Syntheses of Ruthenium Chlorohydroborato Complexes $Cp^*Ru(PMe_3)(\eta^2\text{-}BH_3Cl)$ and $Cp^*Ru(PMe_3)(\eta^2\text{-}BH_2Cl_2)$: Unexpected Chloride Transfer from Ruthenium to Boron

Yasuro Kawano* and Mamoru Shimoi

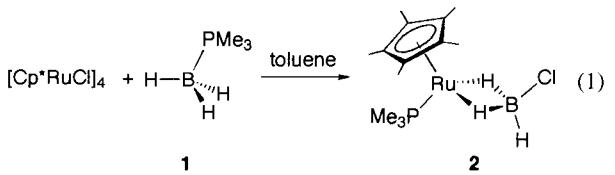
Department of Basic Science, Graduate School of Arts and Sciences, University of Tokyo, Meguro-ku, Komaba, Tokyo 153-8902

(Received May 25, 1998; CL-980399)

Trimethylphosphineborane (**1**) reacted with $[Cp^*RuCl]_4$ to lead the unexpected chloride transfer from ruthenium to boron affording a chlorotrihydroborato ruthenium complex $[Cp^*Ru(PMe_3)(\eta^2\text{-}BH_3Cl)]$ (**2**) in 44% yield. The structure of **2** was elucidated by X-ray crystallography. Reaction of **1** with $[Cp^*RuCl_2]_2$ produced a dichlorodihydroborato complex $[Cp^*Ru(PMe_3)(\eta^2\text{-}BH_2Cl_2)]$ (**3**) besides **2**.

Trimetylphosphineborane, $BH_3{\cdot}PMe_3$ (**1**), is an isoelectronic and isostructural compound with methane. Activation of **1** using transition metal complexes is an interesting subject as a synthetic method of borane-metal complexes and in relation to alkane activation as well. We previously reported BH bond activation of **1** using an electron-rich tungsten complex $[Cp^*W(CO)_3CH_3]$, which produces a novel boryl complex $[Cp^*W(CO)_3(BH_2{\cdot}PMe_3)]$.[1] This is a very rare example of activation of tetra-coordinate (sp^3-type) borane to form metal complexes.[2,3] The success of BH activation suggests that electron-rich metal complexes having a Cp* ligand is effective for activation of **1**. Such an idea prompted us to examine the reactions of **1** with $[Cp^*RuCl]_4$[4] and $[Cp^*RuCl_2]_2$.[5] We have found unexpected occurrences of bond rearrangements including a B-P bond activation during the reactions.

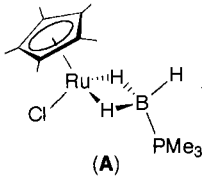
Treatment of $[Cp^*RuCl]_4$ with four equivalents of **1** at room temperature in toluene gave an orange solution. Removal of volatiles and recrystallization of the residue from hexane afforded a chlorotrihydroborato ruthenium complex $[Cp^*Ru(PMe_3)(\eta^2\text{-}BH_3Cl)]$ (**2**) in 44% yield as orange crystals (eq 1).[6]



(1)

1 **2**

Elemental analysis indicated that the formula of the product is identical to that of a simple adduct of the precursors, $[Cp^*RuCl]$ and **1**. On first glance, it seems to suggest that the product is the complex in which $BH_3{\cdot}PMe_3$ coordinates to the ruthenium atom in "Cp^*RuCl" through two BH's (**A**), which completes the 18-



(**A**)

electron rule. Indeed, we have reported group 6 metal complexes, $[M(CO)_5(\eta^1\text{-}BH_3{\cdot}PMe_3)]$ (M = Cr, Mo, W), in which **1** coordinates to the central atom through a BH.[7] In the ^{31}P NMR spectrum of **2**, however, only a sharp singlet was observed at -1.6 ppm indicating that trimethylphosphine does not bind to boron but directly to the ruthenium center. The methyl signal of the Cp* ligand of **2** in the ^1H NMR spectrum appeared at 1.69 ppm as a doublet with the coupling constant of 1.4 Hz, which is the typical value in complexes possessing a $[Cp^*M(PR_3)]$ moiety. The coordinating BH's and the terminal one resonate at -11.27 ppm and 6.34 ppm, respectively. Furthermore, the ^1H-decoupled ^{11}B NMR spectrum exhibits a broad signal in the typical region for η^2-borohydrido complexes, 37.7 ppm. In the IR spectrum, the ν(BH) band is found at 2476 cm^{-1} while the ν(RuHB) bands appear at 1923 and 1772 cm^{-1}. These observations clearly demonstrate that the structure of **2** is the one depicted in eq 1. Complex **2** is the first example of metal complexes of borohydrido ligand including a halogen atom. Chlorotrihydoroborate ion does not exist as a free ion. Thus, $[BH_3Cl]^-$ ion is stabilized by complexation in **2**. It is quite probable that the strong coordinating power of PMe_3 toward ruthenium is a part of the driving forces for the formation of **2**, although the reaction mechanism is not clear currently. We note that similar tetrahydroborato complexes, $[Cp^*Ru(PR_3)(\eta^2\text{-}BH_4)]$ (PR_3 = PMe_3, PPh_3, PPh_2Me, $PiPr_3$, PCy_3, PEt_3), were prepared by the reduction of $[Cp^*RuCl_2(PR_3)]$ using $NaBH_4$ in THF by Suzuki and co-workers.[8]

The structure of **2** is further confirmed by single crystal X-ray structural analysis.[9] Crystals of **2** suitable for X-ray analysis were obtained by slow cooling of the hexane solution. An ORTEP diagram of **2** is shown in Figure 1. As expected from the NMR spectra, the $[BH_3Cl]^-$ ion coordinates to the ruthenium

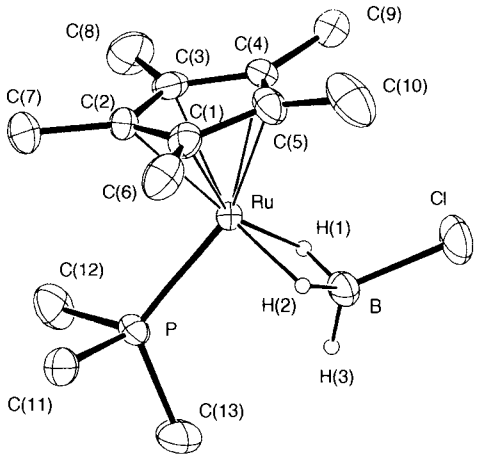
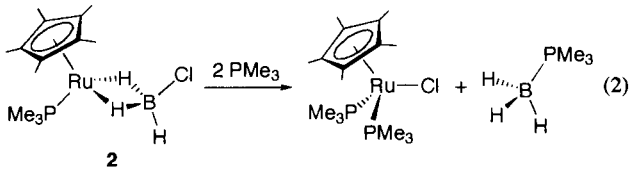


Figure 1. The crystal structure of **2**. Selected interatomic distances (Å) and bond angles (°): Ru–P 2.295(1), Ru···B 2.122 (8), Ru–H(1) 1.76(5), Ru–H(2) 1.70(5), B–H(1) 1.15(5), B–H (2) 1.37(6), B–H(3) 1.00(6), Cl–B 1.862(7); P–Ru–B 93.3(2), H(1)–Ru–H(2) 73(3), Ru–H(1)–B 91(3), Ru–H(2)–B 87(3), Ru–B–Cl 120.6(3), Ru–B–H(3) 115(3), H(1)–B–H(2) 109(3), Cl–B–H(3) 124(3).

atom in a bidentate fashion, and the PMe_3 ligand directly binds to the ruthenium center. The Ru–P distance is 2.295 (1) Å. Positions of hydrogen atoms attached to boron were determined by the difference-Fourier synthesis and refined. The Ru–H(1) and Ru–H(2) bond lengths are 1.76(5) and 1.70(5) Å, respectively. The interatomic distances between boron and bridging hydrogen atoms, B–H(1) and B–H(2), are 1.15 (5) and 1.37 (6) Å. They are longer than that between the boron and the terminal hydrogen atom, B–H(3) (1.00 (6) Å). It is attributable to the reduction of the bond order between the boron and the bridging hydrogen atoms caused by the coordination to the ruthenium atom. This is a common phenomenon for not only borohydrido complexes but other σ complexes.[10] The Ru···B distance, 2.122(8) Å, is a reasonable value for those in bidentate borohydrido complexes.[11] The chlorine atom is located on the same side as the Cp* ligand with respect to the four membered ring defined by Ru, B, H(1), and H(2) atoms. Although two isomers are possible depending on the position of the chlorine atom, only one spicies was observed in the solid state and in solution as evidenced by NMR.

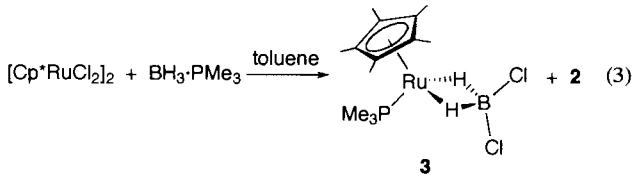
The chlorotrihydroborato complex **2** readily reacted with two equivalents of PMe_3 to afford $[Cp^*Ru(PMe_3)_2Cl]$[12] and $BH_3{\cdot}PMe_3$ quantitatively, involving chloride transfer from boron to ruthenium (eq 2). This makes a sharp contrast to the reactivity



2 (2)

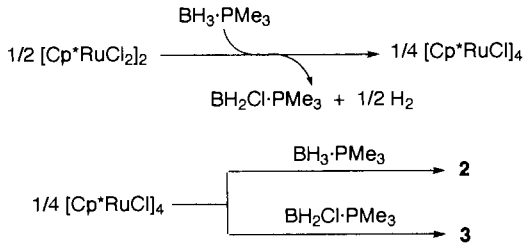
of other borohydrido complexes, which undergo symmetrical cleavage by phosphines to give the corresponding hydrido complexes and phosphineboranes (It can be closely related to the symmetrical cleavage of diborane by Lewis bases).[13]

$BH_3{\cdot}PMe_3$ was also activated by another Ru(III) complex, $[Cp^*RuCl_2]_2$. Interestingly, a dichlorodihydroborato complex **3** was produced besides **2** (eq 3).[14] In this case, two chlorides



3 (3)

were transferred to the boron atom. During this reaction, the color of the solution changed from purple (the color of the precursor, $[Cp^*RuCl_2]_2$), to blue-green, and finally to orange (the color of both the product **3** and of $[Cp^*RuCl]_4$). At the stage when the solution color was blue-green, H_2 gas vigorously evolved. It is noteworthy that a similar change of color and gas evolution are observed in the preparation of $[Cp^*RuCl]_4$ by reduction of $[Cp^*RuCl_2]_2$ using $Li[BHEt_3]$.[4] In the reaction shown in eq 3, **1** probably acts as a reducing agent toward the Ru(III) complex giving $[Cp^*RuCl]_4$ and $BH_2Cl{\cdot}PMe_3$, and then they react to afford **3**. The formation of **2** in this reaction can be explained by the reaction of formed $[Cp^*RuCl]_4$ with remaining **1** (Scheme 1). In fact, **3** can be exclusively synthesized by the reaction of $BH_2Cl{\cdot}PMe_3$ with $[Cp^*RuCl]_4$ in toluene as red-



Scheme 1.

orange crystals in 72% yield. Complex **3** is heat sensitive and slowly decomposes at room temperature to give $[Cp^*RuCl_2(PMe_3)]$.[8]

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

References and Notes

1 Y. Kawano and M. Shimoi, "Advances in Boron Chemistry", pp. 393-396, The Royal Society of Chemistry (1997).

2 Fehlner et al. have reported the synthesis of an unstable cobalt boryl complex, $[(OC)_4Co(BH_2{\cdot}THF)]$, by the reaction of $[Co_2(CO)_8]$ with $BH_3{\cdot}THF$: J. D. Basil, A. A. Aradi, N. K. Bhattacharyya, N. P. Rath, and T. P. Fehlner, *Inorg. Chem.*, **29**, 1260 (1990).

3 Many examples of activation of tri-coordinate borane (mainly catechol-borane) are known: for example, a) P. Knorr and J. S. Merola, *Organometallics*, **9**, 3008 (1990). b) S. A. Westscott, N. J. Taylor, T. B. Marder, R. T. Baker, N. J. Jones, and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, **1991**, 304. c) C. Dai, G. Stringer, T. B. Marder, A. J. Scott, W. Clegg, and N. C. Norman, *Inorg. Chem.*, **36**, 272 (1997). d) R. T. Baker, D. W. Ovenall, and J. C. Carabrese, *J. Am. Chem. Soc.*, **112**, 9399 (1990). f) J. Hart and S. R. De Gala, *J. Am. Chem. Soc.*, **116**, 3661 (1994).

4 P. J. Fagan, M. D. Ward, and J. C. Calabrese, *J. Am. Chem. Soc.*, **111**, 1698 (1989).

5 a) T. D. Tilley, R. H. Grubbs, and J. E. Bercaw, *Organometallics*, **3**, 274 (1984). b) N. Oshima, H. Suzuki, and Y. Moro-oka, *Chem. Lett.*, **1984**, 1161.

6 Data for **2**: ^1H NMR (500 MHz, C_6D_6) δ -11.27 (br, 2H, Ru*H*B), 1.01 (d, J = 8.8 Hz, 9H, PMe_3), 1.69 (d, J = 1.4 Hz, 15H, C_5Me_5), 6.34 (q, br, $J \cong$ 120 Hz, 1H, BH). ^{13}C NMR (125.7 Hz, C_6D_6) δ 11.2 (C_5Me_5), 20.6 (d, J = 26.4 Hz, PMe_3), 89.0 (C_5Me_5). ^{11}B NMR (160.4 MHz, C_6D_6) δ 37.7 (br). ^{31}P NMR (202 MHz, C_6D_6) δ -1.6. IR (CH_2Cl_2, cm^{-1}) 2476 (m, ν(BH)), 1923, 1772 (w, ν(RuHB)). Anal. Calcd. For $C_{13}H_{27}BClPRu$: C, 43.17; H, 7.52; Cl, 9.80. Found: C, 42.97; H, 7.56; Cl, 9.47%.

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

8 H. Suzuki, D. H. Lee, N. Oshima, and Y. Moro-oka, *Organometallics*, **6**, 1569 (1987).

9 Crystallographic data for **2**: Red-orange block-like crystals. $C_{13}H_{27}BClPRu$, fw = 361.66, Monoclinic, $P2_1/n$ (variant of no. 14), a = 16.102 (2), b = 11.564 (2), c = 9.4643 (1) Å; β = 100.844 (9) °; V = 1730.8 (4) Å^3), R = 0.052 for 3535 reflections with $I > 3\sigma(I)$.

10 R. H. Crabtree, *Angew. Chem., Int. Ed. Engl.* **32**, 789 (1993).

11 T. J. Marks and Kolb, J. R. *Chem. Rev.* **77**, 263 (1977), and references cited therein.

12 T. D. Tilley, R. H. Grubbs, and J. E. Bercaw, *Organometallics*, **3**, 274 (1984).

13 For example: S. Nlate, P. Guenot, S. Sinbandohito, L. Toupet, C. Lapinte, and V. Guerchais, *Angew. Chem., Int. Ed. Engl.*, **33**, 2218 (1994); Q. Jiang, P. J. Caroll, and D. H. Berry, *Organometallics*, **12**, 177 (1993).

14 Data for **3**: ^1H NMR (500 MHz, C_6D_6) δ -10.13 (br, 2H, Ru*H*B), 1.21 (d, J = 8.8 Hz, 9H, PMe_3), 1.57 (d, J = 1.4 Hz, 15H, C_5Me_5). ^{13}C NMR (125.7 Hz, C_6D_6) δ 11.3 (C_5Me_5), 21.5 (d, J = 26.4 Hz, PMe_3), 90.3 (C_5Me_5). ^{11}B NMR (160.4 MHz, C_6D_6) δ 36.2 (t, J_{BH} = 83 Hz). ^{31}P NMR (202 MHz, C_6D_6) δ -1.5. IR (CH_2Cl_2, cm^{-1}) 2013, 1953 (w, ν(RuHB)). Anal. Calcd. For $C_{13}H_{26}BCl_2PRu$: C, 39.42; H, 6.62; Cl, 17.90. Found: C, 39.15; H, 6.66; Cl, 17.60%.