (**2a**: $M = Cr$; **2b**: $M = W$) and $[M(CO)_4(\eta^2\text{-}B_2H_4\cdot 2PMe_3)]$ (**3a**: $M = Cr$; **3b**: $M = W$; Eq. (1)) [5]. Since the diborane ligand $B_2H_4\cdot 2PMe_3$ is isoelectronic with ethane, these complexes can be regarded as a model system for ethane complexes [6]. Our preliminary NMR studies on the monodentated complexes, **2a** and **2b**, revealed that the bridging hydrogen atom is rapidly exchanging position with its geminal hydrogen [5]. We have since acquired more NMR data for **2a** and **2b** on

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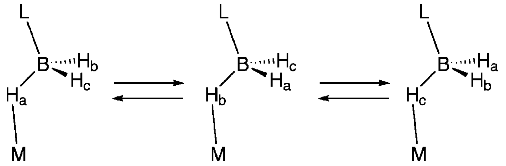
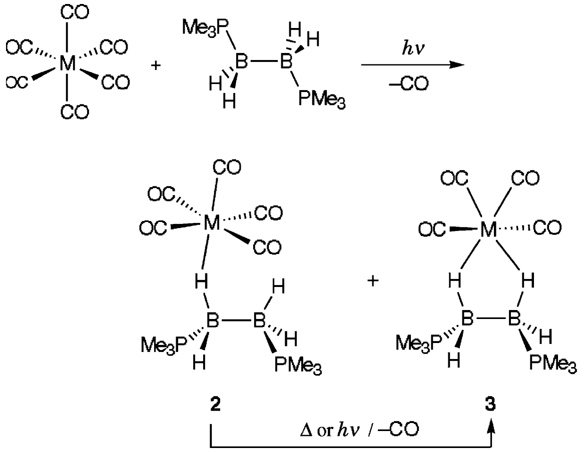


Scheme 1.

higher field instruments to further investigate the fluxional process of these complexes. In this paper, the findings are described, and compared with the reported behavior of alkane complexes.



(1)

## 2. Experimental

The borane complexes, **2a** and **2b**, were prepared by the reported methods [5]. Dichloromethane-$d_2$ and $C_6H_5CH_3$-$d_8$ were dried over molecular sieves 3A and potassium mirror, respectively. These solvents were distilled on a vacuum line into NMR sample tubes containing the samples, to prepare solutions immediately before the measurements. NMR spectra were recorded on JEOL FX-90Q, Varian XL-200, Varian XL-300, GX-400, or XL 500 spectrometers. The temperature-dependent NMR spectra were analyzed with the use of a line shape analysis program, DNMR3 [7].

## 3. Results and discussion

The NMR data pertinent to the discussion in this section are listed in Tables 1 and 2. $^{11}$B-, $^{31}$P-, or $^{1}$H-single-frequency decoupling experiments confirmed the signal assignments that are indicated in the table. In the temperature range from −50 to 0 °C, the 300 MHz $^{1}$H-NMR spectrum of the chromium complex, **2a**, consists of four signals. The methyl proton (CH) signals from two nonequivalent $PMe_3$ appear at 1.28 and 1.22 ppm, each as a doublet. The borane proton (BH) signals are at 0.1 and −6.5 ppm in a 1:1 intensity ratio. The observed spectrum is consistent with the monodentated structure in which the bridging hydrogen and its geminal hydrogen are exchanging positions rapidly (Path A in Scheme 2).

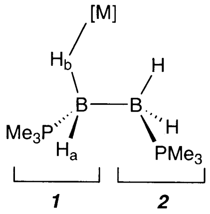
The exchange rate decreases significantly at low temperatures. Thus, as the temperature is decreased, the −6.5 ppm signal broadens and is lost in the base line at −112 °C. At −122 °C, a newly developed, broad signal is clearly visible at −13.7 ppm. Another broad signal is expected to develop simultaneously at around 0.5 ppm. Although this 0.5 ppm signal is severely overlapped with the signals at 0.1 (BH), 1.16 (CH) and 1.22 ppm (CH), a broad rise of base line in this region of the spectrum indicates the presence of the broad signal. See Table 1 and Fig. 1 (the two CH signals appear as one signal in the figure due to the compressed horizontal axis and truncation of the signal peak).

The $^{1}$H-NMR spectra of the tungsten complex, **2b**, in the comparable temperature range are also consistent with the monodentated, fluxional structure, see Table 1. However, the broadening and subsequent splitting of high field BH signal (−3.9 ppm) does not occur at the lower temperatures. Apparently, the geminal hydrogen atom exchange is faster for the tungsten complex than that for the chromium complex. Another notable difference is that, although each of the two CH signals is a doublet for **2a**, corresponding signal for **2b** is a virtual triplet until the temperature is lowered to −100 °C where it appears as a simple doublet. These differences between the two compounds will be discussed later in this section.

At +30 °C, the two CH doublet signals of **2a** coalesce (Fig. 2). Likewise, the CH signals of **2b** coalesce to a single virtual triplet at ca. +5 °C. Apparently, at these higher temperatures the metal-coordinated hydrogen exchanges the position with the vicinal hydrogen atoms (Path B in Scheme 2) fast enough to bring about the coalescence of the two CH signals which are only several hundredth of a ppm apart. The two BH signals stay separated in the same temperature range. These two signals are too far apart to coalesce at the practicable temperatures. For the same reason, the two $^{11}$B signals for each of complexes **2**, or the two $^{31}$P signals of **2a** do not coalesce. The single broad $^{31}$P signal of **2b** may be an overlap of two signals. The overall scheme of the fluxional behavior of complex **2** is summarized in Scheme 2. This process includes the fast exchange of the metal-coordinated BH proton with the geminal hydrogen, path A, and slow exchange with vicinal the hydrogens, path B.

The free energy of activation, $\Delta G^{\ddagger}_{173}$, for the geminal hydrogen exchange (Path A) was estimated to be 28 kJ mol$^{-1}$ for **2a**, by the coalescence point methods [8]. The activation energy for the tungsten complex, **2b**, ought to be less than 28 kJ mol$^{-1}$, because of the absence of

Table 1
$^1H$ NMR shift for $[M(CO)_5(\eta^1\text{-}B_2H_4\cdot 2PMe_3)]$ (**2**)



$[Cr(CO)_5(\eta^1\text{-}B_2H_4\cdot 2PMe_3)]$ (**2a**)

| Freq./MHz | Solvent | Temp./ °C | P*Me*$_3$(2) | P*Me*$_3$(1) | B*H*(2) | B*H*(1a) | B*H*(1b) |
|---|---|---|---|---|---|---|---|
| 200 [a] | $C_6D_5CD_3$ | Ambient | | 0.84 (vt) [b] | 0.2 | | −6.3 |
| 300{$^{11}$B} | $CD_2Cl_2$ | −20 | 1.28 (d) [c] | 1.23 (d) [c] | 0.1 | | −6.5 |
| 300{$^{11}$B} | | −122 | 1.22 (d) [c] | 1.16 (d) [c] | 0.1 | ~ 0.5 | −13.7 |

$[W(CO)_5(\eta^1\text{-}B_2H_4\cdot 2PMe_3)]$ (**2b**)

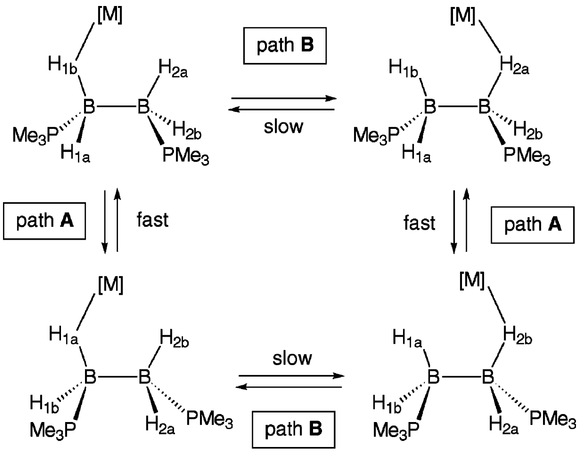
| Freq./MHz | Solvent | Temp./ °C | P*Me*$_3$(2) | P*Me*$_3$(1) | B*H*(2) | B*H*(1a) |
|---|---|---|---|---|---|---|
| 200 [a] | $C_6D_5CD_3$ | Ambient | | 0.86 (vt) [b] | 0.1 | −3.9 |
| 300{$^{31}$P} | $CD_2Cl_2$ | +20 | | 1.30 | 0.3 | −3.9 |
| 300{$^{31}$P} | | −20 | 1.31 | 1.24 | 0.3 | −3.9 |
| 500{$^{11}$B} | | −20 | 1.32 (vt) [b] | 1.25 (vt) [b] | 0.2 | −3.9 |
| 500{$^{11}$B} | | −100 | 1.26 (d) [c] | 1.20 (d) [c] | 0.3 | −3.9 |

[a] Reported in reference 6.
[b] Virtual triplet.
[c] Doublet.

Table 2
$^{11}$B- and $^{31}$P-NMR shift data for $[M(CO)_5(\eta^1\text{-}B_2H_4\cdot 2PMe_3)]$ (**2**) [a]

| Compound | $^{11}$B (96.2 MHz) | | $^{31}$P (121.4 MHz) | |
|---|---|---|---|---|
| | B(2) | B(1) | P(2) | P(1) |
| $[Cr(CO)_5(\eta^1\text{-}B_2H_4\cdot 2PMe_3)]$ (**2a**) | −36.7 | −38.5 | 3.1 | 1.1 |
| $[W(CO)_5(\eta^1\text{-}B_2H_4\cdot 2PMe_3)]$ (**2b**) | −36.3 | −42.8 | 1.51 (br) [b] | |

[a] Shifts in ppm, standards being $BF_3\cdot OEt_2$ and 85% phosphoric acid; solvent, $CD_2Cl_2$; temperature, −20 °C; proton-spin decoupled.
[b] Possibly an overlap of two signals.



Scheme 2.

collapse of the high-field BH signal at −100 °C. These values of activation energy for geminal BH exchange compare with those reported for other related compounds. $\Delta G^{\ddagger}$ value: $<30$ kJ mol$^{-1}$ for $[Cr(CO)_5(\eta^1\text{-}BH_3\cdot PMe_3)]$ (193 K) [4], 41 kJ mol$^{-1}$ for $[FeH(\eta^1\text{-}BH_4)(dmpe)_2]$ (190 K, dmpe = bis(dimethylphosphino)ethane) [9], and 34.7 kJ mol$^{-1}$ for $[Cp_2Ta\{\eta^1\text{-}BH_3(SiH\textit{t}\text{-}Bu_2)\}(PMe_3)]$ (215 K) [10]. The free energies of activation, $\Delta G^{\ddagger}_{285}$, for the vicinal hydrogen exchange (Path B) were estimated to be 64 and 60 kJ mol$^{-1}$ for **2a** and **2b**, respectively. The line shape analysis of the temperature dependent $^1$H{$^{31}$P}-NMR spectra of **2b** provided the activation parameters for this process: $\Delta H^{\ddagger} = 52(2)$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -27(7)$ J mol$^{-1}$ K$^{-1}$. The negative value of the activation entropy suggested that this exchange proceed through a concerted mechanism via an $\eta^2$-interaction of the borane ligand rather than a complete borane dissociation-recombination mechanism. The same analysis could not be performed on **2a** because of the thermal instability of the compound.

The diborane ligand in complexes **2** is in an eclipsed, anticlinal conformation (dihedral angle B–P–B′–P′ ≃ 120°) in crystals, as illustrated in Eq. (1) [5]. Since the steric hindrance among the $M(CO)_5$ group and two $PMe_3$ is minimized in this conformation, this is the most stable configuration in solutions also. When the metal bonded hydrogen atom of complexes **2** changes the role

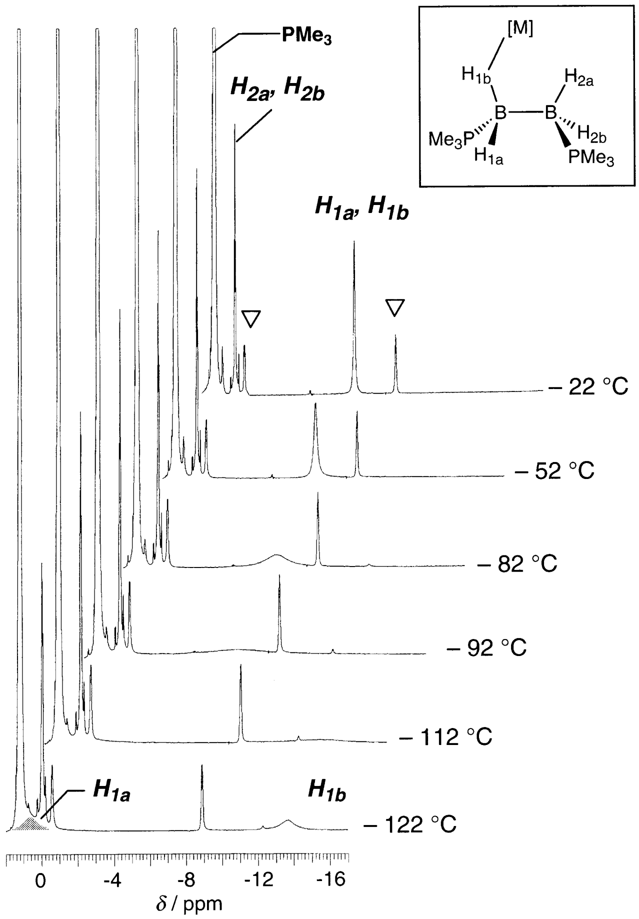


Fig. 1. Temperature-dependent $^{11}$B-decoupled $^{1}$H-NMR spectra of [Cr(CO)$_5$($\eta^1$-B$_2$H$_4$·2PMe$_3$)] (**2a**) (BH region) in a range of −122 to −22 °C (500 MHz, CD$_2$Cl$_2$). The nonequivalent two methyl signals appear as one signal in this figure due to the compressed $X$-axis and truncation of the signal peaks. For the detailed CH region, see Fig. 2. ∇, [Cr(CO)$_4$($\eta^2$-B$_2$H$_4$·2PMe$_3$)] (**3a**).

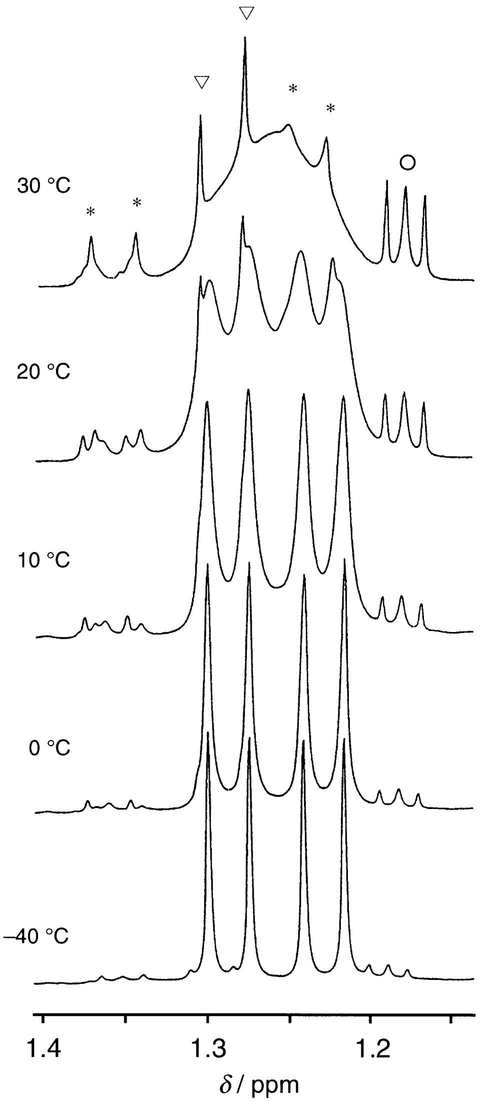
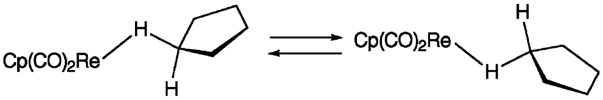


Fig. 2. The CH region of temperature-dependent $^{1}$H-NMR spectra of [Cr(CO)$_5$($\eta^1$-B$_2$H$_4$·2PMe$_3$)] (**2a**) in a range of −40–30 °C (400 MHz, CD$_2$Cl$_2$). Circle, free B$_2$H$_4$·2PMe$_3$; ∇, [Cr(CO)$_4$($\eta^2$-B$_2$H$_4$·2PMe$_3$)] (**3a**); *, impurities.

with its geminal hydrogen, the B–B bond must rotate in order to reassume the most stable configuration, which is the mirror image of the original conformation. The rotation could proceed by going through either the *syn* periplanar (0°) or *anti* (180°) conformation. However, the *syn* conformation is sterically unfavorable because of the severe spatial interaction between the two bulky PMe$_3$ groups. Therefore, the rotation has to proceed by way of the *anti* conformation, which necessarily brings M(CO)$_5$ and P′Me$_3$ close together in the process. Although the M(CO)$_5$ group is bulky too, it is bonded to the boron atom through a bent, long M–H–B bond and the bond is flexible. Therefore, this route of transformation through the *anti* conformation is thought to be feasible. Consequently, the extent of steric interaction between M(CO)$_5$ and P′Me$_3$ becomes crucial to the exchange rates. Since the bond radius of chromium is smaller than that of tungsten [11], the barrier for the B–B rotation is expected to be larger for the chromium system than for the tungsten system. The observed slower exchange rate for the chromium complex **2a**, relative to that for the tungsten complex **2b**, may thus be explained.

As mentioned in an earlier paragraph, the methyl proton signals appear as two deceptively simple doublets for complex **2a**, whereas these are two virtual triplets for complex **2b**. The doublet appearance of the signal is due to the small P–P′ coupling constant, and the virtual triplet appearance is to the large coupling constant [12]. When the geminal hydrogen exchange is slow, the ligand spends correspondingly longer time in the most stable, anticlinal conformation. The value of P–P′ coupling constant for anticlinal conformation being smaller than that for *anti* or *syn* periplanar conformation [13], the effective value of $^{3}J_{\mathrm{PP'}}$ for a slowly exchanging system is expected to be smaller than that for a faster system which would receive more contribution from the *anti*



Scheme 3.

conformation with a large P–P′ coupling constant. Even for fast exchanging **2b** the exchange rate becomes sufficiently slow at −100 °C for the signals to appear as doublets. Thus, the observed appearance of the CH signals is in keeping with the arguments presented in the preceding paragraph.

Recently, a rhenium alkane complex [CpRe(CO)$_2$(*cyclo*-C$_5$H$_{10}$)] was photo-chemically generated, and directly observed by NMR spectroscopy at −100 °C [14]. Its $^1$H-NMR spectrum indicated that the coordinated hydrogen atom of the cyclopentane ligand was exchanging rapidly with the geminal hydrogen atom (Scheme 3). However, the exchange with the vicinal hydrogen atoms was not observed at this temperature. According to theoretical calculations by Zaric and Hall on [W(CO)$_5$(η$^1$-C$_2$H$_6$)], the barrier for the exchange with the vicinal hydrogen atoms is significantly larger than that between the geminal hydrogen atoms [3]. These properties of the alkane complexes parallel the observed fluxional behaviors of diborane complexes **2**.

As the result of this work, the observed parallel relationship in properties between the complexes of borane(3) adducts and those of methane has been extended to the complexes of B$_2$H$_4$·2PMe$_3$ and alkanes containing more than one carbon atom. Metal complexes of electron-precise borane adducts are generally stable enough, relative to those of alkanes, for their convenient characterization. Therefore, results from the studies of borane adduct complexes are expected to be useful for the study of alkane complexes.

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