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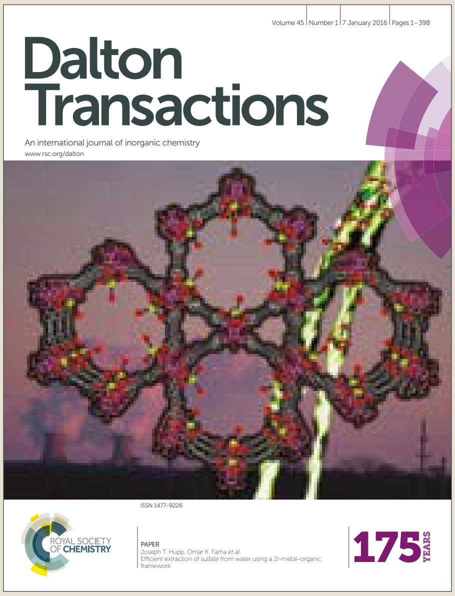

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DOI: 10.1039/C7DT02345F

H/D Scrambling in a Chromium-catalyzed Dehydrocoupling Reaction of Borane–dimethylamine Adduct

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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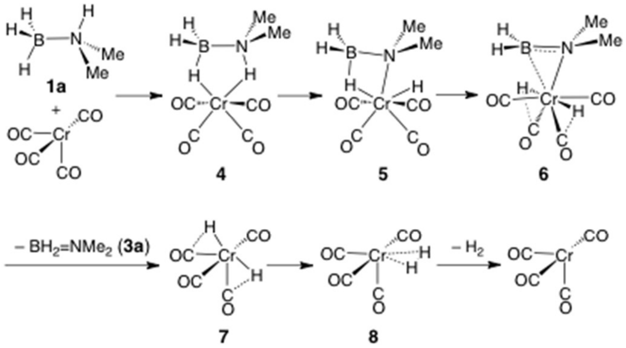
H/D scrambling took place in a chromium-catalyzed dehydrocoupling reaction of deuterium-labeled borane–dimethylamine adduct. In the hydrogen elimination of $BH_3{\cdot}NDMe_2$ (**1a-d$_N$**), H_2, HD and D_2 were generated in 65:30:5 ratio, and 62 % of deuterium atom was incorporated into the major product, dimethylaminoborane dimer. Proton and deuteron nuclei were thus concentrated into the evolved dihydrogen and aminoborane dimer, respectively. The mechanism for the H/D scrambling is understood based upon the reaction pathway of the dehydrocoupling of **1a**, which was previously proposed based on DFT calculations. The H/D distribution in the products is explained by the energy difference according to the deuterated position in an intermediate of the dehydrocoupling reaction.

Introduction

Much attention is focused on transition metal-catalyzed dehydrocoupling reactions of borane–amine adducts.[1-14] The products of this reaction, aminoboranes and borazines, can be good precursors of BN ceramics. In addition, the large hydrogen content and its effective release in this reaction strongly suggest the potential utility of amine–boranes (in particular ammoniaborane) as chemical hydrogen storage materials.[15-22] Thus, research in this area can influence the development of new energy systems such as fuel cells.



Scheme 1

Previously, we reported borane dehydrocoupling reactions catalyzed by group-6 metal carbonyls, $[M(CO)_6]$ (M = Cr, Mo, W).[3] When a borane–secondary amine adduct $BH_3{\cdot}NHR_2$ (**1**) is photolyzed in the presence of catalytic amount of $[M(CO)_6]$, a dimeric or monomeric aminoborane $[BH_2NR_2]_n$ (**2**: n = 2, **3**: n = 1) is produced according to the bulkiness of the amine substituents. If a primary adduct $BH_3{\cdot}NH_2R$ is employed as a precursor, a borazine derivative $[BHNR]_3$ is provided. The mechanism for the dehydrocoupling of secondary adducts was investigated by DFT calculations. This reaction proceeds in an intramolecular stepwise mechanism, and the dehydrogenation follows 1,2-elimination (Scheme 1). Borane **1a** is coordinated to the active catalyst $[Cr(CO)_4]$ through a BH and the NH hydrogen atoms, and the resulting chelate complex **4** undergoes NH and BH activation to generate an aminoborane(dihydride) complex **6** via an intermediate **5**. Complex **6** readily releases an aminoborane molecule **3**, and the remained dihydride $[Cr(CO)_4H_2]$ (**7**) liberates H_2 to regenerate $[Cr(CO)_4]$ after isomerization to a dihydrogen aduuct **8**. When the amine substituents are small, aminoborane **3** dimerizes to yield a cyclic dimer $[BH_2NR_2]_2$ (**2**). During the dehydrogention reaction, a borane σ complex $[Cr(CO)_5(\eta^1\text{-}BH_3{\cdot}NHR_2)]$ is observed by NMR spectroscopy. This species acts as a reservoir of $[Cr(CO)_5]$, which is readily converted to the active catalyst $[Cr(CO)_4]$ in the reaction system.

To further confirm this reaction mechanism and to know what occurs on the metal atom during the dehydrocoupling process, we carried out deuterium labeling experiments. We thought that the intramolecular 1,2-H elimination could be ascertained by the dehydrogeation of $BH_3{\cdot}NDMe_2$. However, we observed unexpected H/D scrambling to yield an H-rich dihydrogen isotopomeric mixture and D-introduced dimethylaminoborane dimer. We report here this observation and discuss the mechanism of the H/D scrambling on the basis of a DFT study.

Results and discussion

Dehydrocoupling of $BH_3{\cdot}NDMe_2$. The H/D scrambling was found to occur when the Cr-catalyzed dehydrocoupling reaction of $BH_3{\cdot}NDMe_2$ (**1a-d$_N$**) was monitored using ^1H, ^2H, and ^{11}B NMR spectroscopy. Thus, a benzene solution and a benzene-d_6 solution of **1a-d$_N$** containing $[Cr(CO)_6]$ (5 mol %) were sealed in Pyrex NMR sample tubes, and were photolyzed for 40 min and then left at room temperature for 2 days to complete the dehydrocoupling reaction. On the basis of the intramolecular 1,2-dehydrogenation mechanism, only HD should be expected to evolve as a dihydrogen isotopomer. In actual, however, all the isotopomers, H_2, HD and D_2 were observed. The ^2H NMR spectrum of the resulting benzene solution exhibited resonances of HD and D_2 as a doublet (4.50 ppm, $^1J_{HD}$ = 42.7 Hz) and a singlet (4.45 ppm) signal, respectively. Their relative quantity was 64:11 as judged by comparing the signal intensity. Likewise, the relative quantity of H_2 and HD evolved in this reaction was determined to be 140:64 based on their signal intensity in the ^1H NMR spectrum of the benzene-d_6 solution

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Electronic Supplementary Information (ESI) available: Cartesian coordinates, electronic energies and Gibbs free energies of the geometry-optimized species. See DOI: 10.1039/x0xx00000x

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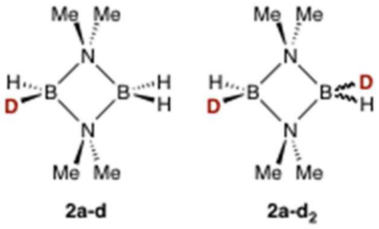
(H_2: singlet, 4.46 ppm; HD: triplet, 4.43 ppm, $^1J_{HD}$ = 42.7 Hz). Hence, H_2, HD, and D_2 were generated in 65:30:5 ratio in the dehydrocoupling of **1a-d$_N$**. In generated dihydrogen, the content of ^{1}H nucleu was much higher than that of ^{2}H. The percentage of ^{1}H nuclei amounts to 80 %. Also, the observed isotopomer distribution almost equals the statistical distribution of proton and deuteron under this ^{1}H content (64:32:4).

Previously, Pacchioni has reported that H/D scramling occurs via $[Cr(CO)_4(H_2)(D_2)]$ when $[Cr(CO)_6]$ is photolyzed under H_2/D_2 atmosphere.[23] In our reaction system, redistribution of dihydrogen isotopomers would also occur through $[Cr(CO)_4(H_2)(D_2)]$. D_2 can be formed via this process.



2a-d **2a-d$_2$**

Chart 1

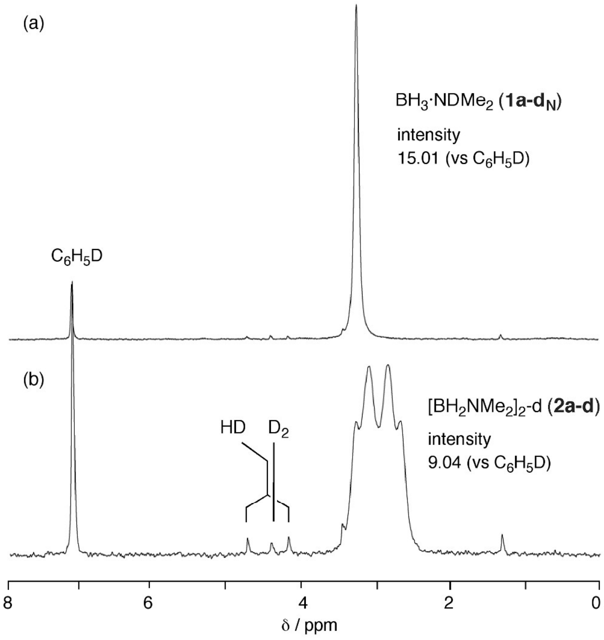


Figure 1. ^{2}H NMR spectral change (76.7 MHz, C_6H_6) during the Cr-catalyzed dehydrocoupling of **1a-d$_N$**. (a) $BH_3{\cdot}NDMe_2$ (**1a-d$_N$**) / $[Cr(CO)_6]$ (5 mol%), before irradiation. (b) After irradiation (40 min) + RT 2d.

Figure 1 exhibits the ^{2}H NMR spectral change during the dehydrocoupling of **1a-d$_N$**. Before the reaction, only a resonance of the nitrogen-attached deuterium is observed at 3.28 ppm as a broad singlet. After the completion of the dehydrogenation reaction, however, this signal disappeared and a boron-coupled quartet resonance appeared alternatively at 3.00 ppm. This resonance is assigned to the BHD moiety of deuterated aminoborane dimers, **2a-d** and **2a-d$_2$** (Chart 1). The deuterium incorporation into the aminoborane was further confirmed by the appearance of a ^{2}H-coupled triplet resonance in the $^{11}B\{^1H\}$ NMR spectrum (Figure 2). When the signal of C_6H_5D in the solvent is used as the internal standard in the ^{2}H NMR spectrum (Figure 1), it has been shown that 62 % of deuterium has been introduced into the aminoborane product. Thus, in the dehydrocoupling of **1a-d$_N$**, proton and deuteron nuclei were concentrated into the produced dihydrogen and dimethylaminoborane dimer, respectively.

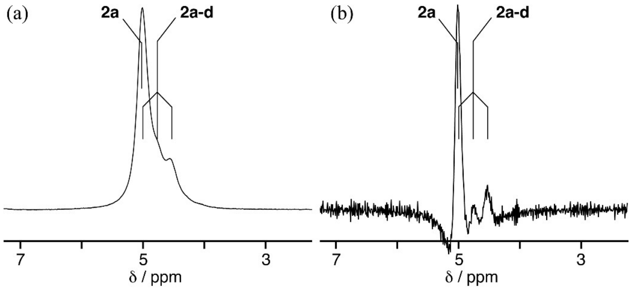


Figure 2. $^{11}B\{^1H\}$ NMR spectra of **2a-d** in the reaction mixture of the dehydrocoupling of **1a-d$_N$**. (a) a common spectrum (b) a resolution-enhanced spectrum obtained by the use of sin-bell type window function.

Computational Approach to the Intramolecular H/D Scrambling. Here we consider the mechanism for the H/D scrambling on the basis of the reaction pathway of the chromium-catalyzed borane dehydrocoupling. Figure 3 exhibits the free energy profile for the transformation of **1a-d$_N$** on $[Cr(CO)_4]$, which was suggested by DFT calculations using the PBE0 functional.[24] Its left half is essentially the same as the dehydrogenation pathway of **1a**, which we reported in the previous paper.[3] However, the relative free energy values are slightly perturbed by the deuterium substitution. After $[Cr(CO)_4]$ was chelated by **1a-d$_N$** with a BH and the ND atoms, the ND and BH bond activation steps proceed successively, forming a $BH_2{=}NMe_2$ ligand on the metal atom. In the first step, the chromium atom is inserted into the ND bond to generate the amidoborane(deuteride) complex **5-d$_N$**. The BH_2NMe_2 moiety in the amidoborane ligand then rotates 90° around the Cr–N axis, leaving the metal-bound BH hydrogen atom, thereby the BH activation is accomplished. Note that in the resulting intermediate **6-d$_{Cr}$**, the hydride and deuteride ligands, which were originally attached to boron and nitrogen respectively, are located at mutually equivalent positions with respect to the BH_2NMe_2 ligand.

<<Figure 3>>

The borane dehydrocoupling is achieved by dissociation of the aminoborane ligand from **6-d$_{Cr}$** and subsequent release of HD from the resulting hydride(deuteride) complex. The aminoborane dissociation from **6-d$_{Cr}$** is 13.8 kcal mol^{-1} endothermic in electronic energy and only 0.2 kcal mol^{-1} endergonic in free energy. Remarkably, the reversion of complex **6-d$_{Cr}$** to the reactants, $[Cr(CO)_4]$ plus **1a-d$_N$**, can also occur easily. The highest barrier for the reversion process is

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13.1 kcal mol^{-1}, which is taken for the conversion of **5-d$_N$** to **TS1-d$_N$**. On the initial step of the reversion, if the aminoborane ligand of **6-d$_{Cr}$** rotates so that the boron end approaches the hydride ligand, **4-d$_N$** will only be reproduced via **TS2-d$_N$**, **5-d$_N$**, and **TS1-d$_N$**. On the contrary, if the aminoborane group rotates so that the boron end is brought close to the deuteride ligand, the boron-deuterated intermediate **5-d$_{B(b)}$** will be formed. This species can readily be converted to **4-d$_{B(b)}$**, which then releases $BH_2D{\cdot}NHMe_2$ (**1a-d$_B$**). In fact, the boron-attached deuteron assignable to **1a-d$_B$** is observed in the ^{2}H NMR spectrum (2.04 ppm, a broad quartet) of the reaction mixture just after the photolysis. This boron-deuterated adduct can coordinate to $[Cr(CO)_4]$ through a BH and the NH hydrogen atoms to release H_2, yielding $BHD{=}NMe_2$ (**3a-d**), via an intermediate **6-d$_B$** (Figure 4). Product **3a-d** dimerizes (or associates with **3a**) to produce **2a-d$_2$** (or **2a-d**).

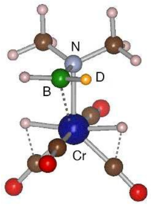

Figure 4. The boron-deuterated intermediate **6-d$_B$**.

The barriers for interconversion among the intermediates for the H/D scrambling are sufficiently low, that the intermediates can be in a quasi equilibrium. Accordingly, the isotope distribution in generated dihydrogen and dimethylaminoborane should be prescribed by the relative free energy of the isotopomers of intermediate **6**, which finally release aminoborane and dihydrogen. In the intramolecular H/D scrambling, **6-d$_{Cr}$** releases **3a** and HD while **6-d$_B$** liberates **3a-d** and H_2. Frequency calculations showed that **6-d$_B$** is 0.33 kcal mol^{-1} stable relative to **6-d$_{Cr}$** in free energy. Based on this energy difference, the relative abundance of **6-d$_B$** and **6-d$_{Cr}$** is expected to be 63.4:36.6 in the reaction system. This value is well consistent with the observed deuteration percentage in the obtained aminoborane **2a** (62 %). Furthermore, it is also expected that a dihydrogen isotopomeric mixture with H:D = 81.7:18.3 is produced on the basis of this value. This also well accords with the observation.

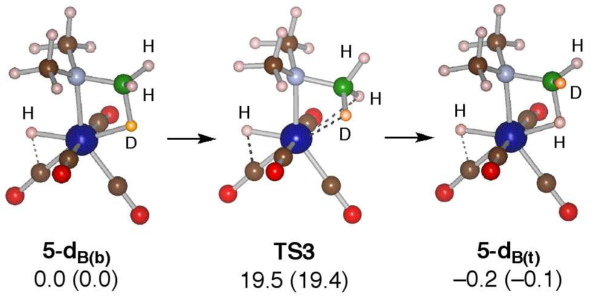

Figure 5. Rotation of the BH_2D group of **5-d$_{B(b)}$** involving site exchange of the deuterium atom. The relative free energy values are given in kcal mol^{-1}. The zero-point corrected electronic energies are also given in parentheses.

Evolution of H_2 and formation of **3a-d** can also take place through rotation of the BH_2D group of intermediate **5-d$_{B(b)}$** followed by the BH activation of resulting **5-d$_{B(t)}$**. This proceeds via **TS3**, which involves an η^2-interacting borane group (Figure 5).[25] However, the energy barrier for the BH_2D rotation, 19.5 kcal mol^{-1}, is substantially higher than that for the aforementioned mechanism including dissociation and recoordination of **1a-d$_B$**.

Conclusions

In this work, we found intramolecular H/D scrambling in the chromium-catalyzed dehydrocoupling reaction of borane–dimethylamine adduct. Their mechanisms can be explained with the reaction pathway of the dehydrocouplng. These findings embody a dynamic behavior of the metal-coordinated amine–borane molecule and its hydrogen atoms, which move around the coordination sphere of the metal centre.

Experimental

All manipulations were carried out under high vacuum or dry nitrogen atmosphere. Reagent-grade THF was distilled under nitrogen atmosphere from sodium-benzophenone ketyl immediately before use. Benzene and benzene-d$_6$ were dried over a potassium mirror and vacuum transferred into NMR tubes directly before use. $BH_3{\cdot}NHMe_2$ (**1a**) were prepared by treatment of $NaBH_4$ with the corresponding ammonium salt in THF according to the literature.[26] $BH_3{\cdot}NDMe_2$ (**1a-d$_N$**) was prepared by dissolving **1a** in D_2O.[27] $[Cr(CO)_6]$ (Strem), $NaBD_4$ (Aldrich), $[NH_2Me_2]Cl$ and D_2O (Wako Pure Chemicals) were purchased and used as received. ^{1}H, ^{2}H, and ^{11}B NMR spectra were recorded on a JEOL α-500 spectrometer.

Dehydrocoupling Reaction of $BH_3{\cdot}NDMe_2$ (1a-d$_N$). A Pyrex NMR sample tube equipped with a Teflon stop cock was charged with **1a-d$_N$** (15 mg. 0.25 mmol) and $[Cr(CO)_6]$ (2.8 mg, 1.3×10^{-2} mmol), and connected to a vacuum line. Dry benzene (0.4 mL) was introduced onto the sample, and the NMR tube was flame-sealed under high vacuum. This solution was irradiated using a 450W medium pressure Hg lamp for 2 hours, and was then allowed to stand at room temperature for 2 days to complete the dehydrocoupling reaction. The ^{2}H NMR spectrum of the reaction mixture showed resonances of HD (4.50 ppm, doublet, $^1J_{HD}$ = 42.7 Hz), D_2 (4.45 ppm, singlet), and deuterated dimethylaminoborane dimers (3.00 ppm, broad quartet, $^1J_{BD}$ = 101.4 Hz). By comparing the signal intensity, the relative quantity of HD and D_2 was determined to be 64:11. In a similar manner, a benzene-d$_6$ solution of **1a-d$_N$** (16 mg, 0.27 mmol) containing $[Cr(CO)_6]$ (2.9 mg, 1.3×10^{-2} mmol) was prepared, photolyzed and then left at room temperature. The ^{1}H NMR spectrum of this reaction mixture showed the formation of H_2 and HD along with aminoborane dimer (H_2: singlet, 4.46 ppm; HD: triplet, 4.43 ppm, $^1J_{HD}$ = 42.7 Hz). In this solution, the ratio of H_2 and HD was 140:64 as determined by the signal intensity. Thus, the relative quantity of H_2, HD, and

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D_2 evolved in the dehydrocoupling reaction was estimated to be 13:6:1 by the normalization using HD as a standard.

In addition, before the reaction the ^{2}H NMR signal intensity of the ND atom of **1a-d$_N$** was 15.01 relative to the signal of C_6H_5D (natural abundance), while after the reaction, the relative intensity of BH*D* signal of deuterated aminoboranes was 9.04. Thus, 62 % of deuterium migrated onto the boron atom.

Computational Details. To obtain thermochemical parameters, frequency calculations were carried out on deuterated isotopomers of the species that participate in the dehydrocoupling reaction of **1a**, whose structures were previously optimized and reported.[3] This computation was performed at the DFT/PBE0 level of theory.[24] Chromium was described with the effective core potentials (ECP) of Hay and Wadt with a double-ζ valence basis set (LANL2DZ)[28] augmented with f-polarization functions (α = 1.941).[29] A double ζ plus polarization valence basis set augmented with diffuse functions, 6-31++G(d,p) was employed for B, N, BH, CrH and NH hydrogen atoms, which directly participated in the dehydrocoupling. For the other atoms, a standard 6-31G(d) basis set was applied. These functional and basis sets are the same as those employed for the geometry optimizations. Thermochemical parameters thus obtained, including zero point energies and Gibbs free energy contributions, were then added to the solvation free energy obtained by the SCRF (self consistent reaction field) calculations using the CPCM model.[30] As reported previously, on the SCRF calculations, Stuttgart-Dresden ECP and valence triple-ζ plus f-polarization basis set (SDD) were used for chromium,[31] and Dunning's aug-cc-pVDZ was employed to describe the other atoms.[32] The free energy values are given as those at 298 K and 1 atm in benzene. All calculations were performed with the Gaussian 03 package of programs.[33]

Conflict of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research (No. 21550056) from Ministry of Education, Culture, Sports, Science and Technology, Japan.

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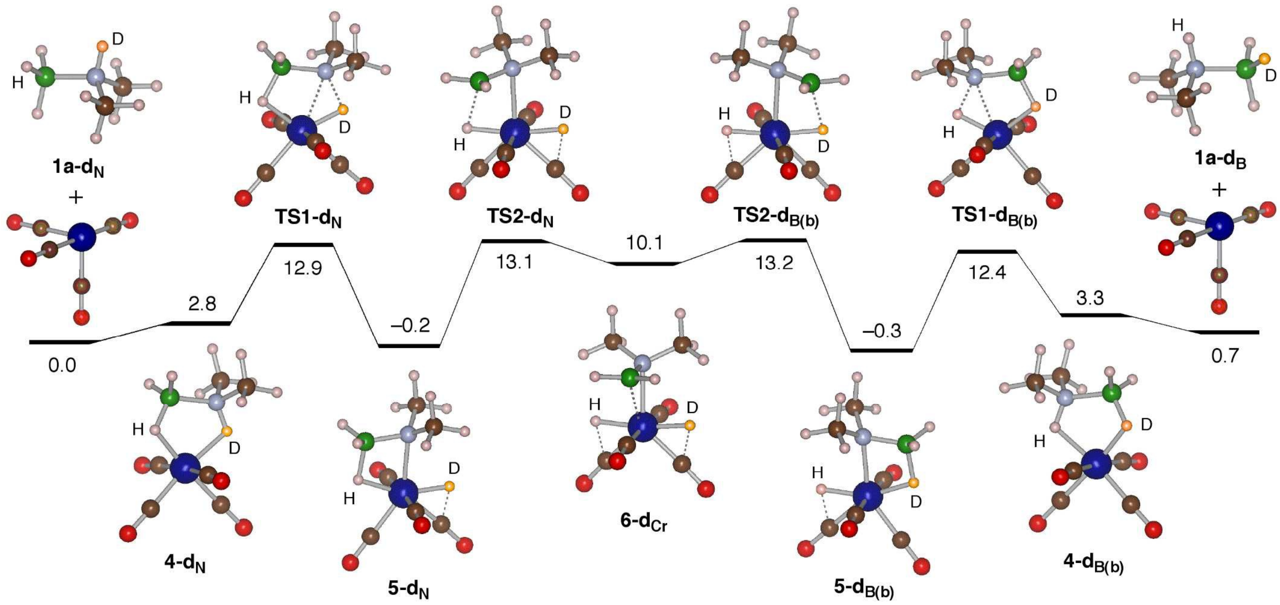

Figure 3. Free energy profile of the H/D scrambling of **1a-d$_N$** on [Cr(CO)$_4$]. The energy values are given in kcal mol^{-1}. Indigo = Cr, green = B, blue gray = N, red = O, brown = C, pink = H, orange = D.

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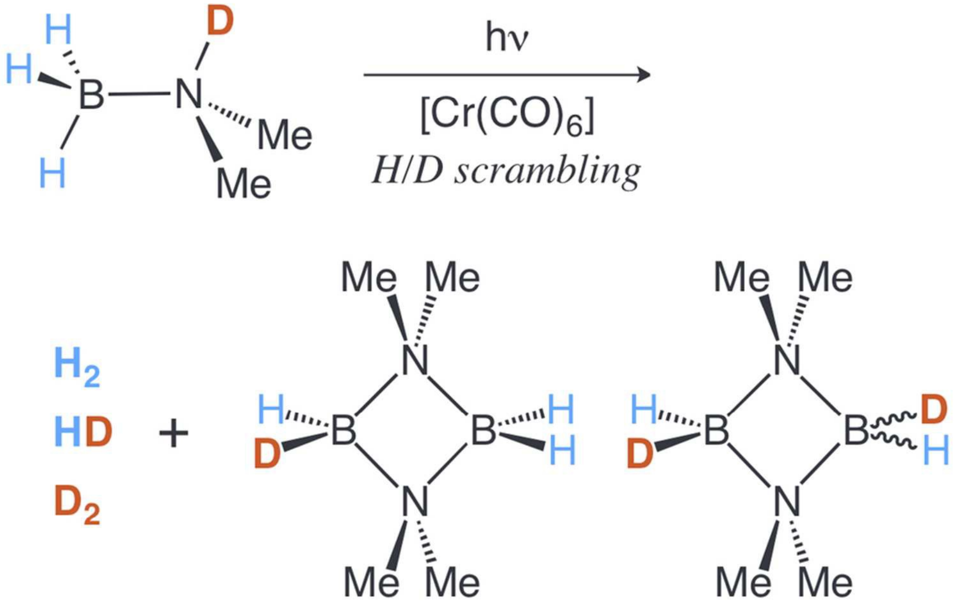
DOI: 10.1039/C7DT02345F



H/D scrambling took place in a chromium-catalyzed dehydrocoupling reaction of deuterium--labeled borane–dimethylamine adduct.

84x70mm (300 x 300 DPI)