Tuning Dihydrogen Bonds: Enhanced Solid-State Reactivity in a Dihydrogen-Bonded System with Exceptionally Short H···H Distances**

Radu Custelcean and James E. Jackson*

The unconventional hydrogen bonds (dihydrogen bonds) between the hydridic hydrogen centers, or more accurately the σ-bonding electrons of M–H bonds (M = B, Ga, Ir, Re, W, Os), and traditional hydrogen-bonding partners H–X (X = N, O) have received considerable attention in the last five years.[1] Very recently, we demonstrated that dihydrogen bonds can be used for topochemical assembly of covalent materials, because of their ability to react by H_2 loss, trading the weak H···H interactions for strong covalent bonds.[2] Solid-state decomposition of the triethanolamine (TEA) complex of $NaBH_4$, whose crystal structure shows multiple dihydrogen bonds between the BH_4^- ions and the OH groups from TEA, proved to be topochemical, leading to a polymeric trialkoxyborohydride which is not achievable from solution or melt. However, the relatively low melting point and solid-state reactivity of this dihydrogen-bonded system made its solid-state decomposition extremely slow (weeks!), which hampered the systematic study of this topochemical process. Moreover, a phase transition preceding the H_2 loss complicated the topochemical relationship between the structures of the initial complex and the final decomposed material.

A special consideration of the acidity and basicity of the protonic and hydridic partners is essential, in order to allow the crystallization of these systems prior to their decomposition by H_2 loss, but still to induce relatively high solid-state reactivity. Substitution of Li for Na in the $NaBH_4 \cdot TEA$ complex appeared to be the most straightforward way to tune the solid-state reactivity in this particular system. The Li^+ would complex the TEA more strongly, making the OH sites more acidic and consequently more reactive. Here we describe the structure and reactivity of $LiBH_4 \cdot TEA$ (**1**), a dihydrogen-bonded system with very short H···H distances and enhanced solid-state reactivity toward H_2 loss with topochemical covalent bond formation.

The complex **1** was crystallized by slow evaporation of a 1:1 TEA/$LiBH_4$ mixture in 2-propanol, as a white crystalline compound which does not melt up to 300 °C. It differs spectroscopically[3] from $LiBH_4$, suggesting different environments for the BH_4^- and Li^+ ions. The X-ray crystal structure[4] of **1** is presented in Figure 1. Each Li^+ is pentacoordinated by the N and three O atoms from a TEA molecule and by an O atom from a different TEA molecule, forming $\{Li^+(tea)\}_2$ dimers, in contrast to the Na analogue, where $\{Na^+(tea)\}_n$ chains were present.[2]

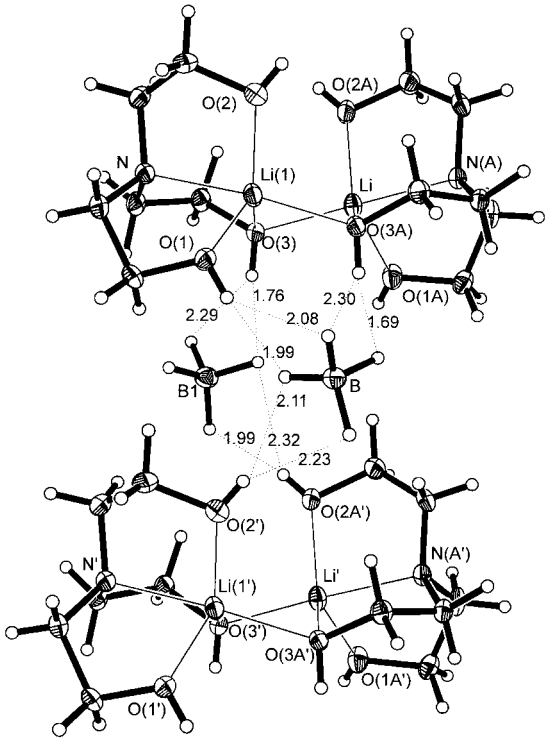

Figure 1. Dihydrogen bonding network in crystals of **1**. H–H contact distances [Å] are not normalized. Selected bond lengths [Å]: O(1)–Li(1) 2.05, O(2)–Li(1) 1.94, O(3)–Li(1) 2.11, N–Li(1) 2.16, O(3A)–Li(1) 2.05, O(1A)–Li 1.95, O(2A)–Li 1.97, O(3A)–Li 2.17, N(A)–Li 2.15, O(3)–Li 2.02, O(1)–H(1) 0.81, O(2)–H(2) 0.74, O(3)–H(3) 0.87, O(1A)–H(1A) 0.88, O(2A)–H(2A) 0.75, O(3A)–H(3A) 0.89, B–H(B) 1.11, 1.16, 1.13, 1.11, B1–H(B1) 1.14, 1.06, 1.15, 1.18.

Multiple dihydrogen bonds connect the dimers through BH_4^- pairs, giving rise to extended ribbons. The dihydrogen bonding network is asymmetrical: one BH_4^- ion forms hydrogen bonds with three OH groups (O(2′), O(1), and O(3A)) in a total of six dihydrogen bonds, while the second BH_4^- ion only forms hydrogen bonds with two of the remaining OH groups (O(2A′) and O(3)) in a total of four dihydrogen bonds. The O(1A)H groups are not involved in any dihydrogen bonding; instead they form conventional hydrogen bonds with O(1)s from the neighboring ribbon, creating thus overall two-dimensional layers. The H–H contact distances range between 1.69 and 2.32 Å.[5] All hydrogen atoms were unambiguously located from the difference Fourier map, making these distances sufficiently reliable. The shortest dihydrogen bonds are 1.69 and 1.76 Å, which after the normalization of the O–H and B–H bonds become 1.62 and 1.67 Å, respectively.[6] These are the shortest H–H distances reported so far for dihydrogen bonds.[7] Notably, both OH groups involved in these two dihydrogen bonds contain bridging O atoms coordinating two Li^+ ions, which undoubtedly results in increased acidity of their corresponding protons, and thus enhanced hydrogen-bonding ability. All the other OH groups complex only one Li^+ ion, leading thus to H–H separations that are significantly longer. The OH···H–B angles range between 75.8 and 106.1° (av 95.0°), while

[*] Prof. J. E. Jackson, R. Custelcean
Department of Chemistry
513 Chemistry Building
Michigan State University
East Lansing, MI 48824 (USA)
Fax: (517)353–1793
E-mail: jackson@curie.cem.msu.edu
custelce@argus.cem.msu.edu

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the O–H···HB angles are larger, ranging between 130.0 and 170.7° (av 150.8°).

The very short H–H distances and the expected acidity increase of the OH groups due to their complexation of Li^+ ions predicted enhanced solid-state reactivity for this system. Indeed, when heated for 1 h at 120 °C under argon, the complex completely decomposed, as indicated by X-ray powder diffraction (Figure 2), ^{11}B solid-state MAS NMR and IR spectra of the resulting material. Only 24 h were necessary for decomposition at 82 °C, the temperature

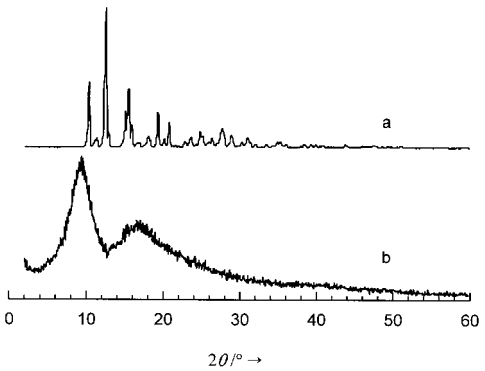

Figure 2. X-ray powder diffraction pattern of **1** (a) and final decomposed material (b).

used for the solid-state decomposition of $NaBH_4 \cdot TEA$, which took about six weeks! Three moles of H_2 per mole of **1** were lost, as indicated by the hydride content of the initial complex and final decomposed material. The resulting solid is insoluble in common organic solvents and does not melt up to 300 °C, indicating a polymeric nature. Its ^{11}B solid-state MAS NMR spectrum exhibits a single peak at $\delta = -4.6$, which, together with the hydride content of one per molecule, suggests a trialkoxyborohydride structure for the decomposed material. The $\tilde{\nu}_{B-H}$ of 2247 cm^{-1} for the same material is also significantly shifted from the 2290 cm^{-1} in the initial complex. No phase transition was observed in this case when the decomposition was monitored by X-ray powder diffraction.

The loss of three moles of H_2 from **1** points to a topochemical relationship between the final decomposed material and the initial complex, where two BH_4^- ions and six OH groups are in close proximity due to the crystal packing imposed by the dihydrogen bonding network. Unlike in the $NaBH_4 \cdot TEA$ case where two-dimensional covalent layers were likely to have formed, a topochemical reaction in the present example is expected to yield a one-dimensional covalent structure, according to the crystal structure of **1**. However, due to the modest crystallinity of the final material[8] (Figure 2b), a definitive knowledge of its structure remains elusive.

In direct contrast, decomposition of **1** in DMSO at 120 °C under argon for four days, yielded a material with no hydridic hydrogen left as shown by its hydride content and IR spectrum. Its ^{11}B solid-state MAS NMR chemical shift ($\delta = -5.9$) is slightly different from the corresponding value in the solid-state decomposition product. In a parallel reaction run in [D_6]DMSO, unconverted BH_4^- and completely alcoholyzed $B(OR)_4^-$ were the only boron species found by ^{11}B NMR spectroscopy in solution throughout the reaction. Such behavior is expected for a reaction in which the $BH_x(OR)_{4-x}^-$ intermediates are more reactive than the starting BH_4^-, and susceptible to disproportionation.[9] Thus, the decomposition process in solution differs qualitatively from that in the solid state, demonstrating again the ability of dihydrogen bonding to exert topochemical control in the BH···HO to B–O conversion.

In summary, we have described a new dihydrogen-bonded system with extremely short H···H distances, presumably induced by the increased acidity of the proton donor OH sites due to strong complexation by Li^+ ions. This system also displays the high solid-state reactivity expected from these structural characteristics. The present study offers the best defined example to date of topochemical assembly of covalent materials using dihydrogen bonds, a developing application of this new and intriguing intermolecular interaction.

Experimental Section

1: $LiBH_4$ (0.22 g, 10 mmol) and TEA (1.4 mL, 10 mmol) were dissolved in 2-propanol (20 mL). Slow evaporation of most of the solvent under argon followed by addition of CH_2Cl_2 (20 mL) afforded 0.95 g (56 %) of complex **1**. X-Ray quality crystals were grown by diffusion of a diethyl ether layer into a solution of **1** in 2-propanol. ^1H NMR (300.1 MHz, [D_3]CH_3CN, 25 °C): $\delta = 4.21$ (s, 3H; OH), 3.60 (t, $J = 5.1$ Hz, 6H; CH_2), 2.58 (t, $J = 5.1$ Hz, 6H; CH_2), −0.23 (q, J (B,H) = 81.0 Hz, 4H; BH_4); ^{13}C NMR (125.89 MHz, [D_3]CH_3CN, 25 °C): $\delta = 53.5$ (CH_2), 58.4 (CH_2); ^{11}B NMR (96.23 MHz, [D_3]CH_3CN, 25 °C, $B(OCH_3)_3$): $\delta = -55.98$ (quintet, J(B,H) = 80.9 Hz; BH_4); ^{11}B MAS NMR (128.33 MHz, 5997 Hz, 25 °C, $B(OH)_3$): $\delta = -48.7$ ($\Delta\nu_{1/2} = 1586$ Hz); ^7Li MAS NMR (155.44 MHz, 6000 Hz, 25 °C, LiCl): $\delta = 2.8$ ($\Delta\nu_{1/2} = 1735$ Hz); IR (KBr): $\tilde{\nu} = 2290$ cm^{-1} (B–H); elemental analysis calcd for $C_6H_{19}O_3NBLi$ (%): C 42.15, H 11.11, N 8.19; found: C 42.39, H 11.56, N 8.17.

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[3] Data for $LiBH_4 \cdot TEA$ ($LiBH_4$) are as follows: IR: $\tilde{\nu}_{B-H}$ 2290 (2301) cm^{-1}; ^{11}B solid-state MAS NMR: $\delta = -48.7$ (−50.2); ^7Li solid-state MAS NMR: $\delta = 2.8$ (1.5).

[4] Crystal data for **1**: Data were collected on a Siemens SMART CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL package (structure analysis program 5.1, Brucker AXS, Inc., Madison, WI, **1997**). Absorption corrections were applied using SADABS, part of the SHELXTL package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from

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difference Fourier map and refined isotropically. Crystal dimensions: $0.44 \times 0.23 \times 0.21$ mm; $T = 173$ K; monoclinic, space group $P2_1$, $a = 7.7156(5)$, $b = 17.0039(11)$, $c = 7.8656(5)$ Å, $\beta = 98.133(1)^\circ$, $V = 1021.55(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.112$ g cm^{-3}; 5330 reflections collected, 3229 independent; $2\theta_{max} = 50^\circ$; 370 parameters; $R_1 = 0.0417$, $wR_2 = 0.0768$ for $I > 2\sigma(I)$; residual electron density: 0.145 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-105289. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[5] The typical normalization of O–H and B–H bonds to 0.96 and 1.21 Å, respectively, leads to the more realistic H–H distances of 1.62 – 2.28 Å.

[6] These corrections are still likely to overestimate the H–H contact distances as they represent typical values for noninteracting partners. A similar analysis of the three close BH···HO contacts in the X-ray structure of $NaBH_4 \cdot 2H_2O$ ($NaBD_4 \cdot 2D_2O$) yielded distances 0.04 Å longer on average than the final neutron diffraction values.

[7] We found the 1.73 Å as the shortest reliable H–H contact distance for a dihydrogen bond reported so far (ref. [1a]). Another value of 1.68 Å was reported, but the disorder of the proton donor solvent as well as the uncertainty in its N–H proton location make this distance somewhat less reliable. See: B. P. Patel, W. Yao, G. P. A. Yap, A. L. Rheingold, R. H. Crabtree, *Chem. Commun.* **1996**, 991 – 992.

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Contactless Electrodeposition of Palladium Catalysts**

Jean-Claude Bradley* and Zhongming Ma

In principle, electrodeposition offers a convenient method of modulating the properties of metal catalysts. It has been used extensively to prepare metal catalysts on conductive substrates such as carbon, metals, or conductive oxides.[1–4] Underpotential deposition to form surfaces with modified catalytic behavior could be considered a related technology.[5, 6] A critical limitation of electrodeposited catalysts is that the deposited area is essentially limited to the electrode surface. To increase the available surface area of electrodeposited catalysts, electrodeposition of metal structures within polymers such as polyvinylpyridine,[7, 8] poly(vinylacetic acid),[9] and nafion[10–13] has been actively explored. A recently developed, related approach is electrodeposition in thin gel coatings.[14] However, such approaches are limited to coatings only a few micrometers thick because of the difficulty of assuring an ohmic or electron-hopping contact with the growing electrodeposit while maintaining a highly permeable structure for rapid diffusion of the reagents and high surface area. Furthermore, small isolated deposits cannot usually be obtained by this method because of the necessity of having an electrically contiguous structure that extends from the electrode into the matrix. Here we describe an electric-field method for preparing electrodeposited catalysts which does not require physical contact between the power source and the deposits. This approach, referred to as bipolar electrodeposition, not only enables electrodeposition across several centimeters of the support but also allows the position of the deposit to be controlled.

Other attempts to increase the thickness of electrodeposited catalysts include the use of electrically conductive polymers such as polypyrrole,[15–17] polyaniline,[18–21] or viologen-based polymers.[22] However, due to anisotropic field distributions and the finite resistivity of the conductive polymer, it is unlikely that homogeneous electrodeposition will be possible in deposits more than a few micrometers thick with this approach. Furthermore, the choice of support is limited to conductive polymers in electrical contact with an electrode.

One method that avoids electrical contact with the conductive support is photoelectrodeposition onto semiconductor particles. This has been used extensively as a method of electrodepositing catalytically active metals (e.g. Au, Pt, Pd, Ag, Rh, Ir) onto a dispersed semiconducting support (e.g. TiO_2, ZnO, SnO_2, ZrO_2, ThO_2, CdS, WO_3).[23–39] In this case photons promote electrons from the valence band into the conduction band of the semiconductor particles to give a situation in which anodic and cathodic processes occur on different regions of the same particle. Although this method was successful in producing catalysts, it requires a semiconductor whose bandgap is tuned to the wavelengths that can penetrate into the sample. Furthermore, due to absorption of light, homogeneous exposure across large volumes is not possible without prolonged mixing.

Here we describe a novel method for creating electrodeposited catalysts over large volumes of nonconductive supports with a much more homogenous distribution than available by other electrodeposition techniques. Our method relies on the polarization of conductive micrometer-scale particles in a nonconductive matrix. This represents another application of our approach to toposelectively (site-selectively) functionalize or otherwise modify particles by using electric fields. We earlier demonstrated toposelective electrodeposition onto isolated millimeter-[40, 41] and micrometer-sized[42] copper particles to form wires with diameters as small as 0.3 μm. We refer to the objects generated from such toposelective manipulation as toposomes.[43]

The preparation of the catalyst is shown schematically in Figure 1. Graphite particles (nominally 1 – 2 μm in diameter) were dispersed onto one side of 60-μm-thick cellulose paper by nebulizing an acetone suspension of the particles. The papers were then stacked to a thickness of 0.5 cm and sandwiched between two flat graphite electrodes with dimensions of 2×2 cm. After immersion in a 1 mM solution of $PdCl_2$

[*] Prof. J.-C. Bradley, Dr. Z. Ma
Department of Chemistry
Drexel University
32nd and Chestnut Streets
Philadelphia, PA 19104 (USA)
Fax: (+1) 215-895-1265
E-mail: bradlejc@post.drexel.edu

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