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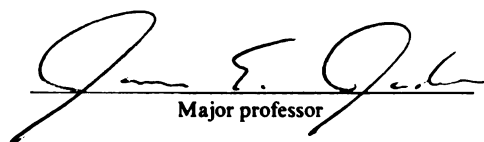
TOPOCHEMICAL ASSEMBLY OF COVALENT MATERIALS
USING DIHYDROGEN BONDING

presented by

Radu Custelcean

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry


Major professor

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TOPOCHEMICAL ASSEMBLY OF COVALENT MATERIALS
USING DIHYDROGEN BONDING

By

Radu Custelcean

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements

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ABSTRACT
TOPOCHEMICAL ASSEMBLY OF COVALENT MATERIALS
USING DIHYDROGEN BONDING

By
Radu Custelcean

This study explores the potential of the unconventional hydrogen bonds (dihydrogen bonds) between hydridic hydrogens in $X-BH_3^-$ ($X = H, CN$) and traditional AH ($A = O, N$) proton donors to serve as preorganizing interactions for the topochemical assembly of covalent materials. Such weak $A-H\cdots H-B$ interactions can indeed be used to organize and hold a structure's form while it is more firmly fastened together by $A-B$ bond formation, transferring thus the initial order from the starting crystal to the newly formed covalent frame. This strategy makes dihydrogen bonding a potentially powerful tool for the rational assembly of crystalline covalent solids with controlled structures and properties, a class of compounds generally accessible only by empirical methods or serendipitous discoveries.

Evidence of such crystal lattice control in the transformation $O-H\cdots H-B \rightarrow O-B + H_2$ was first obtained in studies of the solid-state structures and reactivities of triethanolamine (TEA) complexes with various metal borohydrides ($MBH_3X \cdot TEA$: $M = Na, X = H$; $M = Na, X = CN$; $M = Li, X = H$). Thus, solid-state decomposition of $NaBH_4 \cdot TEA$, whose crystal structure shows multiple dihydrogen bonds between the BH_4^- ions and the OH groups from TEA, is topochemical, leading to a polymeric trialkoxyborohydride, in sharp contrast to the $NaBH_4$ and hydride-free polymeric borate

disproportionation products obtained from decomposition in solution or melt. With its less basic hydridic sites, the dihydrogen-bonded $\text{NaNCBH}_3\cdot\text{TEA}$ complex could not be decomposed in the solid state, losing H_2 only at ca. 100 °C above its melting point. Thus, in addition to close H-H contacts, the relative acidity/basicity of the proton/hydride partners is also critical for the reactivity of the dihydrogen-bonded systems. The $\text{H}\cdots\text{H}$ interactions were conveniently tuned by substituting Li^+ for Na^+ in the $\text{NaBH}_4\cdot\text{TEA}$ complex, which led to shorter H-H contacts and enhanced solid-state reactivity, as a result of stronger complexation by Li^+ and consequently higher acidity of the OH sites. Mechanistic investigations using in situ solid-state ^{11}B NMR, optical microscopy, FT-IR, and XRD, found that, like most solid-state reactions, the topochemical decomposition of $\text{LiBH}_4\cdot\text{TEA}$ is heterogeneous, with nucleation of the product phase from the parent crystal. Kinetic analysis and H/D exchange experiments established that proton transfer along the $\text{H}\cdots\text{H}$ bond, at the reactant/product interface, is the rate limiting step, with activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 20.1 ± 2.4 kcal/mol and -16.8 ± 6.2 e.u., comparable with the analogous values found for the aqueous hydrolysis of BH_4^- in neutral water.

Finally, the concept of crystallinity transfer from dihydrogen- to covalent-bonded crystals was demonstrated by the crystal-to-crystal decomposition of $\text{NaBH}_4\cdot\text{THEC}$ (THEC = N,N',N'',N''' -tetrakis-(2-hydroxyethyl)cyclen), in which self-assembly into dihydrogen-bonded closed-loop large globular dimers minimized the unit cell shrinkage accompanying the $\text{O-H}\cdots\text{HB}$ to O-B conversion. Further elaboration of these dihydrogen-bonded building blocks offers real prospects for the rational assembly of extended $\text{H}\cdots\text{H}$ bonded, and ultimately covalent solids with controlled architectures.

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O(2)H...H-B 117.8, O(3)H...H-B 116.1, O(1)-H...HB 166.8, O(2)-H...HB 155.1, O(3)-
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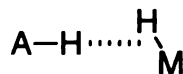
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1. Dihydrogen Bonding: A Literature Review

1.1. Introduction

Hydrogen bonding¹ occupies a prominent position in modern chemistry. It is fundamental for molecular recognition and supramolecular synthesis, and holds a central role in biology.² Typically, this noncovalent interaction occurs between the positively charged hydrogen of an A-H (A = O, N, halogen, C) proton donor, and the lone pair of an electronegative element, or the π electrons of a multiple bond or aromatic ring, representing the proton acceptor. Recently, an unusual type of hydrogen bonding, in which a σ M-H bond (where M is less electronegative than H) acts as the electron donor, has attracted considerable attention.³



With strength and directionality comparable with those found in conventional hydrogen bonding, this proton-hydride interaction, or dihydrogen bonding, can influence the structure, reactivity, and selectivity in solution and solid state, thus finding potential utilities in catalysis, crystal engineering, and materials chemistry. This review summarizes the emergence and development of this topic, starting with the early observations of H $\cdots$ H bonding, continuing with its comprehensive structural and energetic description, and concluding with the implications of this interaction in supramolecular synthesis, as well as its influence on reactivity and selectivity in both fluid and condensed phases.

1.2. Structural and Energetic Characterization

A. Dihydrogen Bonding in the Main Group Hydrides. Chemists had intuitively thought about proton-hydride interactions long before these associations were formally categorized as hydrogen bonds. In 1934, Zachariasen and Mooney reported the crystal structure of ammonium hypophosphite ($\text{NH}_4^+\text{H}_2\text{PO}_2^-$),⁴ and noted that “the hydrogen atoms of the hypophosphite group behave toward ammonium as if they were H^- ions”.⁵ Thirty years later, Burg suggested the presence of $\text{N-H}\cdots\text{H}_3\text{B}$ interactions comparable to hydrogen bonds in liquid $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$, based on the perturbation of the N-H and B-H bands in the IR spectrum.⁶ Titov et al. explained the enhanced chemical reactivity of aminoboranes toward H_2 loss by the “close spatial arrangement of the oppositely-charged hydrogen atoms”.⁷ However, the first to recognize this interaction as a true hydrogen bond were Brown and coworkers in the late 1960’s.⁸ Based on a thorough analysis of the IR spectra of the boron coordination compounds of the type $\text{L}\cdot\text{BH}_3$ ($\text{L} = \text{Me}_3\text{N}$, Et_3N , Py , Et_3P) and $\text{Me}_3\text{N}\cdot\text{BH}_2\text{X}$ ($\text{X} = \text{Cl}$, Br , I) in the presence of proton donors such as MeOH , PhOH and $p\text{-F-C}_6\text{H}_4\text{-OH}$ in CCl_4 , they proposed the formation of a novel type of hydrogen bond in which the BH_3 and BH_2 groups acted as proton acceptors, despite their lack of lone pairs or π electrons. They measured the strengths of these interactions by variable temperature IR spectroscopy, finding association energies in the range of 1.7-3.5 kcal/mol, comparable with moderately strong conventional hydrogen bonds.⁹ Similarly, they inferred the occurrence of intermolecular $\text{NH}\cdots\text{HB}$ hydrogen bonding in $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and $(\text{RNH}\cdot\text{BH}_2)_3$ ($\text{R} = \text{Pr}$, Bu), from the temperature and concentration dependence of their N-H stretching absorptions in CCl_4 .⁸

In a recent study, Epstein and coworkers confirmed the ability of boron hydrides to act as proton acceptors in hydrogen bonds.¹⁰ They studied the interaction of neutral NEt_3BH_3 and $\text{P(OEt)}_3\text{BH}_3$ as well as ionic $\text{Bu}_4\text{N}^+\text{BH}_4^-$ with different alcohols as proton donors, by IR and NMR spectroscopy in CH_2Cl_2 , C_6H_{14} and C_6D_{12} , and concluded that the properties of these unconventional $\text{OH}\cdots\text{HB}$ interactions are similar to those found in classical hydrogen bonds. Their association energies were found to increase proportionally with the proton donors' acidities, being situated in the range 1.1-3.6 and 2.5-6.5 kcal/mol, for the neutral and ionic boron hydrides, respectively. Theoretical calculations (RHF/6-31G) confirmed the attractive nature of these proton-hydride interactions.

The solution studies, however, cannot unambiguously establish whether these unusual interactions involve the boron atom, the hydridic hydrogen, or the BH group as a whole. The X-ray and neutron crystal structures of $\text{NaBH}_4\cdot 2\text{H}_2\text{O}$ were recently determined by Jackson et al., in order to probe the existence of $\text{O-H}\cdots\text{H-B}$ dihydrogen bonding in the solid state, and provide a detailed structural description of it (Figure 1.1).¹¹

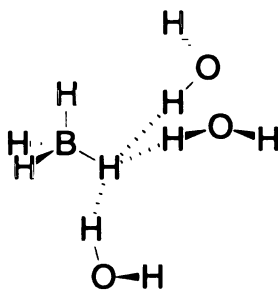


Figure 1.1. $\text{O-H}\cdots\text{H-B}$ dihydrogen bonds found in $\text{NaBH}_4\cdot 2\text{H}_2\text{O}$ in the solid-state.

Three close H...H contacts of 1.79, 1.86, and 1.94 Å were found, substantially shorter than the 2.4 Å distance corresponding to twice the Van der Waals radius of a H atom. The O-H vectors clearly point toward the middle of the B-H bonds, suggesting association with the σ -bond electrons, rather than B or H atoms.

The same conclusion can be drawn from the systematic *Cambridge Structural Database* (CSD) search done by Crabtree et al. for boron-nitrogen compounds.¹² The twenty-six intermolecular N-H...H-B short contacts found in the range 1.7-2.2 Å, for which Crabtree suggested the term “dihydrogen bonds”, showed a strong preference for a bent geometry, with NH...H-B angles typically situated between 95 and 120°, and N-H...HB angles tending to be larger (150-170° in most of the cases). These side-on structures were rationalized by the presence of negative charges on both B and H atoms, which avoid the unfavorable alignment of the dipoles that would result from a linear N-H...H-B arrangement. They also investigated theoretically the NH₃BH₃ dimer, whose C₂ symmetrical geometry (Figure 1.2) optimized at the PCI-80/B3LYP level of theory showed two identical H...H interactions, with contact distances of 1.82 Å, and NH...H-B and N-H...HB angles of 98.8 and 158.7°, respectively, falling in the range found by the CSD search.

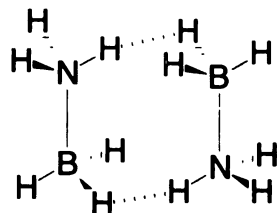


Figure 1.2. C₂ isomer of the NH₃BH₃ dimer.

The calculated dimerization energy of -12.1 kcal/mol corresponds to 6.1 kcal/mol per N-H...H-B interaction, which, as suggested by Crabtree, could account for the strikingly higher melting point of aminoborane (+104 °C) relative to the isoelectronic ethane (mp -181 °C).¹²

A similar head-to-tail arrangement was also found by Cramer and Gladfelter in their theoretical study of the (NH₃BH₃)₂ dimer.¹³ However, using HF, DFT, or MP2 methods, they found a *C*_{2h} symmetrical structure as the global minimum (Figure 1.3), which lies only 0.2 kcal/mol lower in energy than the *C*₂ isomer reported by Crabtree et al. This geometry allows the formation of bifurcated dihydrogen bonds with H-H distances of 1.990 Å, and NH...H-B and N-H...HB angles of 88.6 and 144.8°, respectively, as calculated at the MP2/cc-pVDZ level. The association energy obtained at the same level of theory is -15.1 kcal/mol.

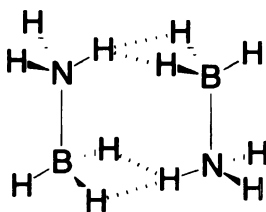


Figure 1.3. *C*_{2h} isomer of the NH₃BH₃ dimer.

For comparison, the crystal structure of NH₃BH₃ recently determined by Crabtree and coworkers by neutron diffraction shows a packing that results in three short intermolecular N-H...H-B interactions, with the shortest one exhibiting a H-H distance of 2.02 Å and values for the NH...H-B and N-H...HB angles of 106(1) and 156(3)°, respectively (Figure 1.4).¹⁴ Again, the N-H vectors point toward the middle of the B-H

bonds, suggesting that the σ -bond as a whole represents in fact the proton acceptor partner in these interactions.

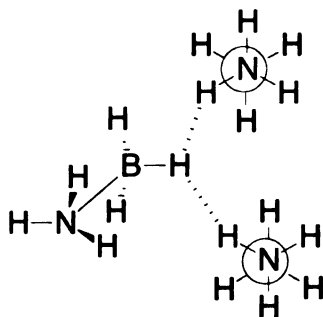


Figure 1.4. The shortest N-H...H-B contacts found in NH_3BH_3 in the solid-state.

Further insight into the nature of the N-H...H-B interaction was provided by Popelier, who applied the “atoms in molecules” theory on the same $(\text{NH}_3\text{BH}_3)_2$ dimer, and concluded that this interaction can indeed be classified as a hydrogen bond.¹⁵

Intermolecular N-H...H-B interactions have also been described by Nöth et al., who recently reported the crystal structure of $(\text{CH}_3)_2\text{NH}-\text{BH}_2-\text{N}(\text{CH}_3)_2-\text{BH}_3$, which self-assembles into dihydrogen-bonded dimers, as illustrated in Figure 1.5.¹⁶

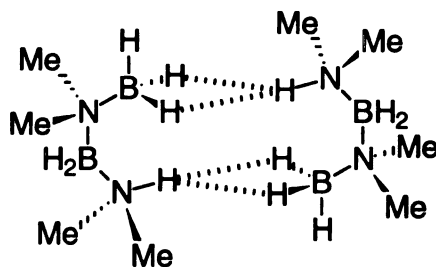
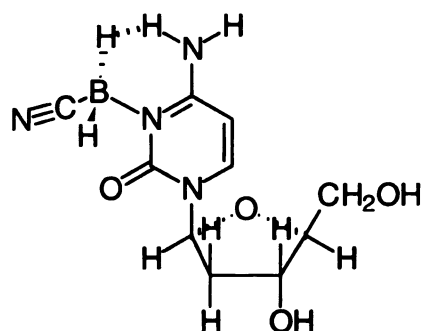


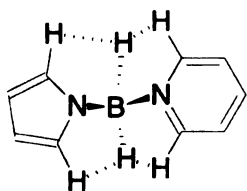
Figure 1.5. Dihydrogen-bonded dimers found in $(\text{CH}_3)_2\text{NH}-\text{BH}_2-\text{N}(\text{CH}_3)_2-\text{BH}_3$ in the solid-state.

The N-H...H-B dihydrogen bonding can also form intramolecularly, as found in the crystal structure of the 2'-deoxycytidine-*N*(3)-cyanoborane (**1**), which shows a H...H close contact of 2.05 Å.¹⁷

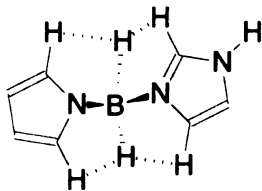


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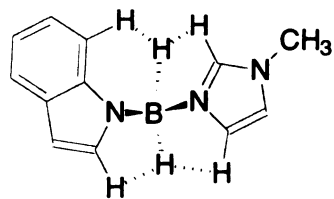
Intramolecular C-H...H-B close contacts are present in the aminoboron hydrides **2-6**, which could be responsible for the stabilization against disproportionation in these complexes.¹⁸



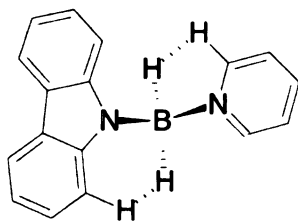
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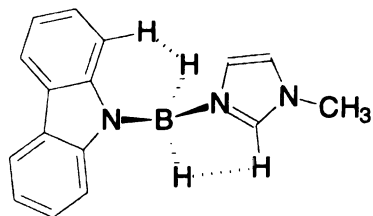
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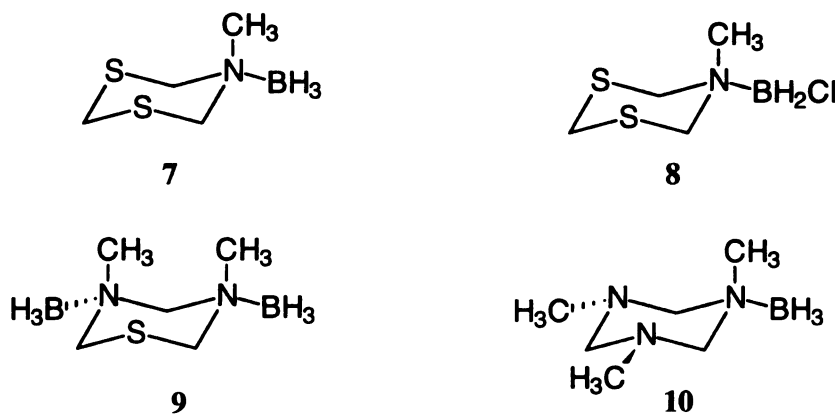
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6

Their X-ray crystal structures show multiple H-H distances below 2.65 Å, which was considered the threshold intermolecular distance for H...H interactions in this study. The heterocyclic rings adopt almost coplanar orientations relative to the B-H bonds, thus maximizing the intramolecular H...H associations. The relatively small H-C-N exocyclic angles next to the B-H bonds in some of these complexes, compared to the free heterocycles, also suggest attractive interactions between the protonic hydrogens on the α -carbons and the hydridic BH hydrogens. In solution, the formation of similar dihydrogen bonds was explored by NOE experiments. For instance, **2** adopts a conformation comparable to the one found in the solid state, allowing again short C-H...H-B contacts.

Intramolecular C-H...H-B dihydrogen bonds were also demonstrated to play a decisive role in controlling the conformation of the heterocyclohexane-borane adducts **7-10**.¹⁹



The BH₃ groups are always found in the equatorial position in these complexes, which appears to be the result of favorable attractive interactions between the hydridic B-H hydrogens, and the positively charged H atoms of the α -CH₂ groups (Figure 1.6).

Associations with the C-H hydrogens of the N-CH₃ group also seem to stabilize these structures, as indicated by the short H-H distances and the decrease of the H₃C-N-BH₃ angles relative to the H₃C-N-CH₃ angle in the (CH₃)₂N⁺ derivative.

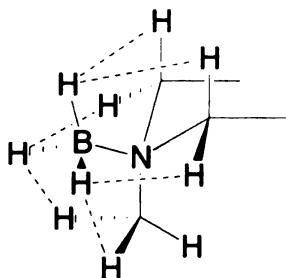
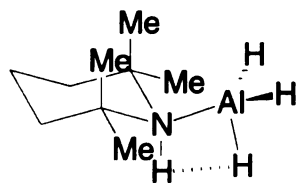


Figure 1.6. C-H...H-B close contacts in **7-10**.

The hydrides of the heavier group 3 elements are also capable of forming dihydrogen bonds. Thus, in 1994, Raston and coworkers provided X-ray crystallographic evidence for an intramolecular N-H...H-Al interaction in the alane-piperidine adduct **11**.²⁰ The H-Al-N-H unit has an eclipsed conformation in the solid state, allowing the two oppositely charged hydrogen atoms to approach to 2.31 Å, in direct contrast to the previously reported structures of aminoalanes, which are known to exhibit a staggered conformation about the Al-N bond. This arrangement, Raston noted, represents an intermediate prior to H₂ evolution, to form an amidometal species.



11

Computational studies at the MP2/cc-pVDZ level, by Cramer and Gladfelter,¹³ revealed a staggered, C_{3v} symmetrical geometry for NH_3AlH_3 , which upon dimerization forms a C_2 symmetrical structure (Figure 1.7) that contains two short intermolecular N-H $\cdots$ H-Al hydrogen bonds, with an H-H separation of 1.781 Å, and NH $\cdots$ H-Al and N-H $\cdots$ HAAl angles of 119.4 and 172.0°, respectively. The dimerization energy calculated at the same level of theory is -11.8 kcal/mol, which corresponds to about 6 kcal/mol per N-H $\cdots$ H-Al dihydrogen bond.

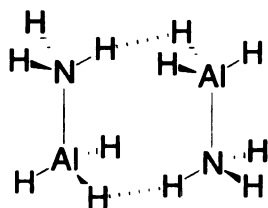


Figure 1.7. Calculated structure of the NH_3AlH_3 dimer.

Cyclotrialumazane ($(\text{NH}_2\text{AlH}_2)_3$) was found theoretically²¹ (MP2/VDZ) to prefer the twist-boat over the chair conformation in the gas phase, by as much as 2.8 kcal/mol, due to favorable electrostatic N-H δ^+ - δ^- H-Al flagpole interactions (Figure 1.8).

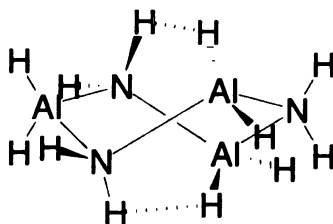


Figure 1.8. Calculated structure of $(\text{NH}_2\text{AlH}_2)_3$.

In the solid state, however, it is likely that it will adopt the chair arrangement for a more efficient packing, as also observed in the analogous boron and gallium systems. Based on this consideration, the chair conformer was used for the calculation (RHF/cc-pVDZ) of the preferred geometry in the $[(\text{NH}_2\text{AlH}_2)_3]_2$ dimer. As shown in Figure 1.9, the resulting C_{3v} symmetrical structure exhibits six short H-H contacts, and the enthalpy of dimerization is predicted to be -9.9 kcal/mol at the MP2/cc-pVDZ//RHF/cc-pVDZ level.

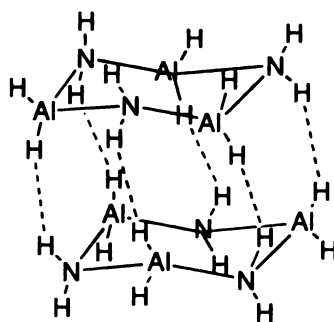
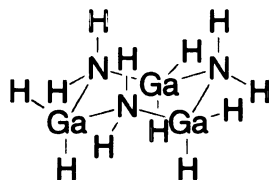


Figure 1.9. Calculated structure of the $(\text{NH}_2\text{AlH}_2)_3$ dimer.

The next element in group 3, gallium, can also be involved in dihydrogen bonding, as Gladfelter's neutron diffraction crystal structure of cyclotrigallazane (**12**) demonstrates.²¹



12

In the solid state, **12** forms an α -network, by participating in four N-H...H-Ga intermolecular interactions, with H-H distances of 1.97 Å (Figure 1.10). The observed NH...H-Ga and N-H...HGa angles are rather close, with values of 131 and 145°, respectively.

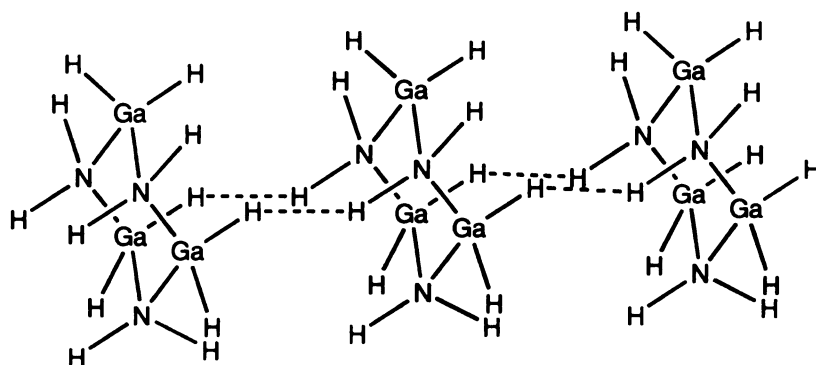


Figure 1.10. Self-assembly of cyclotrigallazane in the solid-state.

The strength of these dihydrogen bonds was estimated by theoretical calculations on the $[(\text{NH}_2\text{GaH}_2)_3]_2$ dimer. As in the aluminum analog, the monomer prefers the twist-boat conformation by 2.6 kcal/mol, thus favoring intramolecular H...H interactions involving the oppositely charged H atoms from the flagpole positions. However, for direct comparison with the solid-state structure, the chair conformation was considered for the geometry optimization of the dimer. The highest dimerization energy was found for the C_s symmetrical structure illustrated in Figure 1.11, from which an interaction energy of about 3 kcal/mol could be estimated for each N-H...H-Ga dihydrogen bond.

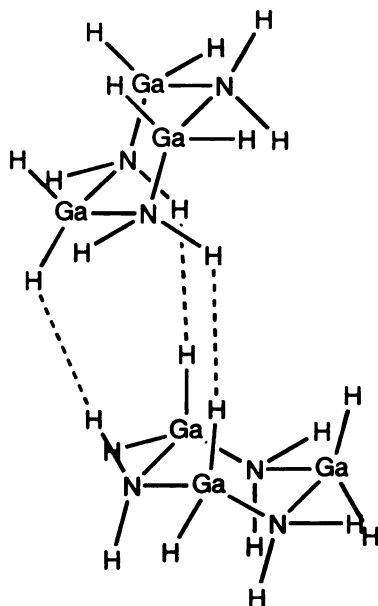


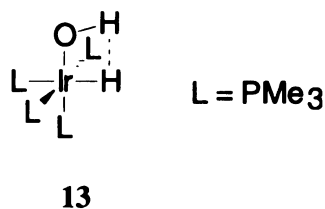
Figure 1.11. Calculated structure of the $(\text{NH}_2\text{GaH}_2)_3$ dimer.

In the case of the $(\text{NH}_3\text{GaH}_3)_2$ dimer, theoretical calculations by Cramer and Gladfelter¹³ predicted a C_2 symmetrical geometry similar to the one found in the Al analog, with N-H $\cdots$ H-Ga dihydrogen bonds of approximately 5 kcal/mol in strength.

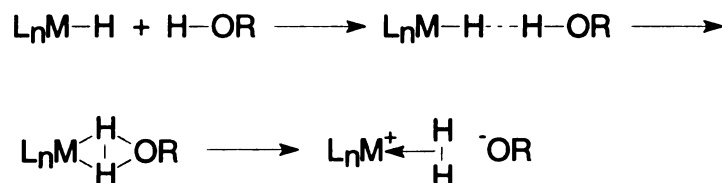
Formation of dihydrogen-bonded complexes by other main group hydrides such as LiH, BeH₂, or the recently discovered XeH₂, has been investigated theoretically by a number of researchers.²² A theoretical study (MP2 and B3LYP) of the dihydrogen-bonded complexes between the hydrides LiH, NaH, BeH₂, MgH₂, CH₄, SiH₄, GeH₄, SnH₄, and hydrofluoric acid, reported by Grabowski, demonstrated the existence of direct correlations between the H $\cdots$ H distances and the H-bonding energies.²³ Also, the H $\cdots$ H

separations have been found to be inversely proportional to the F-H bond lengths, as is seen in conventional O-H...O or N-H...O hydrogen bonds.

B. Dihydrogen Bonding in Transition Metal Hydrides. In 1986, Milstein and coworkers reported the X-ray crystal structure of the iridium hydride complex **13**, in which they noted an unusually small Ir-O-H angle of 91° and an eclipsed H-Ir-O-H conformation, indicating an attractive H...H interaction.²⁴ However, the H-H distance of 2.441 Å was too long for a hydrogen bond. The later neutron diffraction study of the same compound revealed a shorter H-H distance of 2.40 Å, but a wider Ir-O-H angle of 104.4° .²⁵

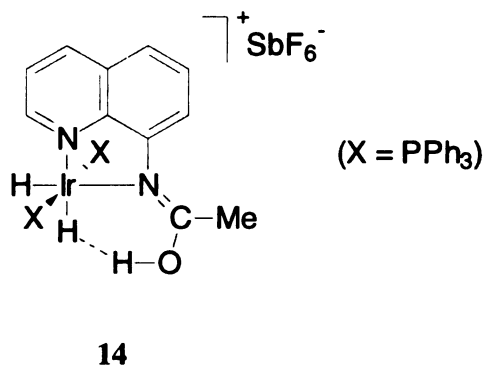


In 1994, Berke and collaborators suggested that the formation of $M-H^{\delta-} \cdots H^{\delta+}-X$ interactions might precede the protonation of transition metal hydrides to yield dihydrogen complexes (Scheme 1.1).²⁶

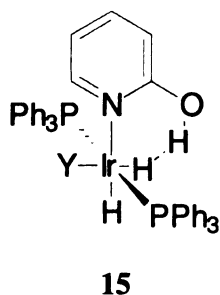


Scheme 1.1

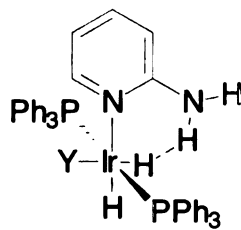
The first unequivocal evidences of dihydrogen bonding involving a transition metal hydride came independently from the groups of Crabtree and Morris in 1994. The X-ray crystal structure of **14** determined by Crabtree et al. showed an unexpected tautomerization of the amide group from the ligand into the iminol form, facilitating thus the interaction between the hydridic Ir-H and the OH proton.²⁷ While the exact H-H distance could not be determined in the solid state due to the failure to locate the Ir-H hydrogen, ¹H NMR *T*₁ relaxation time measurements in solution gave a H...H contact distance of about 1.8 Å. The interaction seems to have some covalent character, as demonstrated by the observed coupling of 3 Hz between Ir-H and O-H hydrogens.



An even higher coupling of 5.5-5.6 Hz was found in **15** (Y = H, Cl, Br, I), in which the H...H contact distance was estimated around 1.7 Å (Y = Cl), based on *T*₁ relaxation time measurements.²⁸



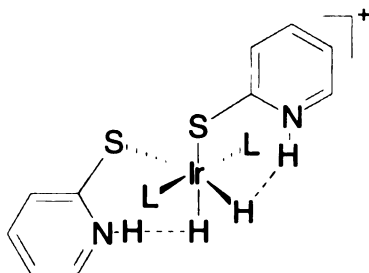
These H...H interactions are fairly strong, competing favorably with the conventional Y...H hydrogen bonds, as demonstrated by the predominance of the O-H...H-Ir dihydrogen-bonded rotamers over the opposite O-H...Y-Ir hydrogen-bonded ones. A quantitative estimation of the strength of these unconventional hydrogen bonds involving iridium hydride complexes was elegantly made by Crabtree's group in the analogous 2-aminopyridine complexes **16** (Y = H, F, Cl, Br, I, CN, CO). They measured the rotation barrier for the NH₂ group, which represents the sum of the H...H interaction energy and the intrinsic rotation barrier around the C-N bond in the ligand. The strongest N-H...H-Ir hydrogen bond (5.0 kcal/mol) was found for the case where Y = H, while the trans Y ligand tends to weaken the interaction in the order: F > Cl > Br > I > CN > CO > H, which can be rationalized by their decreasing electronegativity in the same order.



16

Morris and coworkers demonstrated the presence of H...H interactions in the iridium hydride complex **17** by X-ray diffraction in the solid-state, and NMR spectroscopy in solution.²⁹ The crystal structure of **17** indicated a close contact between the pyridinium protons and the Ir-H hydridic hydrogens, which unfortunately could not be located precisely from the electron density difference maps. Nevertheless, their ¹H NMR data provided clear evidence for N-H...H-Ir hydrogen bonding in CD₂Cl₂, with a

H-H contact distance of about 1.75 Å, calculated from the observed T_1 relaxation times of the protonic and hydridic hydrogens.



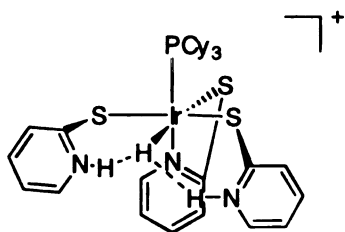
17 (L = PCy₃)

18 (L = PH₃)

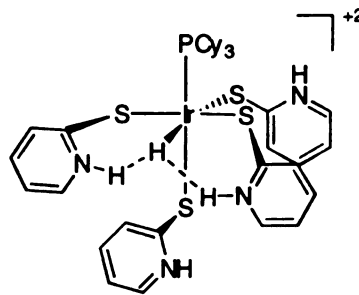
Theoretical calculations by Hoffmann et al.^{22a} on the model complex **18** confirmed the attractive H···H interaction, and concluded that its nature is mostly electrostatic.

Interestingly, when THF was used as a solvent, the dihydrogen bonds were switched off in **17**, presumably by the formation of conventional N-H···O hydrogen bonds with the solvent.

Bifurcated N-H···H(Ir)···H-N dihydrogen bonds were also detected by Morris et al. in **19** and **20** by X-ray crystallography and NMR spectroscopy, and their H-H contact distances were estimated around 1.80 and 1.86 Å, respectively.³⁰

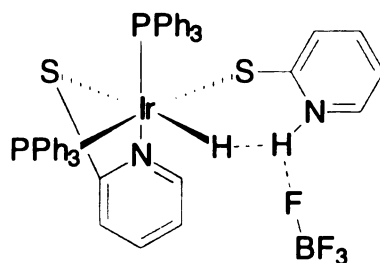


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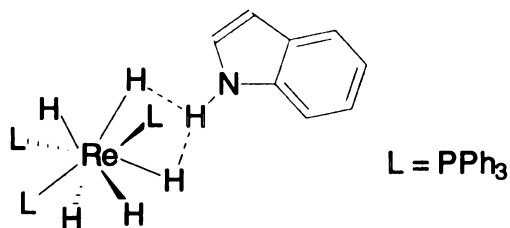
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They also reported an interesting bifurcated Ir-H...H(N)...F-B interaction in complex **21**, in which the N-H proton is shared by a hydridic Ir-H hydrogen and a conventional B-F electron donor from the BF_4^- counterion.³¹



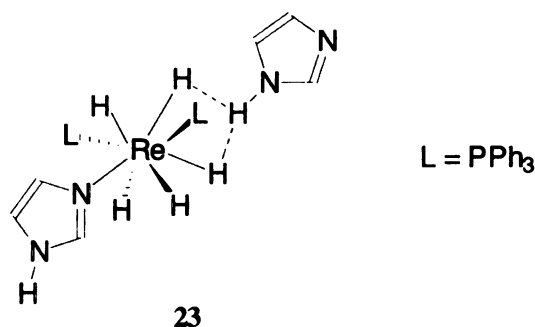
21

The occurrence of intermolecular X-H...H-M dihydrogen bonds was first documented by Crabtree and his collaborators, with the neutron diffraction crystal structure of the rhenium polyhydride complex **22**, which exhibits a three-center interaction between two Re-H hydridic hydrogens and the N-H proton from an indole molecule of crystallization.³² The geometrical parameters for the two H...H contacts, i.e. H-H distances of 1.73 and 2.21 Å, and strongly bent NH...H-Re angles of 119 and 97°, respectively, fall in the range expected for dihydrogen bonding. The strength of the interaction was estimated around 4.3 kcal/mol, from the shift of the N-H stretching band in the solid-state IR spectrum of **22**, relative to free indole.



22

Theoretical calculations using the DFT method on a $[\text{ReH}_5(\text{PH}_3)_3]\cdot\text{NH}_3$ model confirmed the attractive nature of the interaction, and predicted a similar three-center H-bond with $\text{H}\cdots\text{H}$ distances of 1.92 and 2.48 Å, and an interaction energy of 8 kcal/mol in the gas phase. The intermolecular $\text{N-H}\cdots\text{H-Re}$ hydrogen bonding appears to be general, as demonstrated by the X-ray crystal structure of the analogous complex **23**, in which the role of the proton donor is played by an imidazole molecule.^{32b, 33} The H-H distances could not be satisfactorily determined due to the failure to locate the N-H hydrogen from the disordered imidazole. However, the strength of the interaction (5.3 kcal/mol, estimated by IR spectroscopy) is greater than in the similar complex **22**, as expected considering the higher acidity of imidazole relative to indole.



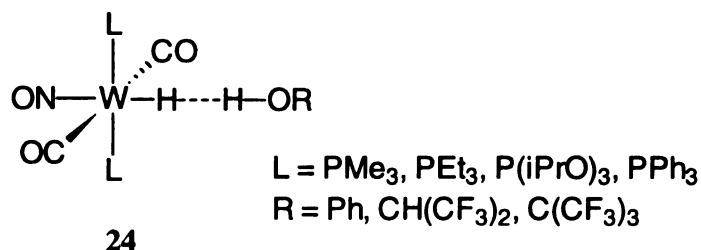
Other weak acids such as 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{OH}$, 2-*t*Bu-6-Me $\text{C}_6\text{H}_3\text{OH}$, pyrrole, PhNHPh , PhNHBn , PhNHMe , also associate with $\text{ReH}_5(\text{PPh}_3)_3$, as shown by the IR of the thin films obtained by evaporation of CH_2Cl_2 solutions containing a 1:1 mixture of the polyhydride and the proton donor.³⁴ The $-\Delta H^0$ of the interactions, evaluated from the observed shifts of the NH or OH bands, were found to generally correlate with the acidities of the proton donors, and vary between 3.0 and 5.6 kcal/mol. Replacing the hydridic partner with the $\text{WH}_4(\text{PMePh}_2)_4$ complex resulted in slightly weaker dihydrogen

bonds of 1.1-5.2 kcal/mol. That these interactions involve primarily the hydridic hydrogen and not the d^2 non-bonding electron pairs of the Re or W metals was demonstrated by the analogous d^0 complex $\text{ReH}_7(\text{dppe})$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), that also associated with the same proton donors, with $-\Delta H^0$ in the range 1.3-4.7 kcal/mol.

In solution, the $\text{N-H}\cdots\text{H-Re}$ interactions were studied by Crabtree et al. using UV-vis spectroscopy.³⁵ Thus, the $\text{ReH}_5(\text{PPh}_3)_2\text{L}$ ($\text{L} = \text{pyridine, 4-picoline, 4-dimethylaminopyridine, and 4-carbomethoxypyridine}$) hydrogen bond acceptors interact with indole as the hydrogen bond donor, showing free energies of association, $-\Delta G$, of 3.8-5.0 kcal/mol.

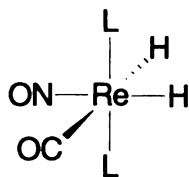
In a thorough analysis, Epstein, Berke, and coworkers surveyed dihydrogen bonding in solution in the tungsten hydride-alcohol complexes **24**.³⁶ Using IR and NMR spectroscopies, they ruled out hydrogen bonding to the CO or NO groups, and proved the exclusive formation of the unconventional $\text{O-H}\cdots\text{H-W}$ interactions. As expected, the strengths of these dihydrogen bonds increase with the donator abilities of the ligand L ($\text{PMe}_3 > \text{PEt}_3 > \text{P(OiPr)}_3 > \text{PPh}_3$) and are directly proportional to the acidities of the proton donors phenol (PhOH), hexafluoro-2-propanol (HFIP), and perfluoro-2-methyl-2-propanol (PFTB) ($\text{PFTB} > \text{HFIP} > \text{PhOH}$). Their magnitude was estimated in the range 4.1-6.9 kcal/mol, from the observed shifts in the corresponding ν_{OH} bands, as well as from the variation of the association constants K with temperature. In addition, NMR experiments (δ shifts, NOE, and T_1 relaxation times), all supported the formation of $\text{O-H}\cdots\text{H-W}$ dihydrogen bonds, with H-H contact distances as short as 1.77 Å in the case of HFIP. A linear $\text{OH}\cdots\text{H-W}$ orientation was arguably suggested for these interactions, in

sharp contrast to the previously established propensity of dihydrogen bonds for a strongly bent geometry.



In an analogous series of rhenium hydride complexes (**25**), the same two research groups proved the occurrence of intermolecular O-H...H-Re dihydrogen bonding in solution.^{37, 38} When PFTB was used as proton donor, interaction energies between 4.5 and 6.1 kcal/mol were calculated from the observed ν_{OH} shifts in the IR spectra in hexane. In toluene, however, the ΔH values, derived from variable temperature NMR spectroscopy, are smaller by about 3 kcal/mol, apparently due to competitive O-H... π interactions with the solvent.³⁸ The H...H contact distances calculated from T_1 relaxation times range between 1.78 and 1.94 Å. The phosphine ligand appears to have an important influence over the regioselectivity of the H-bonding formation. Thus, while in **25a** interaction with one of the hydridic hydrogens is preferred, the NO group competes more and more effectively for the proton donor as the bulk of L increases, to the point where only O-H...ON hydrogen bonds are observed for **25c**. However, DFT calculations on a $\text{ReH}_2(\text{CO})(\text{NO})(\text{PH}_3)_2 \cdot \text{H}_2\text{O}$ model indicated that the H...H interaction is energetically preferred by about 3.0-3.5 kcal/mol.³⁷ Also, a stronger interaction was predicted with the Re-H hydride trans to the NO group ($d_{\text{H}\cdots\text{H}} = 1.49$ Å) compared to the Re-H trans to CO

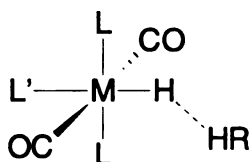
($d_{\text{H-H}} = 1.79 \text{ \AA}$), and confirmed experimentally by the high regioselectivity displayed by both PFTB and HFIP alcohols toward the former, as shown by NMR spectroscopy.³⁸



25

L = PMe₃ (a), PEt₃ (b), PiPr₃ (c)

The experimental results obtained by Epstein and Berke on the intermolecular dihydrogen bonding in solution were complemented by the theoretical work of Scheiner et al. on the Mo and W hydride complexes **26**.³⁹ Their HF/3-21G and DFT (B3LYP, BLYP, B3PW91) calculations confirmed that the H...H interactions are favored over conventional hydrogen bonding involving the NO group.

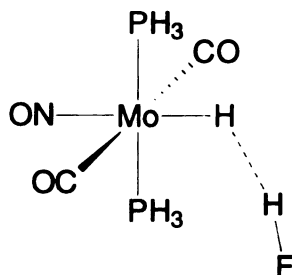


M = Mo, W
L = PH₃, NH₃
L' = NO, Cl, H
R = F, OH, H₂O⁺

26

The dihydrogen bonds in **26** become stronger and shorter with the increases in the donating ability of the *cis*-ligand or the acidity of the proton donor, consistent with experiment. However, the strongly acidic H₃O⁺ induces complete proton transfer, resulting in the formation of an η^2 -H₂ dihydrogen complex. The H-H-M angles are

strongly bent in all the optimized structures, as illustrated in Figure 1.12 for the representative complex **26a**. For this dihydrogen-bonded system, a 2.6 kcal/mol destabilization energy was calculated for a linear F-H...H-Mo orientation.



26a

Figure 1.12. Calculated structure for dihydrogen-bonded complex **26a**; $\angle \text{FH}\cdots\text{H-Mo} = 127^\circ$, $\angle \text{F-H}\cdots\text{HMo} = 174^\circ$.

As with the boron hydrides, C-H sites may participate as protonic partners with transition metal hydrides. Recent X-ray structural studies and CSD surveys confirmed the existence of intra-⁴⁰ as well as intermolecular⁴¹ C-H...H-M close contacts in transition metal hydrides. A large number of these examples were observed in complexes containing $\text{R}_{3-x}(\text{Ph})_x\text{P}$ ($x = 1-3$) ligands, in which one or more *ortho* C-H bonds point toward the M-H hydridic hydrogens (Figure 1.13).^{40a,c,d} While the H...H distances and M-H...H angles in these complexes were found to fall essentially in the same range as observed for the more “conventional” dihydrogen bonds involving N-H or O-H proton donors, the C-H...H angles usually tend to be smaller, due to the inherent constraints imposed by the chelation.^{40a} However, caution is advisable in interpreting some of these

C-H...H-M short contacts, as steric compression by bulky ligands or packing forces may make a significant contribution to the observed H...H close proximities.^{40b}

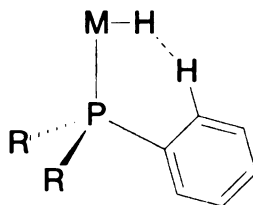
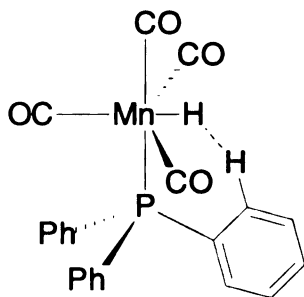


Figure 1.13. Generic representation of C-H...H-M dihydrogen bonds in complexes of transition metal hydrides with $R_{3-x}(Ph)_xP$ ligands.

The comprehensive analysis of the manganese hydride complex **27** carried out by Brammer and collaborators provided convincing evidence for an intramolecular C-H...H-Mn dihydrogen bond.⁴² Their combined low-temperature neutron and X-ray diffraction study revealed a short intramolecular C-H...H-Mn contact of 2.10 Å, with H...H-Mn and C-H...H angles of 126.5 and 129.0°, respectively, and an essentially coplanar relative orientation of the Mn-H and C-H bonds ($\angle \text{Mn-H}\cdots\text{H-C} = 0.7^\circ$). The experimental atomic charges found for the Mn-H hydridic and *ortho* CH protonic hydrogens, of -0.40 and +0.32, clearly indicate an attractive electrostatic interaction, whose magnitude was calculated to be 5.7 kcal/mol. Moreover, topological analysis of the charge density using the “atoms in molecules” theory unequivocally supported the existence of a moderately strong intramolecular C-H...H-Mn hydrogen bond.



27

1.3. Self-Assembly of Extended Dihydrogen-Bonded Systems.

In the previous section it was demonstrated that dihydrogen bonding is a significant interaction, with energetic, electronic, and spectral characteristics, as well as directionality, comparable with those found in conventional hydrogen bonding. A direct consequence of this similarity is that dihydrogen bonds, like traditional H-bonds, could find potential utility in crystal engineering and supramolecular synthesis. That these $\text{H}\cdots\text{H}$ noncovalent interactions are indeed capable of controlling crystal packing was already suggested by the crystal structure of cyclotrigallazane (**12**), which self-assembles into an extended dihydrogen-bonded α -network in the solid state (Figure 1.10), as demonstrated by Gladfelter's group.²¹

The osmium polyhydride complex $[\text{K}(1\text{-aza-18-crown-6})][\text{mer-OsH}_3(\text{CO})(\text{iPr}_3\text{P})_2]$ (**28**) synthesized by Morris et al. also forms polymeric one-dimensional chains in the solid-state (Figure 1.14).⁴³ The $\text{N-H}\cdots\text{H-Os}$ dihydrogen bonds are however complemented by $\text{CO}\cdots\text{K}^+$ interactions in the assembly of the chains.

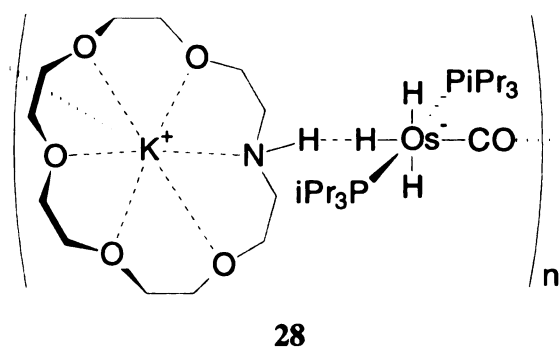


Figure 1.14 Self-assembly of dihydrogen-bonded complex **28** in one-dimensional chains.

When 1,10-diaza-18-crown-6 was used to complex K^+ , similar chains held together exclusively by $N-H\cdots H-M$ dihydrogen bonds (Figure 1.15) could be assembled from the osmium, ruthenium, and iridium anionic polyhydrides $[MH_{x+3}(iPr_3P)_2]^-$ ($M = Os$ (**a**), Ru (**b**), $x = 2$; $M = Ir$ (**c**), $x = 1$) (**29**).^{44, 45} The intermolecular $H\cdots H$ distances in these complexes were estimated from their X-ray crystal structures to be in the range 1.8–1.9 Å. The NH bands in their solid-state IR spectra are broadened relative to the free diaza-crown ether, and shifted to lower numbers by 96, 107, and 132 cm^{-1} , for the Os, Ru and Ir complexes, respectively, in accord with the increasing basicity (and hydricity) of these polyhydrides in the same order. The observed shifts correspond to $N-H\cdots H-M$ interaction energies of about 3 kcal/mol.⁴⁵ Weaker $C-H\cdots H-M$ hydrogen bonds can also be involved in the supramolecular association of the polyhydrides **29a,b** with $K(THF)(1-aza-18-crown-6)$, in which alternating $NH\cdots H-M-H\cdots HN$ and $CH\cdots H-M-H\cdots HC$ units lead to the formation of zigzag chains, as illustrated in Figure 1.16.⁴⁵ The $NH\cdots HO$ s and $NH\cdots HRu$

separations were estimated at 1.7 Å, while the weaker CH...HOs and CH...HRu interactions exhibit longer H-H contact distances of 2.2 and 2.1 Å, respectively.

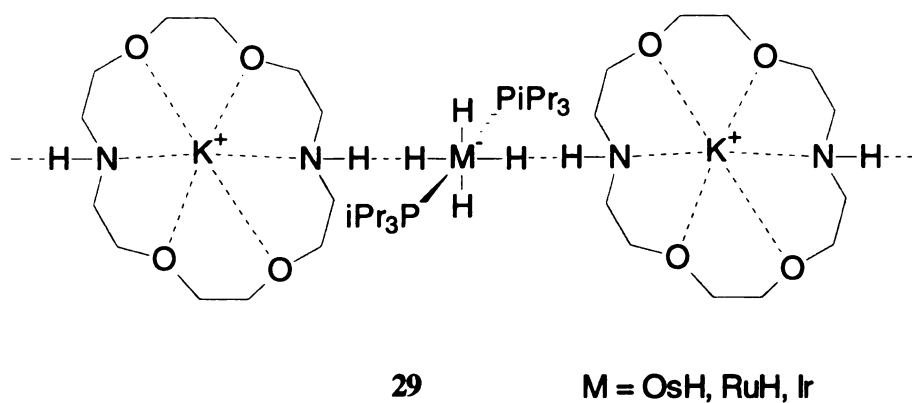


Figure 1.15. Self-assembly of dihydrogen-bonded complexes **29**·[K(1,10-diaza-18-crown-6)] in one-dimensional chains.

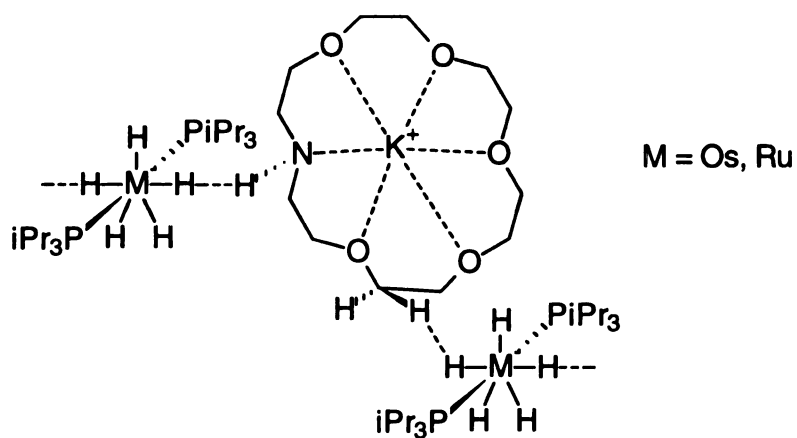


Figure 1.16. Self-assembly of dihydrogen-bonded complexes **29a,b**·[K(THF)(1-aza-18-crown-6)] in one-dimensional chains.

Finally, a similar polymeric chain can be assembled exclusively by weak C-H...H-M interactions (Figure 1.17), as illustrated by the crystal structure of **29b**·[K(THF)(18-crown-6)].⁴⁵ In this case, the observed C-H...H-Ru contact distance is 2.2 Å.

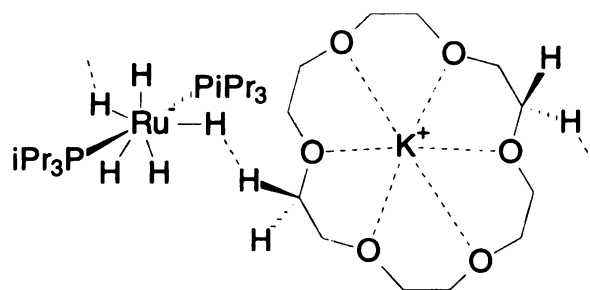


Figure 1.17. Self-assembly of dihydrogen-bonded complexes **29b**·[K(THF)(18-crown-6)] in one-dimensional chains.

As part of early endeavors in the Jackson group directed toward the structural characterization of dihydrogen-bonded systems involving anionic borohydrides, the crystal structure of guanidinium borohydride was explored.⁴⁶ In the solid-state, this salt is organized into extended tapes, in which the alternating BH_4^- and $\text{C}(\text{NH}_2)_3^+$ ions are connected by multipoint dihydrogen bonds, as illustrated in Figure 1.18.

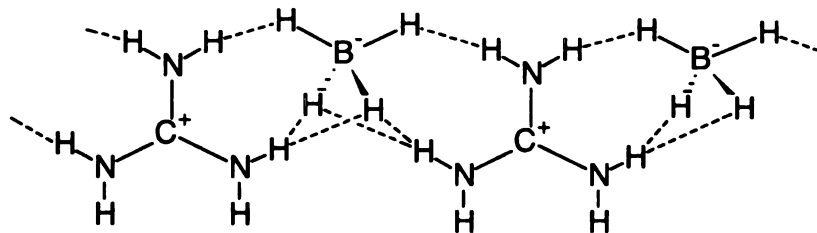
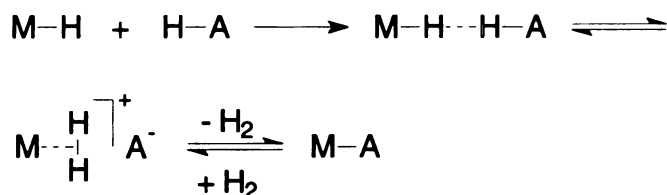


Figure 1.18. Self-assembly of guanidinium borohydride in one-dimensional extended tapes.

1.4. Dynamics of Dihydrogen Bonds

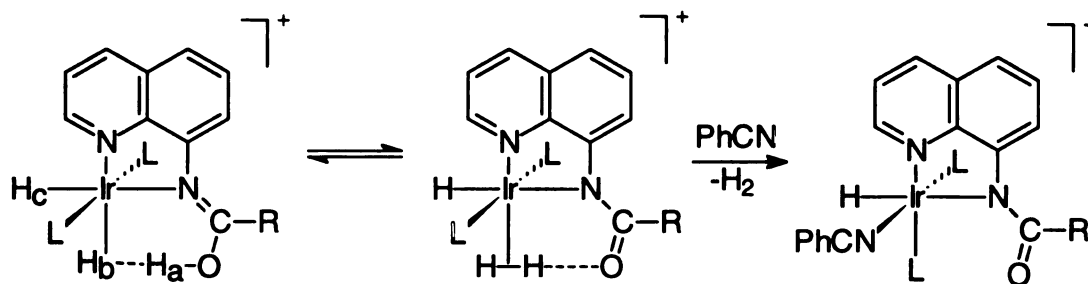
Numerous studies have now established that dihydrogen bonding is an important and general interaction involving element-hydride σ bonds, and its geometrical and energetic features have been described in great detail. The significance of these unusual hydrogen bonds extends, however, beyond their fundamental aspects. With their substantial strength and directionality, they can be used to control reactivity and selectivity of chemical reactions, in the same time finding a place alongside conventional hydrogen bonding in the supramolecular chemists' arsenal of noncovalent interactions. However, what makes dihydrogen bonding particularly interesting is the special reactivity conferred by its peculiar nature. It has been recently demonstrated that $\text{H}\cdots\text{H}$ bonds have a role in the formation of dihydrogen $\eta^2\text{-H}_2$ complexes and the reverse heterolytic splitting of H_2 , as well as σ -bond metathesis (Scheme 1.2).



Scheme 1.2

The Ir-H_b bond in **30** has been found to be activated by dihydrogen bonding for a number of reactions.⁴⁷ Thus, the hydridic and protonic hydrogens H_a and H_b involved in the $\text{H}\cdots\text{H}$ interaction can interchange relatively easily whereas the non-interacting H_c is

exchanged much more slowly with H_a and H_b. The $\Delta H^\ddagger$ for the H_a/H_b exchange has been estimated by variable temperature NMR spectroscopy at around 14-16 kcal/mol and found to go down as the R group becomes more electron-withdrawing, consistent with a mechanism involving proton transfer from the OH group to the Ir-H_a bond, to give an η^2 -H₂ intermediate complex (Scheme 1.3). Rotation of the H₂ ligand in this complex and transfer of the proton back to the oxygen completes the exchange. When the reaction was performed in the presence of benzonitrile, the H₂ ligand could be displaced by PhCN, in a rate-limiting step.



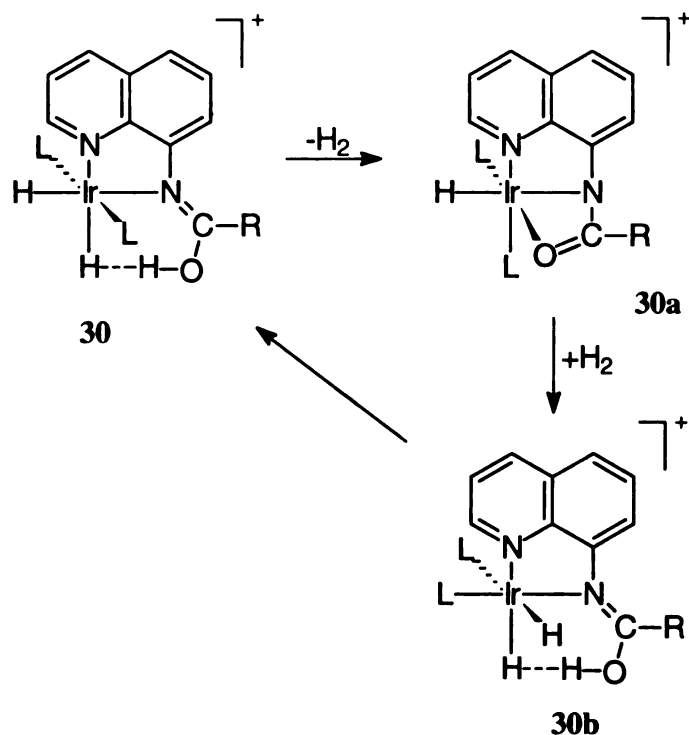
30

L = PPh₃

R = Me, *n*-Bu, *p*-tolyl, Ph, *p*-FC₆H₄, 3,4-C₆H₃F₂

Scheme 1.3

Alternatively, H₂ elimination from **30** by heating in a sealed tube at 80 °C yielded the chelate complex **30a**, in a σ -bond metathesis reaction. The initial complex **30** could be recovered by exposure to H₂ in CH₂Cl₂ at room temperature, via the isomer **30b** (Scheme 1.4).

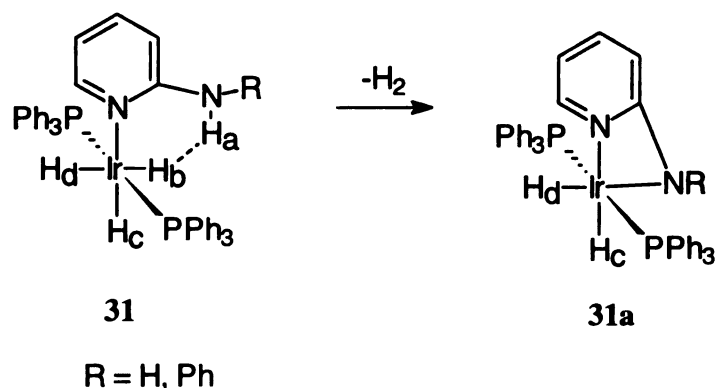


Scheme 1.4

Similarly, hydrogen scrambling between H_a and H_b is facilitated by dihydrogen bonding in complexes **31**, apparently via an $\eta^2\text{-H}_2$ intermediate.⁴⁷ H_2 loss at room temperature was also observed, with the formation of **31a** in a first order reaction, with measured activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 14 ± 2 kcal/mol and -32 ± 6 eu, respectively (Scheme 1.5). The highly negative activation entropy suggests an associative process with a highly ordered transition state.

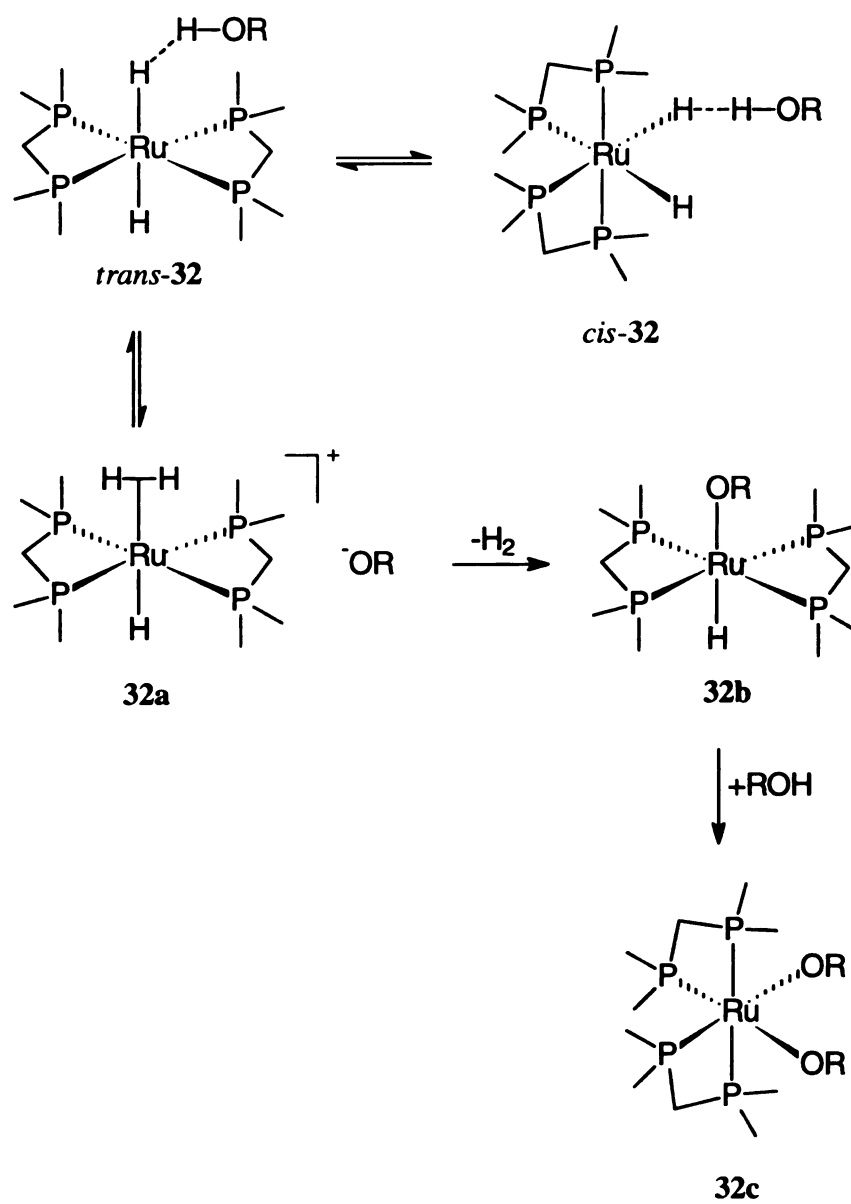
The first direct observation of a dynamic equilibrium between a $\text{H}\cdots\text{H}$ bonded system and an $\eta^2\text{-H}_2$ complex resulting from proton transfer along a dihydrogen bond was made by Chaudret and coworkers, using NMR spectroscopy.⁴⁸ Thus, in the presence of phenol, the ruthenium hydride complex $\text{RuH}_2(\text{dppm})_2$ (**32**) exists as a mixture of dihydrogen-bonded

cis and *trans* isomers in benzene or toluene solutions. The *trans* isomer is also involved in a dynamic equilibrium with the dihydrogen complex **32a**, which lies 17 kcal/mol lower in enthalpy than **32·PhOH** (Scheme 1.6). It was proposed that the reversibility of the process originates in the strong dihydrogen bonding between **32** and phenol. In the presence of the more acidic hexafluoroisopropanol, the corresponding dihydrogen complex **32a** further reacts by H₂ loss, to ultimately give **32c** via **32b**.



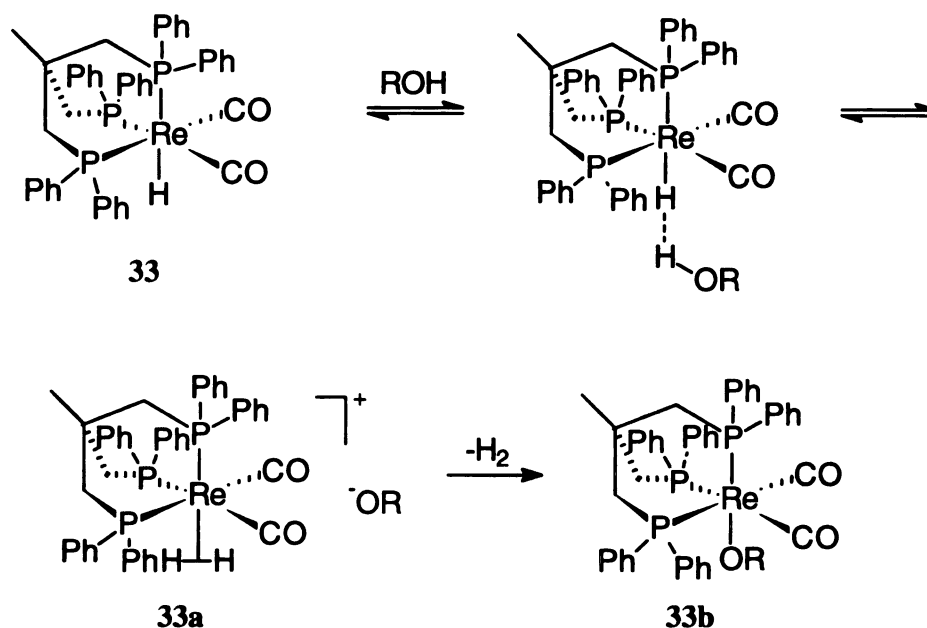
Scheme 1.5

DFT calculations by Scheiner et al. on a HOH...H₂Ru(PH₂CH₂PH₂)₂ model yielded ΔE and $\Delta E^{\ddagger}$ values of -10.7 and 10.0 kcal/mol, respectively, in qualitative agreement with experiment.⁴⁹ However, when the stronger proton donor HF was used in the calculations, no F-H...H-Ru adduct could be identified, and the system evolved directly toward the dihydrogen complex, which in this case lies 23.8 kcal/mol lower in energy than the separated HF and ruthenium hydride complex.



Scheme 1.6

Using in situ IR and NMR spectroscopy, Epstein et al. studied the proton transfer in the dihydrogen-bonded complexes between (triphos)Re(CO)₂H (**33**) and phenol, tetrafluoroboric acid (HBF₄·OMe₂), chloroacetic acid (ClCH₂CO₂H), hexafluoro-2-propanol (HFIP) or perfluoro-2-methyl-2-propanol (PFTB), as proton donors, at 200-260 K (Scheme 1.7).⁵⁰ The η^2 -H₂ complexes **33a** were found again to be thermodynamically more stable than their H···H bonded precursors. Higher temperatures induced H₂ loss with the formation of the covalent products **33b**.



Scheme 1.7

In the case of H₂Re(CO)(NO)(PMe₃)₂ + CF₃COOH, the dihydrogen-bonded complex coexists in equilibrium with the corresponding η^2 -H₂ complex, which loses H₂ upon heating.⁵¹ Similarly, the dihydrogen-bonded adduct

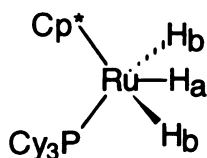
$(\text{CF}_3)_2\text{CHOH}\cdots\text{HW}(\text{CO})_2(\text{NO})(\text{PMe}_3)_2$ was found to undergo proton transfer in the rate-limiting step with the formation of an unstable $\eta^2\text{-H}_2$ complex, which subsequently eliminates H_2 to form a W-OR covalent product.

The proton transfer in the dihydrogen-bonded complex

$(\text{CF}_3)_3\text{COH}\cdots\text{HRu}(\text{Cp})(\text{CO})(\text{PCy}_3)$ was also studied by Epstein et al. using in situ IR spectroscopy, and a relatively high barrier of 15 kcal/mol was found for this process.⁵¹ To model this reaction, Scheiner et al. used the $\text{HRu}(\text{Cp})(\text{CO})(\text{PH}_3)$ ruthenium hydride model, which was allowed to interact with H_3O^+ , CF_3OH or H_2O , representing strong, moderate, and weak proton donors, respectively.⁵² While in the first case spontaneous transfer of proton with the formation of a corresponding hydrated $\eta^2\text{-H}_2$ complex was observed, the other two weaker acids did not transfer the proton at all, suggesting that the activation barrier for this process is largely determined by the proton donor ability of the acidic partner. The critical role of the proton donor acidity has also been recognized recently by Lau et al., who concluded that strongly acidic conditions give $\eta^2\text{-H}_2$ complexes, while weakly acidic conditions favor dihydrogen-bonded species.⁵³

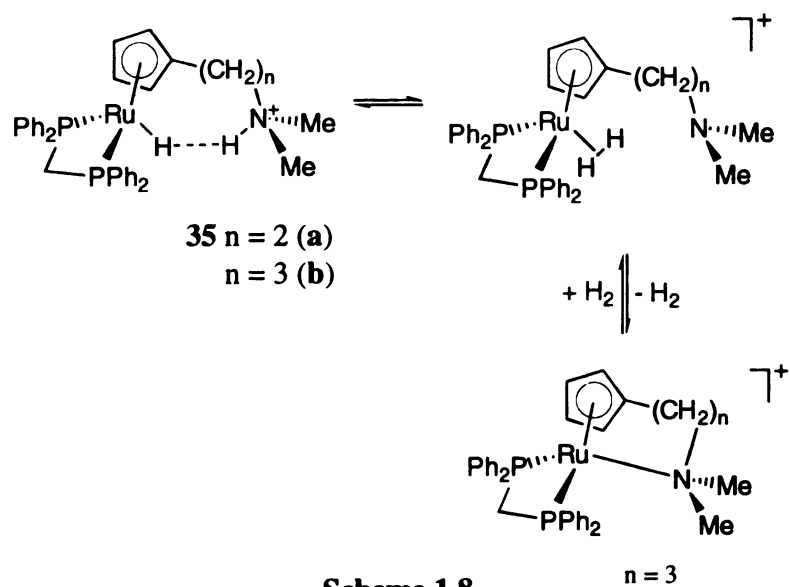
In the ruthenium polyhydride complex **34**, Chaudret et al. noted a substantial increase of the H-H coupling J_{ab} upon formation of dihydrogen bonding with various proton donors in toluene, which was tentatively explained by the decrease of the electron density on Ru, caused by the partial charge transfer from the metal hydride to the hydrogen bond donor.⁵⁴ When the $\text{CDCl}_2\text{F}/\text{CDF}_3$ (2:1) solvent system was used instead, proton transfer with the formation of the $(\text{Cp}^*)(\text{PCy}_3)\text{RuH}_4$ complex was observed at low temperatures, as a result of the unusual property of the Freon mixture to strongly increase its dielectric constant upon cooling, assisting thus the protonation of **37**.⁵⁵ Interestingly,

the reactants can be mixed at room temperature, but the proton transfer only occurs when the temperature is sufficiently lowered to induce an adequate increase in the dielectric constant of the solvent. The same behavior was observed in CD_2Cl_2 , a solvent which is also known to have a strong temperature-dependent dielectric constant.

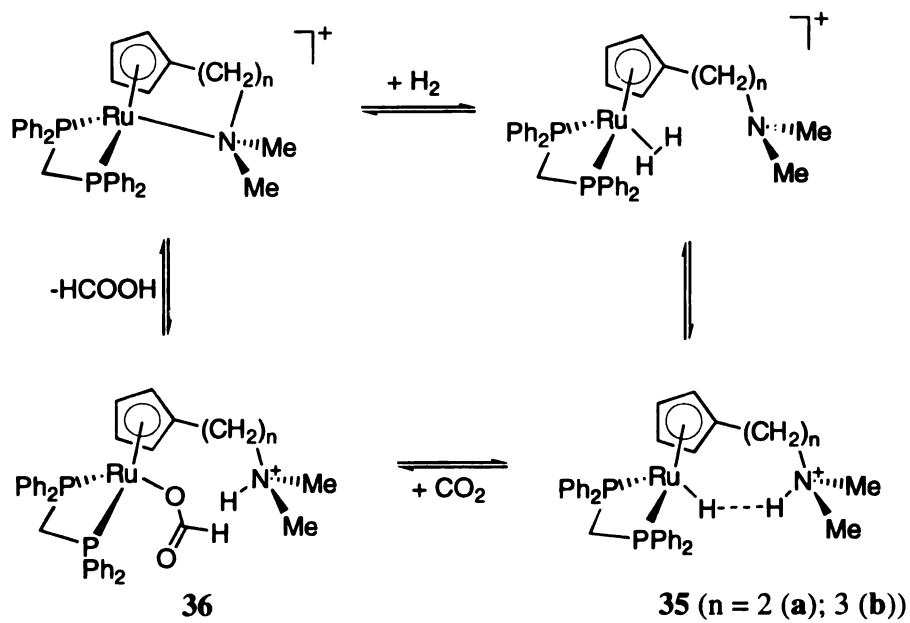


34

According to Lau et al., intramolecular $\text{N-H}\cdots\text{H-Ru}$ dihydrogen bonds also appear to mediate proton transfer and subsequent formation of N-Ru bonds in **35**, as illustrated in Scheme 1.8.⁵⁶ H/D exchange of both protonic and hydridic hydrogen atoms with D_2O strongly suggest the existence of $\eta^2\text{-H}_2$ intermediate species in equilibrium with the $\text{H}\cdots\text{H}$ bonded complexes. H_2 loss with the formation of a Ru-N bonded chelate structure is facile in **35b**, and the reverse Ru-N bond hydrogenolysis can be done at $60\text{ }^\circ\text{C}$ under 60 atm (Scheme 1.8). This system was found to catalyze the reduction of CO_2 to formic acid, although with low yields.⁵⁶ The heterolytic splitting of the H_2 ligand is believed to be a crucial step in the proposed mechanism, which is depicted in Scheme 1.9. The only NMR detectable metal-containing species throughout the reaction is **35**, suggesting that the insertion of CO_2 into the Ru-H bond is the rate-determining step, as also supported by recent theoretical calculations on a similar system.⁵⁷

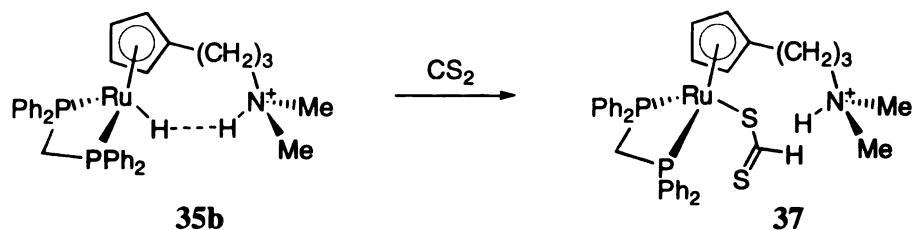


Scheme 1.8



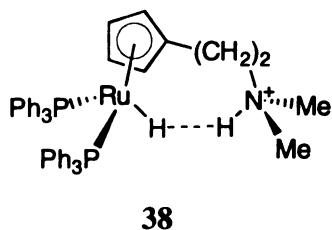
Scheme 1.9

While the proposed metal formate intermediate **36** could not be detected, the analogous dithioformate complex **37** was easily prepared from **35b** and excess CS₂ (Scheme 1.10), and its identity was unambiguously established by IR and NMR spectroscopies.⁵⁶



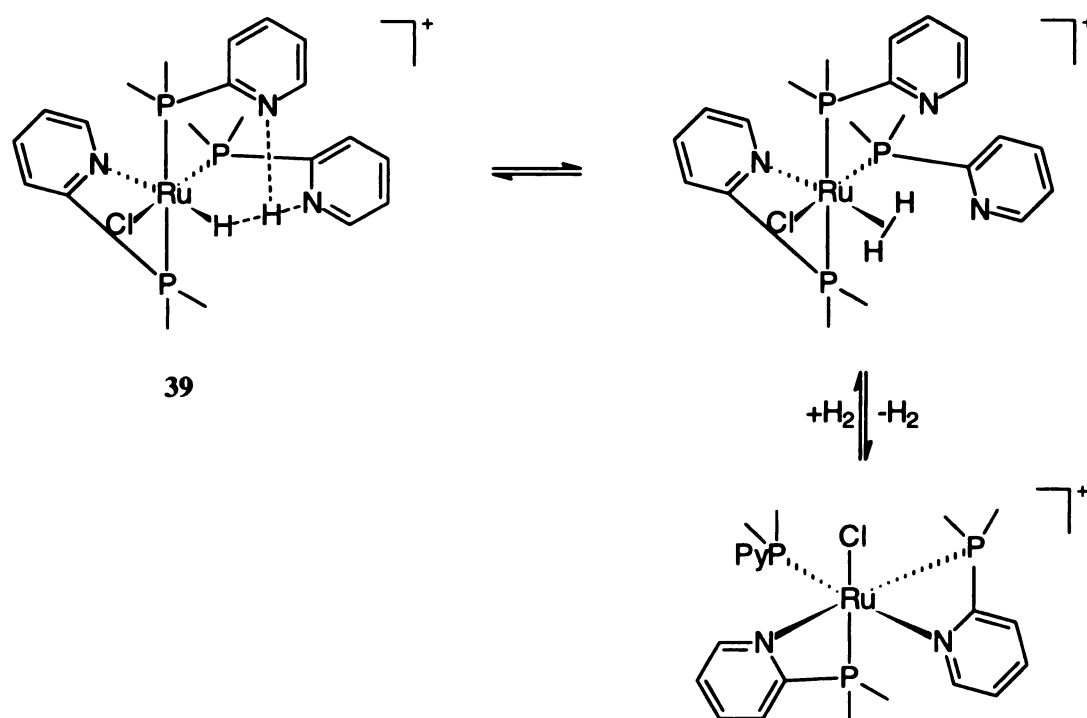
Scheme 1.10

Hydrogen exchange in the structurally related complex **38** was studied by Chaudret et al. using ¹H NMR spectroscopy, and the activation energy for this process was determined to be around 11 kcal/mol.⁵⁸ However, extensive DFT calculations suggested that the mechanism for the exchange does not involve any proton transfer within the N-H...H-Ru dihydrogen bond.



A very interesting dihydrogen-bonded system with its hydrogen exchange dynamics has been recently described by Jalón et al.⁵⁹ They reported a three-center py₂H...H-Ru intramolecular interaction in **39**, in which fast scrambling between the

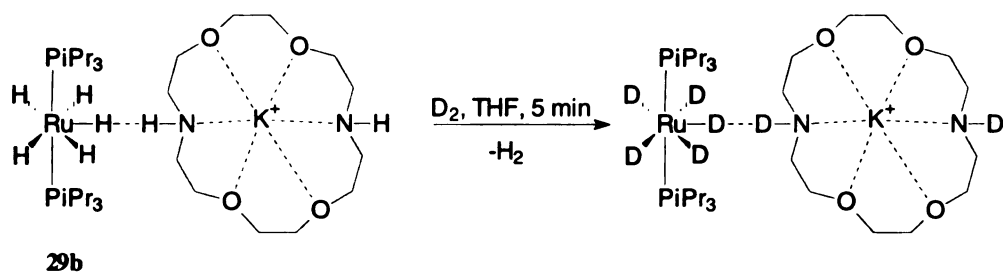
hydridic and protonic hydrogen atoms occurs most probably via an η^2 -H₂ complex intermediate (Scheme 1.11). An activation energy of about 13.6 kcal/mol was determined for this process, using variable temperature ¹H NMR spectroscopy. Moreover, this system proved to be a very active catalyst for D⁺/H₂ exchange. Thus, when a solution of **39** in CD₃OD was exposed to a dihydrogen atmosphere (1 atm) at room temperature, more than 90% of H₂ was exchanged for D₂ in about half an hour.



Scheme 1.11

A similar exchange was reported by Morris et al. in the ruthenium polyhydride complex **29b**·[K(1,10-diaza-18-crown-6)] (Scheme 1.12).⁴⁵ Upon exposure to D₂ gas at 1

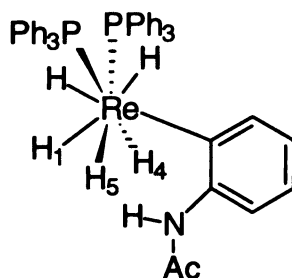
atm and room temperature for 5 min, the intensities of the NH and RuH ^1H NMR (THF-d_8) signals were depleted by 100% and 90%, respectively. For comparison, only 13% decrease in the hydride resonance was observed after 10 days when the much less acidic 18-crown-6 ether was used for complexation, implying efficient activation of the M-H bonds by N-H $\cdots$ H-Ru dihydrogen bonding. The exchange is also significantly slower if the ruthenium hydride is replaced by the less basic analogous osmium hydride (**29a**). While the conjugate acid of **29b**, the known $\text{RuH}_2(\text{H}_2)_2(\text{iPr}_3)_2$ dihydrogen complex, could reasonably play the role of the intermediate in the exchange process depicted in Scheme 1.12, its involvement in this transformation was ruled out by control experiments.



Scheme 1.12

Intramolecular N-H $\cdots$ H-Re interactions can affect hydride fluxionality in $\text{ReH}_5(\text{PPh}_3)_2\text{L}$ ($\text{L} = N\text{-acetyl-2-aminopyridine}$) (**40**).⁶⁰ Thus, the free energy of activation for the turnstile rotation involving the H_1 , H_4 , and H_5 atoms in this complex is 0.7 kcal/mol smaller than for the analogous complex with the NHAc group in the *para* position of the pyridine ring. Stabilization of the transition state by strong N-H $\cdots$ H-Re dihydrogen bonding, which is only possible in the *ortho*-NHAc isomer, seems to be

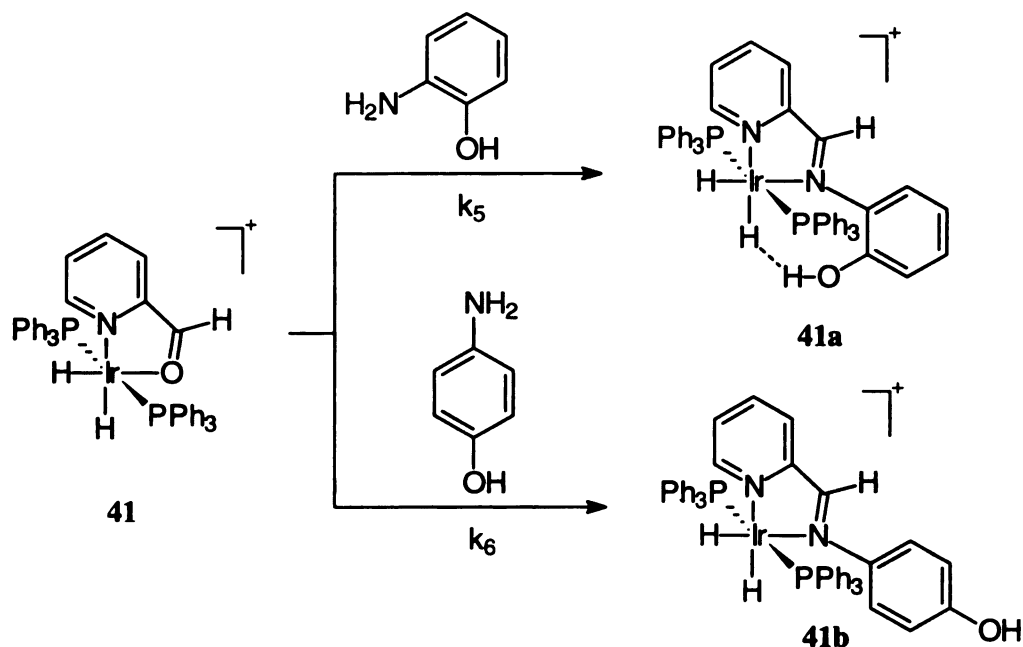
responsible for the observed difference. However, this effect is partly offset by non-bonding repulsive interactions between the two H...H hydrogen atoms, which are forced to approach to 1.49 Å in the transition state, according to theoretical calculations.⁶¹



40

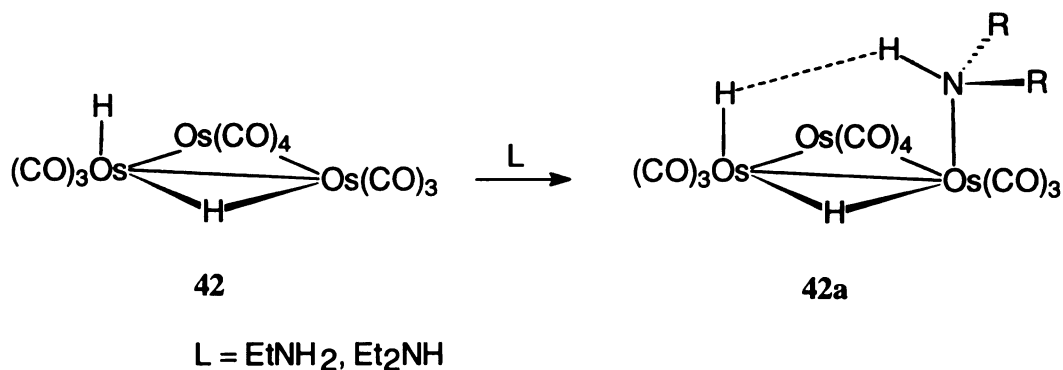
Dihydrogen bonding can have important consequences on the selectivity and stereochemistry of reactions in solution. Thus, the formation of directional and strong H...H interactions can differentially stabilize one particular transition state among two or more possibilities, ultimately controlling the product distribution or stereochemical outcome. An illustration of this concept is the selective imination of the η^1 -aldehyde complex **41** with *ortho*- vs. *para*-aminophenol, carried out by Crabtree et al.⁶² In a competitive experiment using an equimolecular mixture of 2-aminophenol, 4-aminophenol and **41**, a 4.2:1 ratio of the resulting products **41a** and **41b** was obtained (Scheme 1.13), which was calculated to correspond to a k_5/k_6 value of 6. This outcome appears to be the result of O-H...H-Ir dihydrogen bonding stabilization of **41a** (and presumably of the TS leading to it). The two isomers do not interconvert, indicating that the observed product distribution is dictated by kinetic not thermodynamic control. While the observed ratio between the two rate constants is translated into a $\Delta\Delta G^\ddagger$ value of 1.1

kcal/mol, the 4.5 kcal/mol estimated H...H interaction energy in **41a** is substantially larger, the difference being apparently offset by the unfavorable chelate ring conformation required for efficient H-bonding in the transition state.



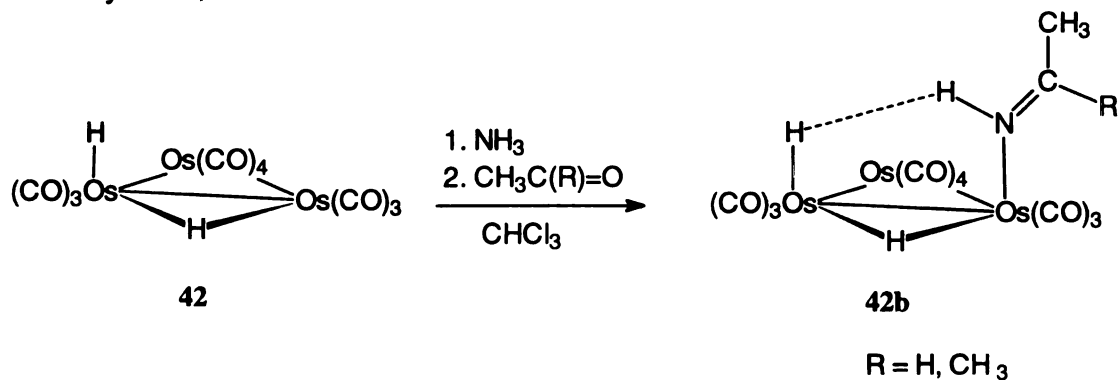
Scheme 1.13

Dihydrogen bonding can also direct the regiochemistry of ligand attachment to transition metal clusters, as demonstrated by Aime and coworkers.⁶³ Thus, reaction of the electronically unsaturated osmium cluster **42** with EtNH₂ or Et₂NH yields exclusively the *syn* product **42a**, stabilized by an intramolecular N-H...H-Os interaction, which would not be possible in the *anti* isomer (Scheme 1.14). Notably, with Et₃N, which lacks the acidic hydrogens required for dihydrogen bond formation, no reaction occurs.



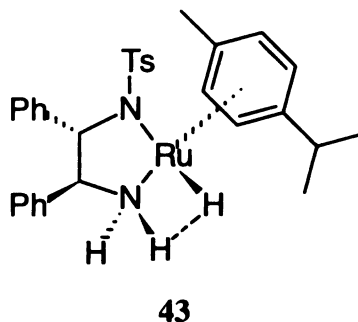
Scheme 1.14

The *syn* isomer is also preponderantly formed when **42** reacts with NH_3 . Subsequent treatment with acetaldehyde or acetone in chloroform leads to the exclusive formation of the dihydrogen-bonded imino-derivatives **42b** with a *syn* configuration (Scheme 1.15).^{64, 65} The intramolecular N-H...H-Os interaction is disrupted in more polar, hydrogen bonding solvents such as methanol or acetone. In this case, the interconversion between the *syn* and *anti* isomers was demonstrated by variable temperature NMR spectroscopy, which suggests that the observed regioselectivity is a result of thermodynamic, rather than kinetic control.

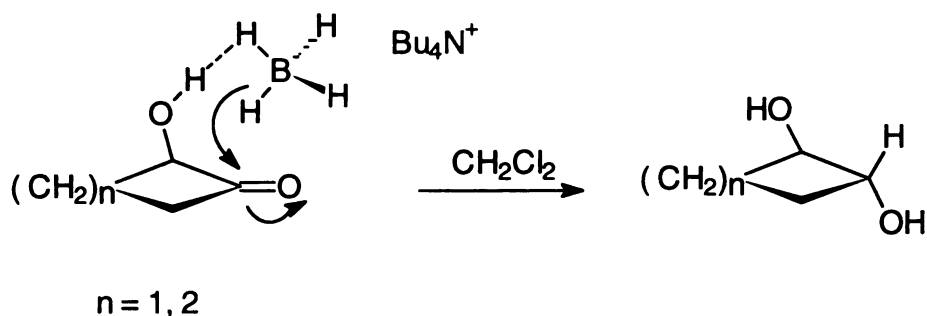


Scheme 1.15

The ruthenium hydride **43**, whose crystal structure shows an intramolecular N-H...H-Ru short contact, was found to efficiently catalyze the asymmetric hydrogenation of ketones to chiral alcohols.⁶⁶ However, the specific contribution of the H...H interaction to the high enantioselectivity observed in these reductions was not analyzed.



Work in our group by Gatling established the ability of O-H...H-B dihydrogen bonds to direct the borohydride reduction of ketones to alcohols.⁶⁷ Thus, reductions of 2-hydroxycyclobutanone or 2-hydroxycyclopentanone with tetrabutylammonium borohydride in the non hydrogen bonding solvents CH₂Cl₂, ClCH₂CH₂Cl, or *o*-dichlorobenzene are accelerated about 150 times relative to the reductions of the corresponding unsubstituted cycloalkanones, and yield almost exclusively trans diols after workup (Scheme 1.16). These effects are greatly reduced in the presence of competing hydrogen bonding alcohols or anions like F⁻, Cl⁻, or Br⁻. Capping of the OH with a trimethylsilyl group also shuts off both the stereodirection and the rate acceleration. AM1 semiempirical calculations predicted a 3.5 kcal/mol preference for the hydride delivery from the OH substituted face of 2-hydroxycyclobutanone. This value is in reasonable agreement with the experimental findings, despite the crude level of theory and the absence of counterions or solvent in the model.

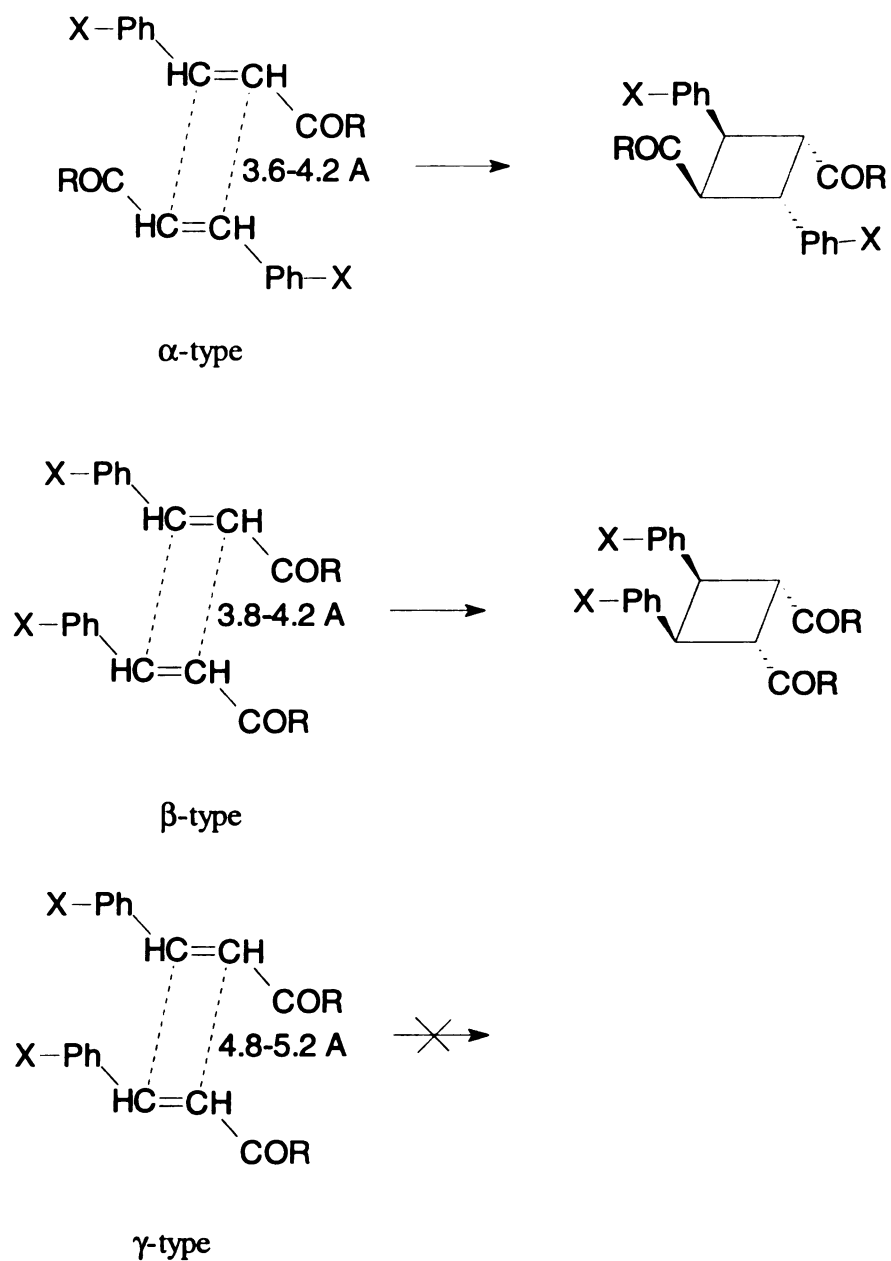


Scheme 1.16

In the solid-state, dihydrogen bonding can control the transformation of cyclotrigallazane (**12**) into nanocrystalline gallium nitride, according to Gladfelter and coworkers.⁶⁸ Initial loss of H_2 at $150\text{ }^\circ\text{C}$ resulted in an amorphous GaN phase, which upon annealing at $600\text{ }^\circ\text{C}$ led to the metastable crystalline cubic gallium nitride, as a 1:1 mixture with the thermodynamically favored hexagonal GaN. The crystallization in the cubic system appears to be dictated by the initial crystal packing in **12**, consisting of $N-H\cdots H-Ga$ dihydrogen-bonded chains (Figure 1.10), which can be considered essentially “hydrogenated” cubic GaN. For comparison, decomposition of cyclotrigallazane in thin films obtained by vapor deposition, a process that presumably disrupts the dihydrogen-bonded network, yields exclusively hexagonal GaN. It is remarkable that despite the huge contraction of the unit cell accompanying the conversion of **12** into cubic GaN, the reaction still maintains partial topochemical character.

2. Organic Solid-State Reactions: Mechanisms and Concepts

Organic solid-state reactions have been reported to occur since the beginning of organic chemistry. The 1828 Wöhler's famous transformation of ammonium cyanate into urea was proven to take place both in solution⁶⁹ and solid-state.⁷⁰ However, it was not until relatively recently that this discipline has developed as a mature field, with the invaluable assistance of physical methods like X-ray crystallography, optical and electronic microscopies, thermal analysis, and solid-state NMR spectroscopy. A fundamental difference between the reactivity in fluid and solid phases is that while the former is dominated by the electronic properties of molecules, reactivity in solids is a balance between packing and electronic effects. In the solid-state, the reactants are usually locked in a fixed orientation with relatively low mobility, and consequently the intrinsic reactivity of the molecules is often less important than their spatial arrangement relative to the neighboring molecules in the crystal. Reactions under such geometrical control can therefore be highly selective, leading sometimes to products and materials otherwise inaccessible.⁷¹ The first to recognize this powerful concept was G. M. J. Schmidt, who in the 1960's articulated the "topochemical" principle, of lattice control over the course of solid-state reactions and stereochemistry of the products.⁷² Thus, in their seminal study of photochemical dimerizations of trans-cinnamic acid derivatives, Schmidt and coworkers found correlations between their orientations in the starting crystals, and their solid-state reactivity, as well as stereochemistry of the resulting dimers (Scheme 2.1).



X = H, OH, Cl, NO₂, CH₃, OCH₃, OC₂H₅, OPr

R = OH, OCH₃, OC₆H₅, NH₂, C₆H₅

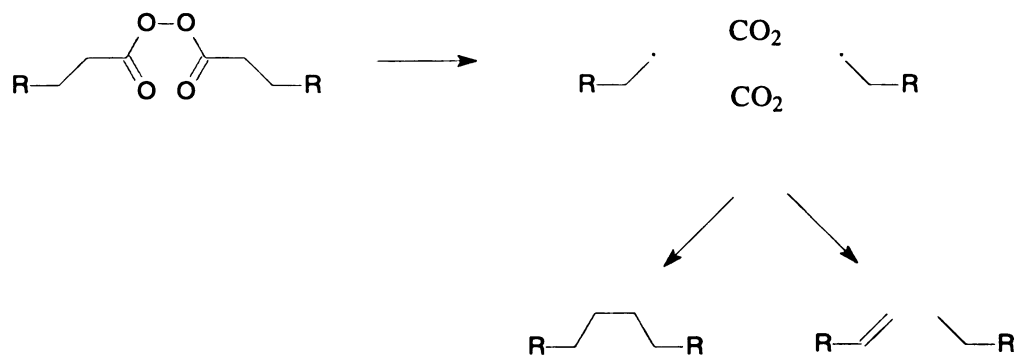
Scheme 2.1

The monomers may have three major types of crystal packings. In the α arrangement, the molecules are anti-parallel, with 3.6-4.2 Å between the double bonds, and yield almost exclusively centrosymmetric dimers. In contrast, dimers with a plane of symmetry are obtained by the irradiation of the β -type crystals, in which the double bonds are oriented in a parallel fashion, approximately 3.8-4.2 Å apart. Finally, the γ -type polymorphs, with distances between the closest double bonds greater than 4.8 Å, are photochemically inert in the solid-state. This study made Schmidt soon realize the imperative of understanding the rules governing the packing of molecules in crystals, which led to the emergence of crystal engineering.⁷²

According to Schmidt, for a reaction to be topochemical, it has to proceed with a minimum of atomic and molecular movement; otherwise, disorganization of the crystalline medium due to excessive molecular motions may lead to loss of lattice control over the reaction. Later, Cohen introduced a new concept, that of the “reaction cavity”, defined as the space occupied by the atoms directly involved in the solid-state reaction.⁷³ The topochemical principle can be thus reformulated to state that those reactions which proceed under lattice control occur with minimal distortion of the reaction cavity, and that formation or removal of any empty space within the cavity should be energetically unfavorable, since they imply substantial changes in attractive and repulsive forces. Gavezzotti quantified this theory by proposing precise methods for molecular volume calculation, and concluded that a prerequisite for crystal reactivity is the availability of free space around the reaction site.⁷⁴

Topochemical control was also noticed in the solid state decomposition of diacyl peroxides which photolyze to a pair of CO₂ molecules and a pair of free radicals (Scheme

2.2).⁷⁵ While in solution or melt the fate of the radicals is complex and variable and mixtures of products are obtained, photolysis of single crystals give radical-radical coupling products in high yields.



Scheme 2.2

At the first inspection one might conclude that the topochemical least-motion principle is obeyed since radical coupling predominates in the solid state over disproportionation, which requires that one radical abstract a hydrogen atom from the more distant second carbon in the other radical. However, low temperature EPR studies of the generated radical pair suggest that the reaction does not follow a least-motion path, as the reactive carbons initially move apart before they finally combine. This behavior appears to be caused by the two CO₂ molecules resulting from photolysis, which cannot be accommodated in the reaction cavity. The pressure created by the forming CO₂ was estimated around 20 kbar from its asymmetric stretching mode, which is sensitive to pressure. The conclusion is that in such gas evolving systems, where there is no possibility that the product molecules would fit into the reaction cavity, the developed

stress could control the course of the reaction. Recently, a unified theoretical formulation of solid-state reactivity, that can be applied to thermal-, light-, and shock-induced reactions as well has been proposed, in which the reaction cavity and steric compression concepts have been quantified.⁷⁶

There are two main mechanisms that may operate in organic solid-state transformations.⁷⁷ The first one, the homogeneous mechanism, involves conversion of "A" molecules of the starting material in the initial crystal lattice, to "B" molecules of the product, with the B molecules remaining in the same region of the lattice initially occupied by the A molecules. A single crystal of the reactant will thus pass through a continuous series of solid solutions, first of B in A and later of A in B, before becoming a single crystal of the product. Minimal structural change is required on going from A to B so that the crystal lattices of reactant and product, which should have very close geometrical parameters, can accommodate each other in the process of conversion. These severe requirements make candidates for the homogeneous mechanism extremely rare. In most of the solid-state reactions the product is structurally incompatible with the reactant lattice, and therefore a heterogeneous mechanism operates, with initiation of reaction at nucleation sites frequently located at crystal imperfections or surfaces, and subsequent growth of the product phase, which usually does not retain the three-dimensional periodicity of the initial crystal, and appears amorphous or polycrystalline. Even under these conditions, the process can be topochemical; a great number of solid-state reactions have shown that there is no strong correlation between the chemical specificity and the long-range crystallographic order of the product phase.⁷⁸

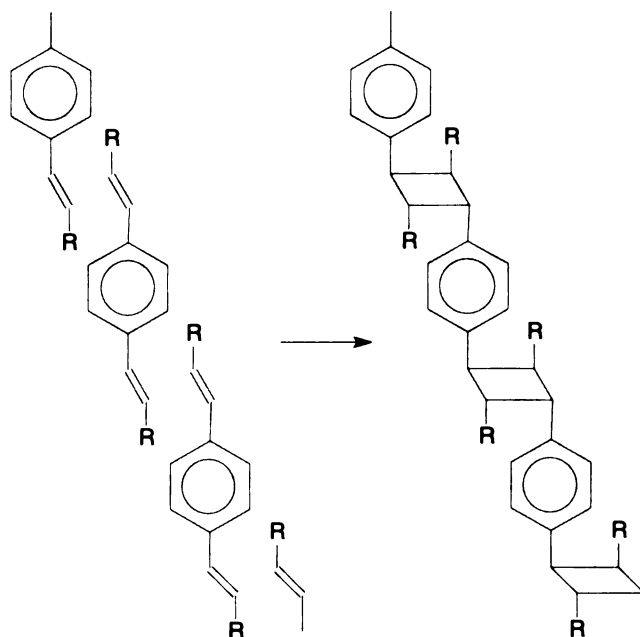
Another term frequently used by solid-state chemists is “topotaxy”, which is concerned with the relationship between the three-dimensional crystallographic orientation of reactants and products.⁷⁹ In a “topotactic” transformation, the lattice parameters, crystal system, and space group of the product are closely related to those of the reactant. The solid-state process does not necessarily have to be homogeneous, as nucleation of the crystalline product at the surface of the initial crystal can lead to oriented growth under the influence of the surface tension, resulting in coincidence between certain crystallographic axes of reactant and product phases. It thus follows that while topochemical control often leads to topotaxy, the latter phenomenon may be completely independent from the occurrence of a topochemical process.

A potential problem in solid-state organic chemistry is that the intermolecular forces in organic crystals are predominantly of van der Waals or hydrogen bonding type, which are significantly weaker than typical covalent bonds. As a consequence, melting or sublimation may occur very often in thermally activated reactions, before any detectable chemical transformation. Another possible complication is the formation of liquid products. It is therefore imperative that these possibilities be ruled out any time the exertion of topochemical control is invoked.

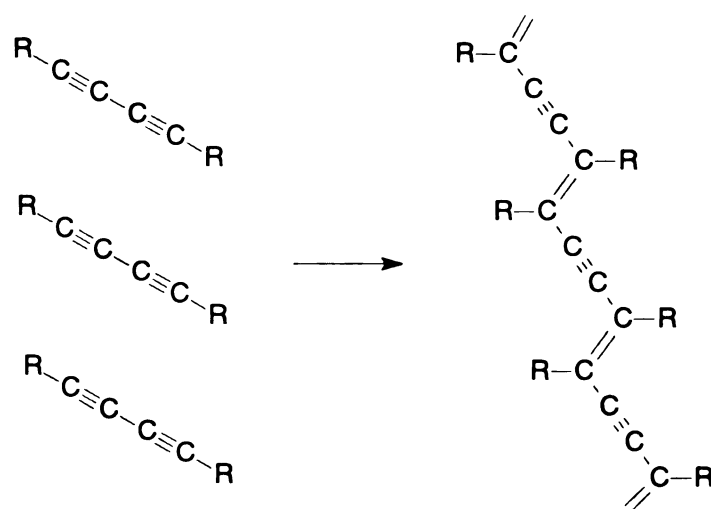
2.1. Topochemical Polymerizations and Polycondensations

In ordinary solid-state polymerizations there is essentially no lattice control over the polymer chain growth, apparently due to the considerable movement that the monomers must undergo to add to the end of the growing chain.⁸⁰ This is the result of the

significant shrinkage that occurs when going from van der Waals distances between molecules to much shorter covalent bonds, leading to a growing gap between the chain end and the next reacting monomer. This means that ultimately the monomer can add to the polymer only by breaking away from the lattice, resulting in the loss of stereoregularity and crystallinity. Hirshfeld and Schmidt argued that this effect could be avoided in crystals of carefully designed bifunctional monomers.⁸¹ It was predicted that in suitable structures, the monomer would attach itself to its neighbor via a rotation about its center of mass, so that the polymerization would not require diffusive motion, and lattice control would be maintained throughout the transformation. Realization of this model has indeed been achieved in divinyl arenes⁸² (Scheme 2.3) and diacetylenes⁷⁹ (Scheme 2.4), which can photopolymerize topochemically, leading to highly stereoregular, sometimes crystalline polymers.



Scheme 2.3

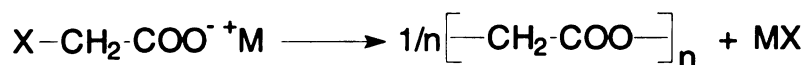


Scheme 2.4

These topochemical polymerizations may proceed either homogeneously or heterogeneously.⁷⁹ In homogeneous cases the polymer is formed as a solid solution, which grows from points randomly distributed throughout the parent crystal. The product is thus isomorphous with the monomer crystal. This mechanism usually operates in the polymerization of diacetylenes, and in some cases, single-crystal to single-crystal transformations can be achieved. In the case of [2+2] photopolymerizations, heterogeneous mechanisms dominate; the reaction starts preferentially at defect sites of the monomer crystal, with nucleation of the polymer phase. The parent crystal typically shatters into a polycrystalline aggregate, or, sometimes, an amorphous phase. Once the crystal is broken, polymerization continues into the crystallites, usually starting from the edges. Comparison of the monomer and polymer crystals showed that in many cases the space group does not change and the modification of the unit cell volume during

polymerization is very small, implying topotactic control. Moreover, when the initial diolefin crystallized in a chiral space group, an absolute asymmetric synthesis with the formation of an optically active polymer could be achieved.⁸³

An interesting solid-state thermal polycondensation occurs in salts of halogenoacetic acids, leading to polyglycolide, the simplest possible polyester (Scheme 2.5).⁸⁴



X = Cl, Br, I;

M = Na, K, Rb, NH₄, Ag

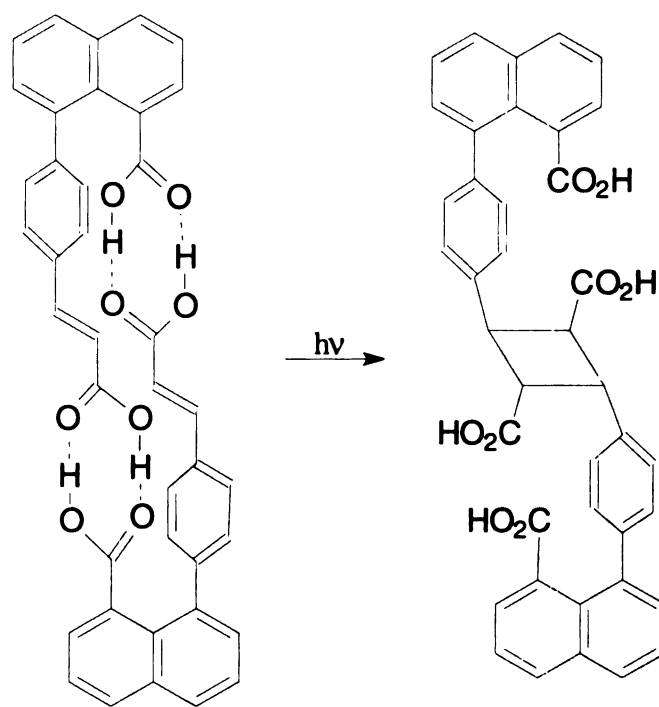
Scheme 2.5

Interestingly, the metal halide byproducts are deposited as small cubic crystallites in the polyglycolide matrix, implying long-range diffusion of the formed M⁺X⁻ ion pairs in the crystals. The salts can be subsequently washed out with water, to leave a highly microporous polymer. Crystal structure analysis in the case of silver chloroacetate indicated that this polycondensation is topochemical, and is driven by the very short Ag-Cl interatomic distance of 2.903 Å, which is only 0.128 Å longer than in silver chloride.⁸⁵ The observed interatomic distance between the reacting carbon and oxygen atoms of 3.25 Å is also within the range expected for high solid-state reactivity.

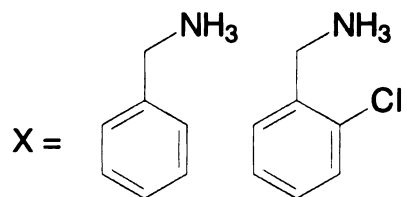
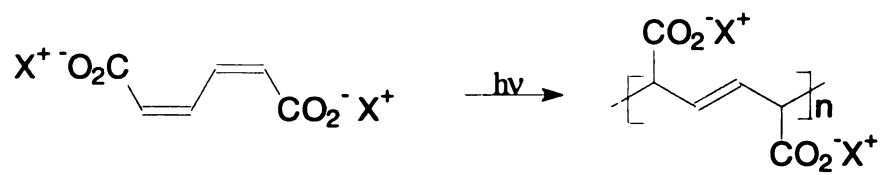
2.2. Hydrogen Bonding Assisted Topochemical Reactions

The topochemical principle is a very powerful concept that can be applied to the assembly of both small molecules and extended covalent networks with controlled topologies. However, the major disadvantage of this approach is the lack of solid-state reactivity in many systems due to misalignment of the reactive functionalities in their crystals. This obstacle can, however, be eliminated by successful application of crystal engineering in designing solid-state reactive molecular solids. Schmidt and Leiserowitz noted as early as 1969 that the probability of α,β -unsaturated amides to crystallize in photodimerizable structures was very high, due to favorable hydrogen-bonded, predictable packings.⁸⁶ Alternatively, they could control crystal packing by introduction of stackable dichlorophenyl units, or by co-crystallization with mercuric chloride, which were shown to be capable of imposing 4 Å periodic arrangements.⁷²

More recently, Feldman and coworkers used the predictable hydrogen bonding dimer motif of the carboxylic acid functionality to properly align olefins for photodimerization (Scheme 2.6).⁸⁷ This example is a nice illustration of using hydrogen bonds as preorganizing interactions, which can be subsequently reinforced by robust covalent linkages. While in this case a discrete dimer was assembled, extension of this strategy to higher-dimensional systems by appropriate design can be easily imagined.⁸⁸ A similar approach was used by Matsumoto et al. for the topochemical photopolymerization of benzylammonium salts of butadiene-1,4-dicarboxylic acid (Scheme 2.7).⁸⁹

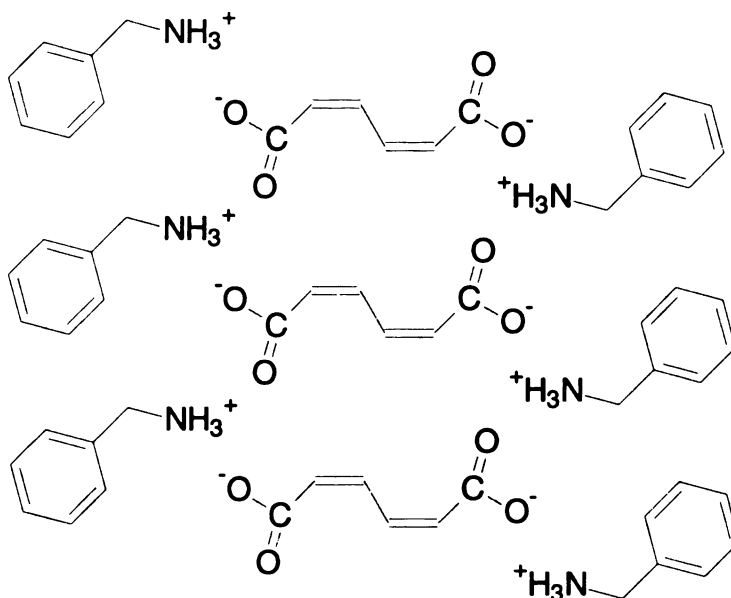


Scheme 2.6



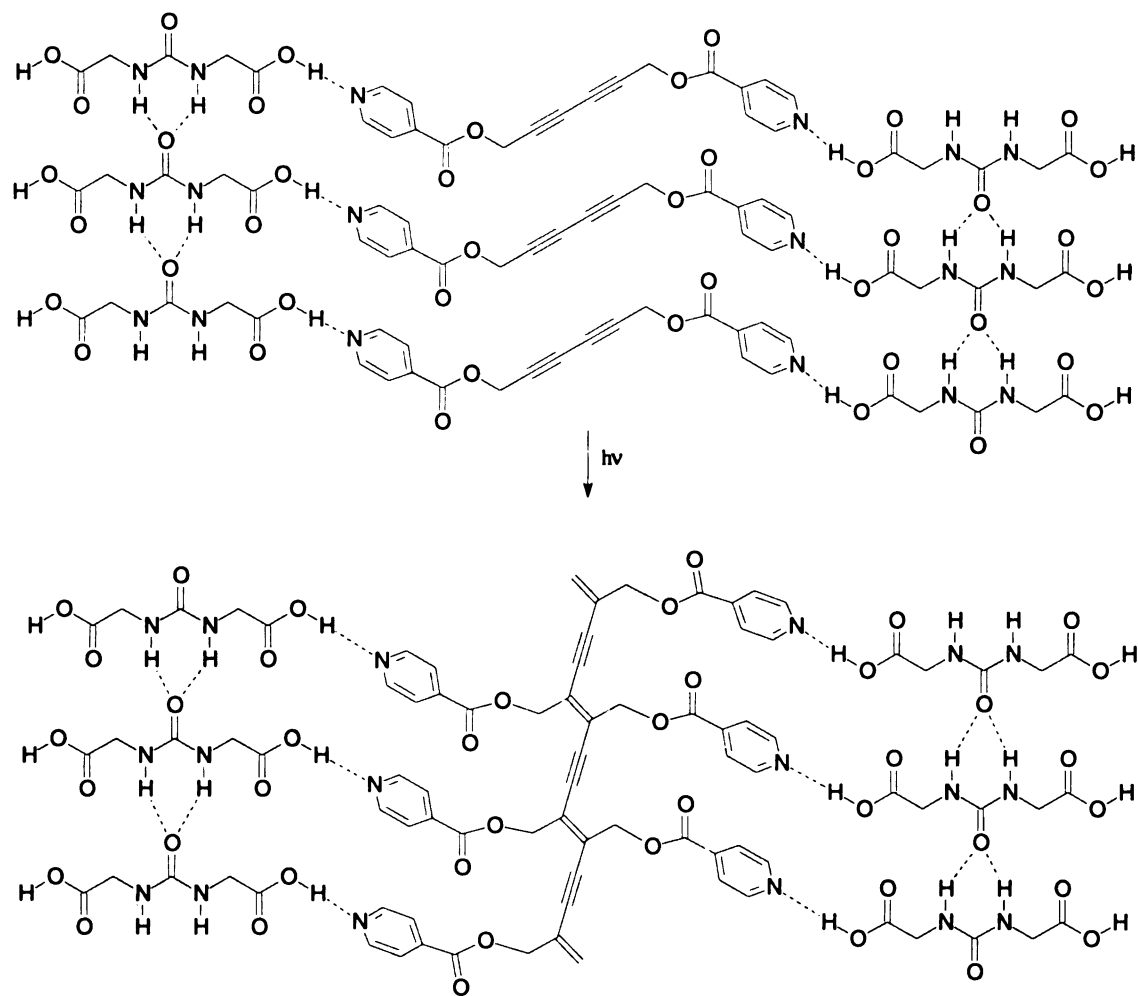
Scheme 2.7

Hydrogen bonding between the NH_3^+ and COO^- groups enforce the required orientation of the butadiene units for solid-state polymerization in this case (Scheme 2.8).

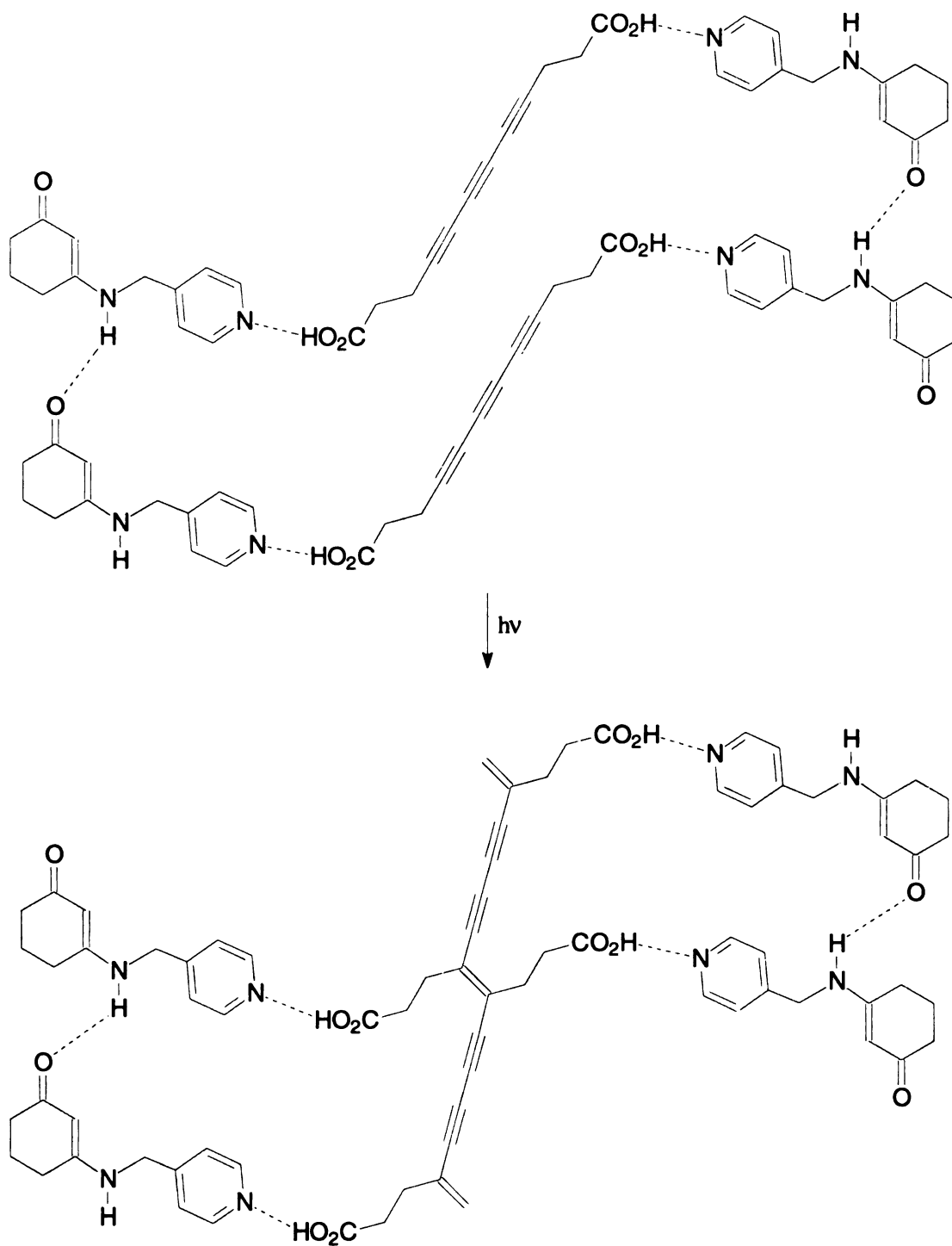


Scheme 2.8

The reliable self-assembly of urea derivatives into hydrogen-bonded α -networks was exploited by Lauher and Fowler to preorganize diacetylenes for solid-state topochemical photopolymerization.⁹⁰ Thus, by co-crystallization of a pyridyl-substituted diacetylene with dicarboxylurea, an anticipated β -network could be assembled, in which the diacetylene units were forcibly aligned into the desired solid-state reactive arrangement (Scheme 2.9). Using a similar strategy, they were recently able to align a triacetylene for solid-state polymerization, which led to an unprecedented 1,6-polytriacetylene via a single-crystal to single-crystal reaction (Scheme 2.10).⁹¹



Scheme 2.9



Scheme 2.10

Besides hydrogen bonding, other noncovalent associations such as phenyl-perfluorophenyl stacking interactions have also been explored as preorganizing elements in the solid-state topochemical polymerization of diacetylenes⁹² and diolefins.⁹³

2.3. Kinetics of Solid-State Decompositions

In this section the focus will be mainly on organic solids which decompose to yield solid and gaseous products,⁹⁴ as also expected from dihydrogen-bonded systems upon heating in the solid-state. This can be represented as:



Decomposition may be initiated by heat, light, or ionizing radiations. The stability toward thermal decomposition may be affected by the previous history of the sample, presence of impurities, aging, sample size, or the nature and pressure of gas atmosphere above the solid.⁹⁵ The rate of the process can be most conveniently followed by measuring the pressure developed in a constant volume system or by using a thermobalance to determine the weight loss under isothermal conditions, although XRD or spectroscopic methods can also be used.^{94b} The fractional decomposition α vs. time curves are typically sigmoid in shape, indicating an autocatalytic reaction. This pattern is almost universally associated with the initiation of reaction at specific sites followed by the growth of nuclei, with the reaction mostly confined to the product/reactant interface. The kinetics is therefore controlled by the number of nuclei present and the total area of the expanding interface. After the inflection point, the growing nuclei start to coalesce, slowing the decomposition rate as the interfacial area decreases, until the reaction eventually stops.

Different kinetic models with their corresponding equations have been elaborated to account for various solid-state decomposition mechanisms.⁹⁴ Among them, the most common are the Avrami-Erofeev equation (1) and the phase boundary model (2):

$$[-\ln(1 - \alpha)]^{1/n} = kt; \quad n = 1-4 \quad (1)$$

$$1 - (1 - \alpha)^{1/n} = kt; \quad n = 1-3 \quad (2)$$

The first one corresponds to a nucleation and growth mechanism, while the second is associated with an inward advancement of the reaction interface from the crystal's edges. The exponent n in Eq. 1 is given by $\beta + \lambda$, where β is the number of steps involved in nucleus formation (typically $\beta = 0$ or 1 , the former corresponding to spontaneous nucleation), and λ is the dimensionality of the nuclei growth.^{94b}

For some decompositions the acceleratory region can be described by an exponential expression (3).^{94a}

$$\alpha = Ce^{-kt} \quad (3)$$

Due to molecular volume change, the formation of product molecules induces strain in the crystal, which produces cracks forming fresh surfaces on which decomposition can occur. The reaction will therefore spread down these crevices into the crystal. Decomposition on these surfaces produces additional strains and hence further cracking and a type of chain branching process thus develops.^{94c} This mechanism can be mathematically described using the Prout-Tompkins equation (4):

$$\ln [\alpha/(1-\alpha)] = kt \quad (4)$$

It should be pointed out, however, that very often there is no single model that can acceptably describe the whole conversion range, as different mechanisms may operate for different stages of decomposition.

A substantial autocatalytic effect has been also observed for some single-phase solid-state polymerizations, which could be explained quantitatively by a strain-dependent rate of chain initiation and propagation model.⁹⁶ Thus, it was demonstrated that the conversion-time curves display a more pronounced sigmoid character as the differences in unit cell parameters between the monomers and polymers increase.

The rate constants obtained from solid-state reactions usually obey the Arrhenius equation. However, special care must be exercised when interpreting the obtained activation parameters, since decompositions of solids are complex processes involving not only chemical steps such as breaking or formation of bonds, but also physical transformations such as phase transitions, diffusion and desorption of gaseous products, and heat transfer. Therefore, chemically specific techniques may be necessary, to obtain mechanistic details at the molecular level. Another important issue is whether the Arrhenius equation has any physical meaning in the solid-state, as its theoretical foundation has been established in the context of collision theory in the gas phase. However, even if the Maxwell-Boltzmann energy distribution is not applicable to the immobilized constituents of a solid, it was demonstrated that energy-distribution functions of similar form (Fermi-Dirac or Bose-Einstein) also give rise to an Arrhenius-type equation.⁹⁷ Thus, its application to solid-state transformations is justifiable not only in terms of a useful empirical parametrization, but is also supported by a rigorous theoretical foundation.

An alternative approach for the kinetic analysis of solid-state reactions is the isoconversional method, applied under isothermal or nonisothermal conditions.⁹⁸ This strategy allows the estimation of the activation energy without assuming a particular

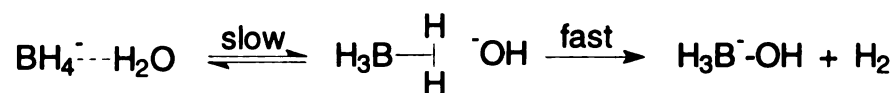
reaction model, and is particularly convenient for analysis of nonisothermal data such as that obtained from DSC and TGA experiments. Under isothermal regime, the activation energy at a particular conversion, E_{α} , can be evaluated using Equation 5:^{98b}

$$-\ln t_{\alpha,i} = \ln[A/g(\alpha)] - E_{\alpha}/RT_i \quad (5)$$

While in some cases it can unmask the complexity of the solid-state process studied, the major disadvantage of this method, however, is that the obtained activation energy varies significantly with the extent of reaction, which complicates the interpretation of the kinetic data.

3. Topochemical Assembly of Covalent Materials Using Dihydrogen Bonding

As illustrated in Chapter 1, many studies regarding the dynamics of dihydrogen-bonded systems in solution have demonstrated that proton transfer from the acidic AH partners to the transition metal hydrides MH, along the H...H bonds, generally leads to η^2 -H₂ non-classical complexes, which subsequently eliminate hydrogen upon heating, with the formation of covalent M-A bonds (Scheme 1.2). An analogous process appears to occur in the case of the borohydride anion. In aqueous solutions, BH₄⁻ is very likely dihydrogen-bonded to H₂O, as suggested by the crystal structure of NaBH₄·2H₂O,¹¹ as well as theoretical and experimental studies by Epstein et al.¹⁰ Under neutral or acidic conditions, borohydrides undergo hydrolysis to boric acid (B(OH)₃), for which the established mechanism involves slow proton transfer resulting in a BH₅ intermediate, followed by fast H₂ loss and B-O bond formation (Scheme 3.1).⁹⁹ Activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 20.6 ± 1 kcal/mol and -22.3 ± 3 eu were measured for the neutral hydrolysis, while under acidic conditions the corresponding obtained values were 8.0 ± 1 kcal/mol and -3 ± 3 eu, respectively.¹⁰⁰ The structure of BH₅, as deduced by theoretical calculations, is best described as an almost planar BH₃ molecule, loosely coordinated by H₂.¹⁰¹



Scheme 3.1

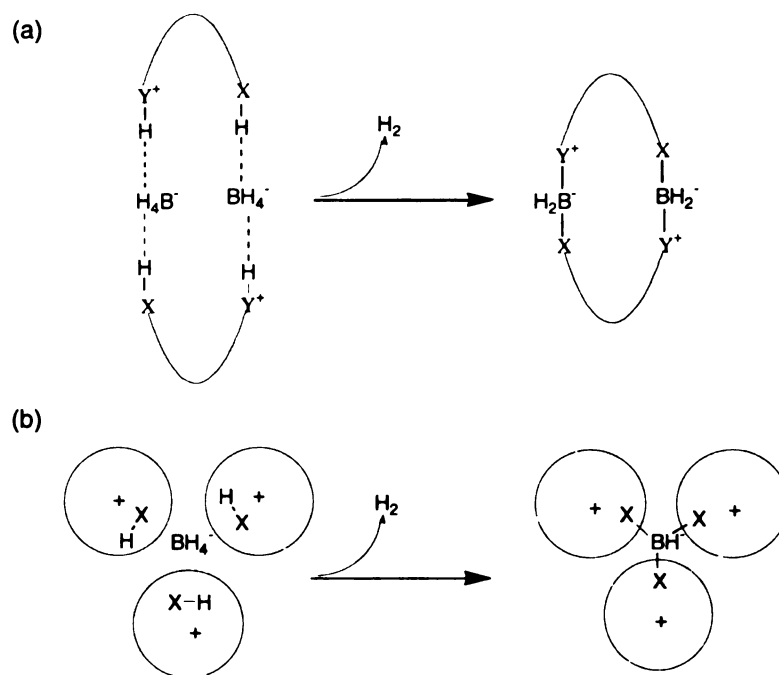
Theoretical work by Elguero et al. indicates that H₂ generation from dihydrogen-bonded borohydrides can also be induced by the internal forces within a crystal.¹⁰² All these premises, together with the established ability of borohydrides to self-assemble into extended dihydrogen-bonded networks, suggest that A-H...H-B dihydrogen bonds could be employed in topochemical assembly of covalent materials. Such weak H...H interactions, in principle, may be used to organize and hold a structure's form while it is more firmly fastened together by A-B bond formation, transferring thus the initial order from the starting crystal to the newly formed covalent frame. This strategy makes dihydrogen bonding a potentially powerful tool for rational assembly of new covalent crystalline materials with controlled structures and properties.

In the topochemical transformation outlined above, the initial H-bond arrangement should determine the final covalent structure. However, when going from the A-H...H-B interaction to a covalent A-B bond there is approximately a 1.5-2 Å change in distance between A and B. This is a considerable shrinkage, and if it were cumulative in the reaction direction, it would lead to an increasing gap between the growing covalent network and the unconverted dihydrogen-bonded molecular units as the decomposition advanced, with eventual loss of lattice control over the reaction. Even under these circumstances, however, the transformation may still be topochemical, as demonstrated by the solid-state conversion of cyclotrigallazane into nanocrystalline gallium nitride reported by Gladfelter et al.⁶⁸, which is accompanied by 62.9% shrinkage of the unit cell. The price to pay was the initial loss of crystallinity and the consequent requirement for high annealing temperatures to restore it. Although this thermal treatment

had no detrimental effect upon the robust GaN product, more delicate structures would not tolerate such high temperatures, limiting the general applicability of this approach.

A low temperature procedure for topochemical dihydrogen to covalent bonding transformations would allow the extension of this strategy into the structurally more diverse domain of organic materials. Like many solid-state processes, this reaction includes two threats to the crystalline order: (a) geometry change upon bond reorganization, and (b) gas generation and diffusion within the lattice. Clearly, careful design of the starting dihydrogen-bonded networks is necessary in order to meet these challenges. Success, however, would mean that the well-developed tools of molecular synthesis could now be applied to the rational construction of crystalline covalent solids with desired structures and functions.

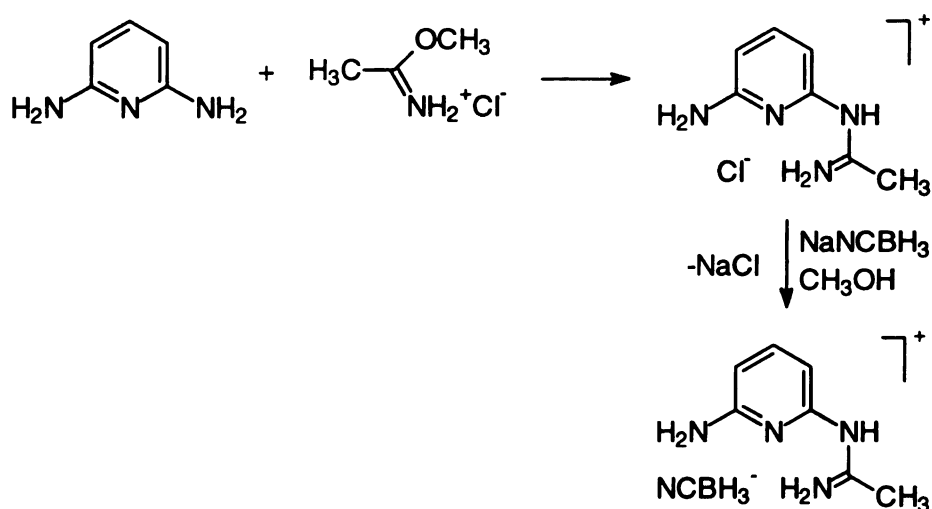
This work involves two strategies to address this problem: (a) design of cations to form closed loops in coordination with hydride-bearing anions, in which case the lattice distortion would not be cumulative, and (b) selection of globular cations large enough that their close packing determines the lattice parameters, with the hydridic anions fitting into the interstitial holes, in which bond formation via flexible arms would induce minimal change in the unit cell (Scheme 3.2).¹⁰³ A dividend of this latter strategy is that the anticipated looseness of the lattice should allow the released H₂ to diffuse readily through and out of the crystal.



Scheme 3.2

3.1. Results and Discussion

***N*-[2-(6-Aminopyridyl)]-Acetamidine (NAPA) Cyanoborohydride: A Closed Loop Dihydrogen-Bonded Structure by Design.**¹⁰³ NAPA H₃BCN (**44**) was synthesized (Scheme 3.3) to explore the prospect of convergent coordination in closed loops, which appeared as a likely possibility due to the bent geometry of the aminopyridyl-acetamidine unit. The cyanoborohydride anion was chosen as the hydridic partner because of its enhanced stability toward acidic substrates relative to BH₄⁻,^{101c} which was decomposed instantaneously in solution by the NAPA cation. The white crystalline compound melts at 119-120 °C with decomposition and gas evolution. The ¹H, ¹³C, and ¹¹B NMR, as well as IR spectra confirmed its structure.



Scheme 3.3

Figure 3.1 shows the X-ray crystal structure for **44**. There are two independent centrosymmetric (NAPA H₃BCN)₂ dimers in the unit cell, each of them exhibiting close H-H contacts: 1.98, 2.12, 2.26 Å, and 2.04, 2.09, 2.31 Å, respectively. Applying the corrections for the N-H and B-H bonds that appear too short from X-ray compared to typical literature values, these H-H contacts become 0.1-0.15 Å shorter. This is well below the 2.4 Å van der Waals contact radius, implying strong and specific interactions. The NH...H-B angles are strongly bent, ranging between 91.6° and 126.3°, with an average of 108.2°, while the N-H...HB angles are larger (range 148.1 - 175.6°; average 158.5°), as expected for dihydrogen bonds. It thus appears that despite the less negative charge on the hydridic hydrogens (-0.18 vs. -0.27 by Mulliken population analysis for MP2/6-311++G** wavefunctions), the NCBH₃⁻ ion is capable of strong dihydrogen bonding, comparable to that of the BH₄⁻ ion in this case, owing to the increased acidity of the proton donor partner. More important, the structure of this very first attempt showed two independent occurrences of the intended closed loop packing, with its potential for topochemical control.

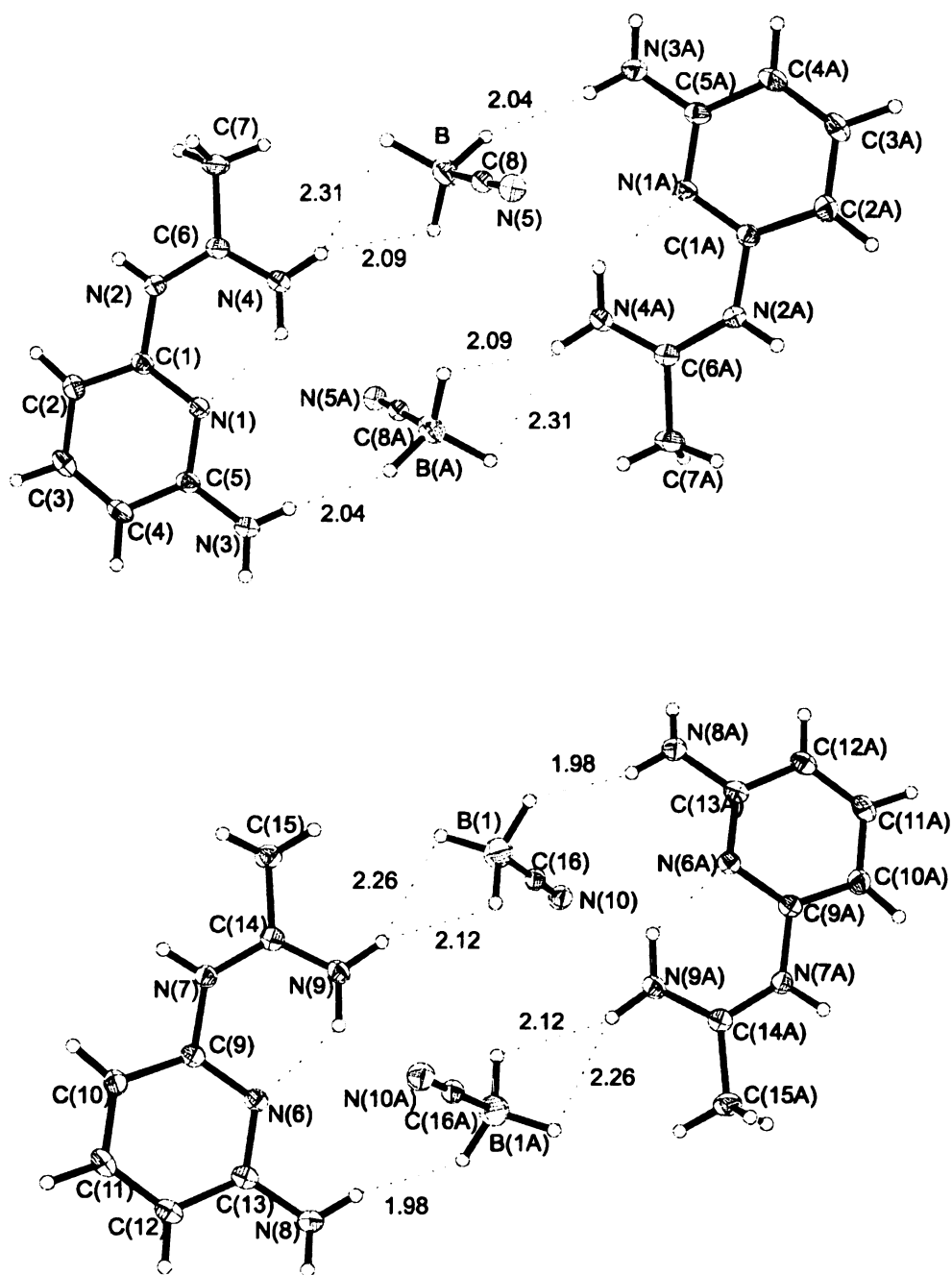
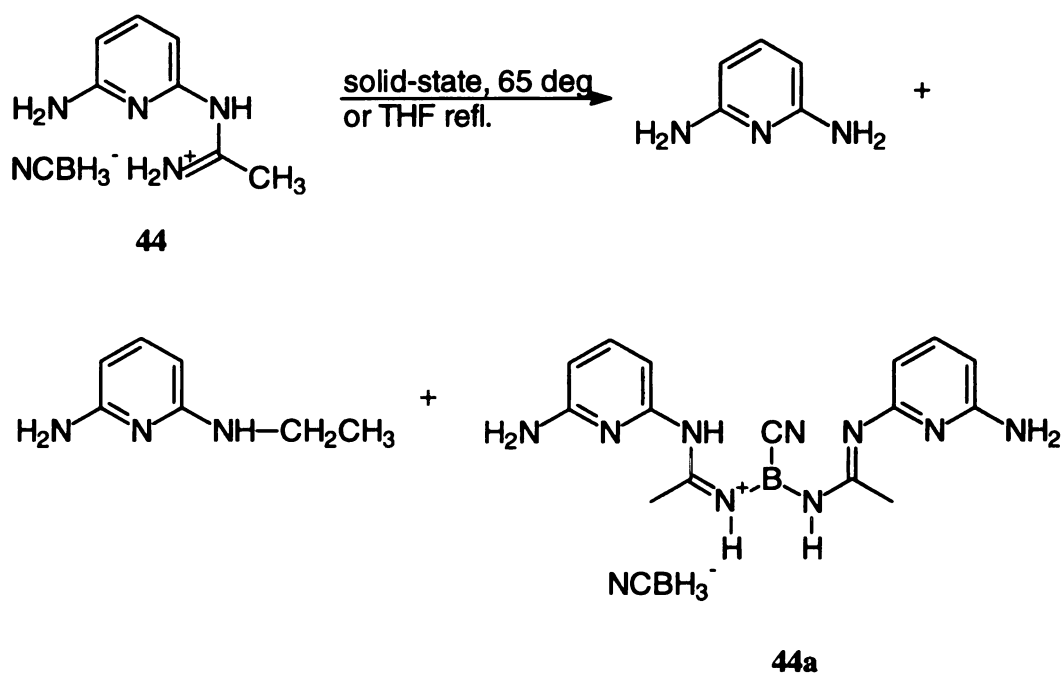


Figure 3.1. X-Ray Crystal Structure of NAPA H₃BCN showing the H...H contacts in Å.

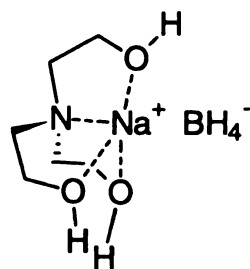
Decomposition in both solid and solution unfortunately led to complex mixtures (Scheme 3.4) via the unwanted reduction of the amidine group by the cyanoborohydride, which accounts for the majority of the decomposition products identified by MS, ^1H , ^{13}C and ^{11}B NMR. Although the decomposition product ratios were slightly different in solid state and solution, we could not attribute that result to topochemical control, since the solid state reaction occurred with partial liquefaction due to the low melting point of some of the products, relative to the temperature required for decomposition ($\sim 65^\circ\text{C}$).



Scheme 3.4

Despite the lack of observable topochemical control, this system demonstrated the ability of NCBH_3^- to form dihydrogen bonds and showed that the closed loop coordination is a viable packing arrangement that can be readily designed into dihydrogen-bonded systems. Additionally, another critical design feature for the next dihydrogen-bonded systems became apparent: their melting point, which should be sufficiently high to allow the decomposition to be carried out in the solid.

Topochemical Control by Dihydrogen Bonding. Structure and Reactivity of $\text{NaBH}_4 \cdot \text{TEA}$ (45).¹⁰³ The complex of NaBH_4 with triethanolamine (TEA) was synthesized as a candidate for the globular cation strategy.



45

The complex precipitated from a stirred mixture of NaBH_4 and TEA in THF as a white crystalline compound, which melts at 107-108 °C with decomposition and gas evolution. The X-ray powder diffraction pattern of the complex is unique and confirms the absence of NaBH_4 . The ^{11}B and ^{23}Na solid state MAS NMR chemical shifts are -47.9 and -9.9 ppm respectively, 2.5 and 6.1 ppm downfield relative to sodium borohydride, indicating different environments for the BH_4^- and Na^+ ions. However, the B-H stretching vibration frequency for **45** (2288 cm^{-1}) is almost identical with the corresponding value in NaBH_4 (2291 cm^{-1}). The X-ray crystal structure is shown in Figure 3.2.

Each Na^+ is hexacoordinated by the N and two O atoms from a TEA molecule and by three O atoms from the two neighboring TEA molecules, forming $\text{TEA} \cdot \text{Na}^+$ linear chains (Figure 3.2a). Two O atoms from each TEA molecule are shared by two adjacent Na^+ cations, but the third oxygen only coordinates the next Na^+ in the chain. Thus, **45** is unlike the previously reported structures of TEA complexes where each cation was complexed by all four heteroatoms from a given TEA molecule.¹⁰⁴ Multiple dihydrogen bonds connect the chains via the BH_4^- anions, giving rise to extended two-dimensional layers (Figure 3.2b). Each BH_4^- H-bonds with two OH groups in one chain and one OH group from the next chain in a total of 5 dihydrogen bonds. The H-H contacts from the three different OH sites are 1.94, 1.93 and 2.12 Å, and 2.16 and 2.13 Å in distance respectively, the latter two being bifurcated H-bonds. Again, typical corrections for O-H and B-H bond lengths lead to H-H distances which are 0.15-0.2 Å shorter. The $\text{OH} \cdots \text{H-B}$ angles vary between 91.8 and 111.7° (average 98.0°) while the $\text{O-H} \cdots \text{HB}$ angles range between 143.9 and 166.7° (average 157.0°). There is no conventional H-bonding; instead all the hydroxylic protons point to the interchain space to form dihydrogen bonds with the borohydrides, demonstrating the importance of these interactions in defining the crystal packing. However, an important driving force for the formation of **45** must be the complexation of Na^+ by TEA, since no complex was formed with $(\text{CH}_3)_4\text{NBH}_4$ or KBH_4 .

Solid-state decomposition of $\text{NaBH}_4 \cdot \text{TEA}$ at 82 °C under Ar or open atmosphere for 30-58 days resulted in a loss of 3 moles of H_2 for each mole of **45**, as indicated by the H⁺ content of the initial complex and final decomposed material. Attempts to use higher decomposition temperatures induced melting. The rate of decomposition seems to be affected by different factors such as sample size, humidity, or the nature or pressure of

gas atmosphere above the solid, which is characteristic for many solid-state reactions.⁹⁵ Thus, decomposition is slower under vacuum than under Ar, and it is considerably faster in open atmosphere, probably due to the presence of humidity. The resulting white solid is insoluble in common organic solvents and it does not melt up to 300 °C, suggesting a polymeric structure. Its ¹¹B solid state MAS NMR shows a single peak at $\delta = -7.1$ ppm. X-Ray powder diffraction of the same material exhibits only a semi-amorphous phase with a broad peak at $2\theta = 9.4^\circ$, but no peaks corresponding to NaBH₄ or to the initial complex (Figure 3.3c). Furthermore, the ¹¹B NMR taken after hydrolysis of this material in neutral D₂O showed only traces of BH₄⁻, indicating the virtual absence of this boron species in the solid-state decomposition product. These data, correlated with the hydride content of the decomposed material (one H⁻ left), suggest a trialkoxyborohydride structure for the decomposed material. The B-H stretching frequency is shifted 5 cm⁻¹ relative to the initial complex (from 2288 to 2293 cm⁻¹). This is not a dramatic change, but it is not surprising since the variation of ν_{BH} in the BH_x(OR)_{4-x}⁻ series is generally small.¹⁰⁵ The loss of 3 moles of H₂ is in agreement with the crystal structure of **45**, where each BH₄⁻ is H-bonded to three -OH groups, two from one chain and one from the next chain. This fact suggests a topochemical relationship between the starting and final materials. Additionally, the two OH from the same chain in **45** belong to different adjacent TEA molecules. A topochemical reaction should therefore lead to a two-dimensional, extended covalent structure, and indeed, the peak at $2\theta = 9.4$ in the powder XRD (Figure 3.3c) corresponds to a d spacing of 9.41 Å in a layered structure. This value is very close to the 9.24 Å inter-layer distance in the initial NaBH₄·TEA.

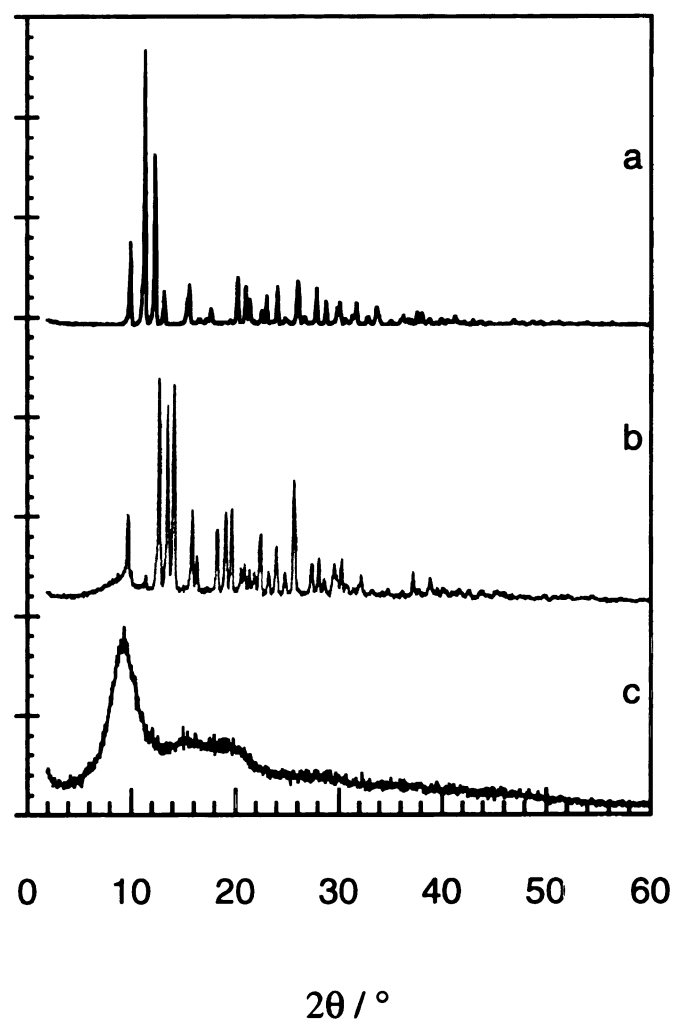


Figure 3.3. Progress of $\text{NaBH}_4\cdot\text{TEA}$ decomposition monitored by X-ray powder diffraction: (a) initial complex; (b) high-temperature polymorph; (c) final decomposed material.

Monitoring the solid-state decomposition by X-ray powder diffraction (Figure 3.3) and H^- analysis revealed a slow (~ 2 weeks), reversible phase transition of the initial complex, prior to any H_2 loss. The IR spectrum for this high temperature polymorph shows the B-H stretching vibration at 2291 cm^{-1} and the ^{11}B solid state MAS NMR spectrum shows a chemical shift at -51.4 ppm . Structure elucidation of this high temperature crystalline intermediate, which somewhat complicates the topochemical relationship between the initial and final structures, would provide useful insight into the intimate mechanism of conversion from the dihydrogen bonding to the covalent networks. Unfortunately, only the low temperature polymorph of **45** has been obtained in recrystallization attempts to date.

An indication for topochemical control is that different reaction products or stereoselectivity are observed in the solid state than in solution or melt. Therefore, we also studied decomposition of **45** in DMSO solution and in the melt. A solution of **45** in DMSO was stirred and heated under Ar at $110\text{ }^\circ\text{C}$ for 55 hours. Like the solid-state decomposition product, the resulting precipitate is insoluble in common organic solvents and does not show any melting below $300\text{ }^\circ\text{C}$. However, H^- analysis and IR showed that this compound has virtually no hydridic hydrogen left. Its ^{11}B solid state MAS NMR chemical shift is slightly different from the solid-state decomposition material ($\delta = -5.0\text{ ppm}$). No other product of decomposition was found by ^{11}B NMR of the mixture resulting from a parallel reaction run in $\text{DMSO-}d_6$, BH_4^- being the only boron species left in solution. On the other hand, when the solid-state decomposition product was stirred in DMSO under the same conditions, no change was observed in the hydridic content or IR spectrum, implying again different products for the solid and solution decompositions.

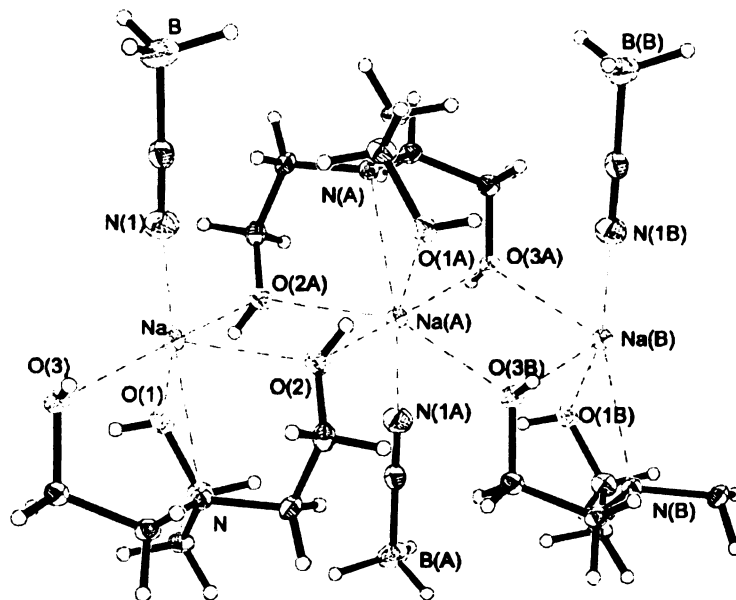
This experiment demonstrated that unlike in the solid state, where the reaction stops at trialkoxyborohydride, decomposition of **45** in solution resulted in complete alcoholysis of BH_4^- to B(OR)_4^- as expected for a reaction in which the $\text{BH}_x(\text{OR})_{4-x}^-$ intermediates, which are more reactive than the starting borohydride, are mobile and therefore susceptible to disproportionation.¹⁰⁶

Similarly, the reaction in the melt at 130 °C under Ar for 2 h resulted in complete alcoholysis of half of the BH_4^- from the initial complex, NaBH_4 being the byproduct of decomposition as indicated by X-ray powder diffraction and ^{11}B NMR. It is remarkable that despite the considerably higher temperature of decomposition in the melt, only 2 moles of H_2 were lost compared to 3 in solid state. The decomposition process in the solid state thus differs significantly from those in solution or melt. These results demonstrate that the particular packing of the molecules in the original crystal, dominated by $\text{H}\cdots\text{H}$ interactions, induced the reaction to take place under topochemical control, leading to an otherwise inaccessible poly-trialkoxymborohydride structure. However, this product showed poor crystallinity, and the reaction times were exasperatingly long due to the relatively low temperature required for decomposition in order to avoid melting.

Influence of the Relative Acidity/Basicity of the Proton/Hydride Partners Upon Solid-State Reactivity of Dihydrogen-Bonded Systems: Structure and Reactivity of $\text{NaNCBH}_3\cdot\text{TEA}$ (46**).**¹⁰³ $\text{NaNCBH}_3\cdot\text{TEA}$ complex was synthesized in order to explore the influence of varying the hydridic donor partner upon the structure and solid-state reactivity of dihydrogen-bonded systems. Due to the smaller negative charge on the hydridic hydrogens, the dihydrogen bonds were expected to make smaller

contributions in defining the solid-state structure and reactivity, compared to the borohydride analog. The complex was crystallized by slow evaporation of a 1:1 triethanolamine- NaNCBH_3 mixture in isopropanol. The X-ray structure is shown in Figure 3.4. The Na^+ cations are heptacoordinated by the four heteroatoms from one TEA molecule, the nitrogen from the cyanoborohydride and two oxygens from neighboring TEAs which bridge adjacent Na^+ cations to form extended chains (Figure 3.4a), crosslinked by dihydrogen bonds. One H from each CNBH_3^- hydrogen bonds to a hydroxylic proton from another chain (Figure 3.4b) with an uncorrected H-H contact distance of 2.16 Å ($\text{OH}\cdots\text{H-B}$ angle = 100.6° ; $\text{O-H}\cdots\text{HB}$ angle = 159.6°), forming a three-dimensional network. There are also $\text{O(1)-H}\cdots\text{O(2)}$ intra-chain conventional H-bonds connecting neighboring TEA molecules. It appears that dihydrogen bonds are less important in the $\text{NaNCBH}_3\cdot\text{TEA}$ crystal packing than in the borohydride analog, with its shorter $\text{H}\cdots\text{H}$ contacts and complete absence of conventional H-bonding. This difference is also reflected in the significantly different solid-state reactivity of the two complexes. While the borohydride complex melted at $107\text{--}108^\circ\text{C}$ with decomposition, the cyanoborohydride analog melts at $85\text{--}86^\circ\text{C}$, and it takes approximately 100 more degrees to finally start decomposing. Thus, close $\text{H}\cdots\text{H}$ contacts do not automatically confer solid-state reactivity; the relative acidity and basicity of the protonic and hydridic partners are also critical. Precise estimates of the basicities of BH_4^- and BH_3CN^- are unavailable, but the bimolecular rate constants for their H_3O^+ -catalyzed hydrolysis are $\sim 10^6$ and 10^{-2} $\text{l/mol} \times \text{sec}$ respectively which may be translated into a pK_B difference of ≥ 8 units.¹⁰⁷

(a)



(b)

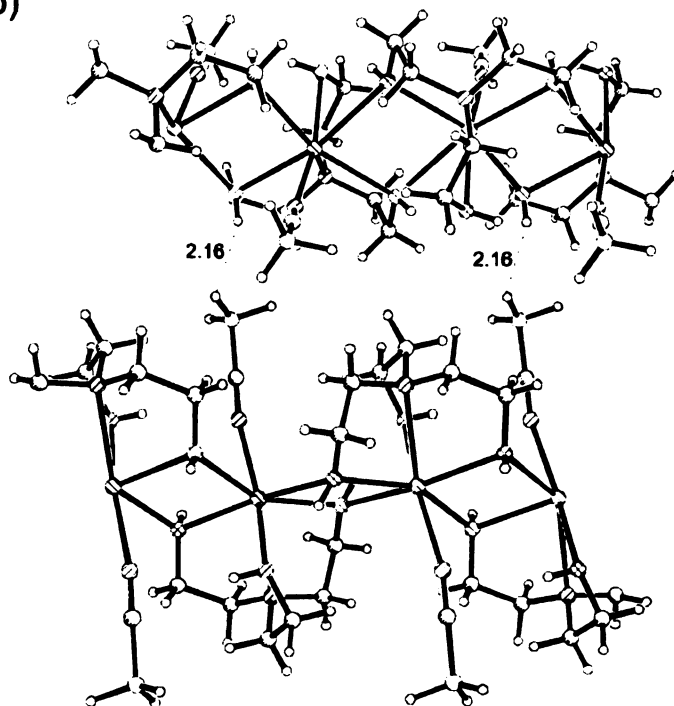


Figure 3.4. X-Ray crystal structure of NaNCBH₃·TEA: (a) coordination of Na⁺; (b) dihydrogen bonds connecting the chains, with H-H contact distances in Å.

Tuning Dihydrogen Bonds: Enhanced Solid-State Reactivity in LiBH₄·TEA

(47).¹⁰⁸ The simplest way to tune the solid-state reactivity in **45** appeared to be the substitution of the Li⁺ cation for Na⁺, which should result in stronger complexation by TEA, thus making the OH sites more acidic, and consequently more reactive. The LiBH₄·TEA complex (**47**) was obtained by slow evaporation of a 1:1 TEA-LiBH₄ mixture in 2-propanol, as a white crystalline compound, which does not melt up to 300 °C. The X-ray crystal structure of **47** is presented in Figure 3.5. 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. Multiple dihydrogen bonds connect the dimers via BH₄⁻ pairs, giving rise to extended ribbons. The dihydrogen bonding network is asymmetrical: one BH₄⁻ H-bonds with three OH groups (O(2'), O(1) and O(3A)) in a total of 6 dihydrogen bonds, while the second BH₄⁻ only H-bonds with two of the remaining OH groups (O(2A') and O(3)) in a total of 4 dihydrogen bonds. The O(1A)H groups are not involved in any dihydrogen bonding; instead they form conventional H-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. 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. All hydrogen atoms were unambiguously located from the difference Fourier map, making these distances sufficiently reliable. The OH...H-B angles range between 75.8 and 106.1° (average 95.0°), while the O-H...HB angles are larger, ranging between 130.0 and 170.7° (average 150.8°).

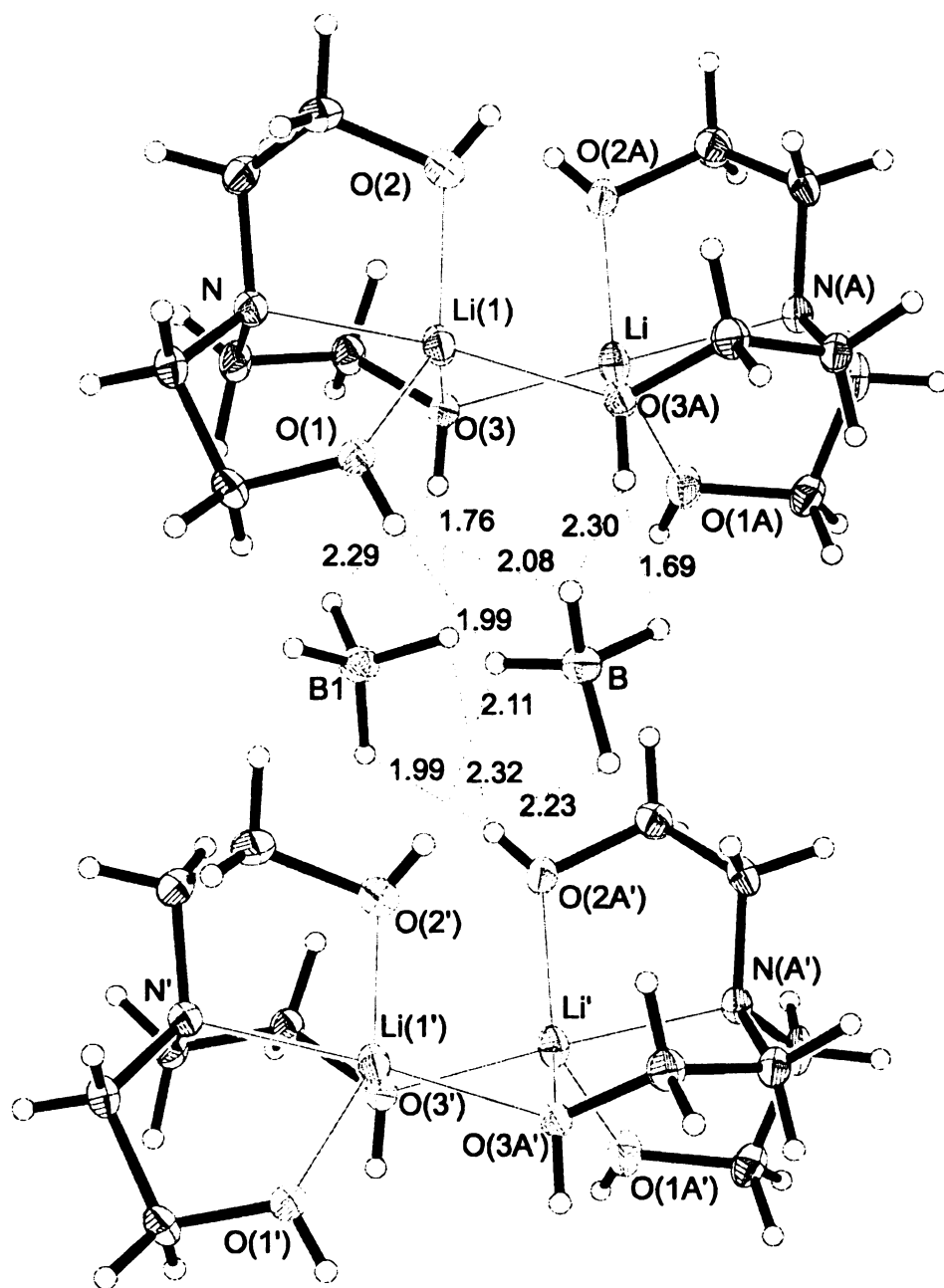


Figure 3.5. X-Ray crystal structure of $\text{LiBH}_4 \cdot \text{TEA}$ showing the $\text{H} \cdots \text{H}$ close contacts in Å.

The shortest dihydrogen bonds are 1.69 and 1.76 Å in distance, which after the normalization of the O-H and B-H bonds become 1.62 and 1.67 Å respectively. These are the shortest H-H distances reported so far for dihydrogen bonds. Notably, both OH groups involved in these two dihydrogen bonds contain bridging O atoms coordinating two Li⁺, 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⁺, leading thus to H-H separations that are significantly longer.

The very short H-H distances and the expected acidity increase of the OH groups due to their complexation of Li⁺ predicted enhanced solid-state reactivity for this system. Indeed, when heated approximately 1 h at 120 °C under Ar, the complex completely decomposed, as indicated by X-ray powder diffraction (Figure 3.6), ¹¹B solid-state MAS NMR and IR spectra of the resulted material. Only about 24 h were necessary for decomposition at 82 °C, the temperature used for the solid-state decomposition of NaBH₄·TEA, which took about 6 weeks. Three moles of H₂ per mole of **47** were lost, as indicated by the H⁺ 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 ¹¹B solid state MAS NMR exhibits a single peak at δ -4.6 ppm, which, together with the H⁺ content, suggests a trialkoxyborohydride structure for the decomposed material. The ν_{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.

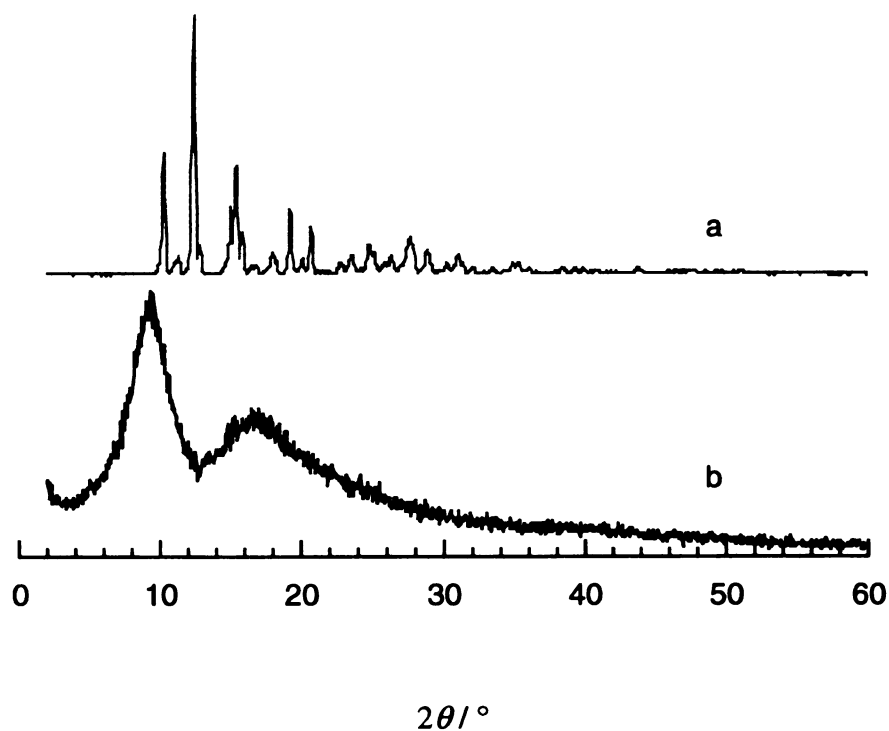
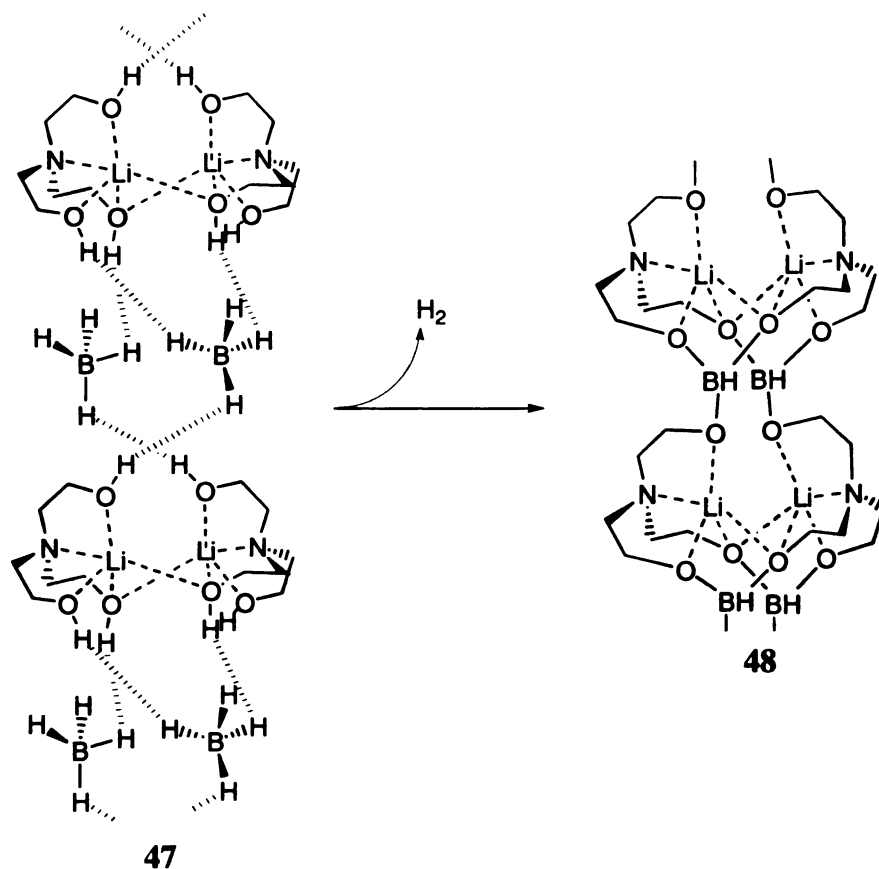


Figure 3.6. X-Ray powder diffraction pattern of $\text{LiBH}_4\cdot\text{TEA}$ (a) and its solid-state decomposition product (b).

The loss of three moles of H_2 points to a topochemical relationship between the final decomposed material and the initial complex, where two BH_4^- and six OH groups are in close proximity due to the crystal packing imposed by the dihydrogen bonding network. Unlike in the $\text{NaBH}_4\cdot\text{TEA}$ 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 (**48**), according to the crystal structure of **47** (Scheme 3.5). However, due to the modest crystallinity of the final material (Figure 3.6b), a definitive knowledge of its structure remains elusive. Using lower temperatures for decomposition (down to 65°C) did not improve the crystallinity of this material.



Scheme 3.5

In direct contrast, decomposition of **47** in DMSO at 120 °C under Ar for 4 days yielded a material with no hydridic hydrogen left as shown by its H⁺ content and IR spectrum. Its ¹¹B solid state MAS NMR chemical shift (-5.9 ppm) is slightly different from the corresponding value in the solid-state decomposition product. In a parallel reaction run in DMSO-d₆, unreacted BH₄⁻ and completely alcoholized B(OR)₄⁻ were the only boron species found by ¹¹B NMR 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 BH₄⁻ and susceptible to disproportionation.¹⁰⁶

It is important to rule out such disproportionation in the solid-state. As depicted in Scheme 3.5, pairs of trialkoxyborohydrides are presumably present in **48**.

Disproportionation into dialkoxyborohydride and borate is therefore conceivable in principle. For instance, in $\text{LiBH}(\text{OCH}_3)_3$, slow disproportionation into $\text{LiBH}_2(\text{OCH}_3)_2$ and $\text{LiB}(\text{OCH}_3)_4$ was observed in THF.^{105a, 109} Table 3.1 presents the experimental ^{11}B NMR chemical shifts for the $\text{BH}_x(\text{OCH}_3)_{4-x}^-$ ($x = 0-4$) anions, for comparison with the experimental data found for **48**. Unfortunately, no NMR data in the literature referring to $\text{BH}_2(\text{OCH}_3)_2^-$ were found. Therefore the ^{11}B NMR chemical shifts for the same series were calculated at the RHF/6-31G* level (Table 3.1), finding good agreement between the experimental^{103, 108, 110} and calculated values for the known $\text{BH}_x(\text{OCH}_3)_{4-x}^-$ anions.

Table 3.1. NMR data for $\text{BH}_x(\text{OCH}_3)_{4-x}^-$, **47**, and **48**.

	^{11}B NMR δ^a (ppm)		^7Li NMR δ^b (ppm)
	calculated	experimental	
BH_4^-	-50.7	-49.7 (solid) ^c -49.5 (solid) ^d	1.5 (solid LiBH_4) ^d
$\text{BH}_3(\text{OCH}_3)^-$	-26.4	-25.1 (THF) ^f	-
$\text{BH}_2(\text{OCH}_3)_2^-$	-12.8	-	-
$\text{BH}(\text{OCH}_3)_3^-$	-10.8	-8.6 (THF) ^f	-
$\text{B}(\text{OCH}_3)_4^-$	-14.9	-15.2 (CH_3OH) ^e -13.0 (THF) ^f	-
47	-	-48.0 (solid) ^d	2.8 (solid) ^d
48 initial	-	-3.9 (solid)	3.1 (solid)
annealed	-	-2.6 (solid)	1.0 (solid)

^a relative to $\text{B}(\text{OCH}_3)_3$. ^b relative to LiCl . ^c reference 103. ^d reference 108. ^e reference 110a. ^f reference 110b.

Compared to these values, however, our decomposed borohydrides exhibit δ values that are consistently shifted downfield. For example, decomposition of **47** or of its Na

analogue in DMSO yielded polymeric borates which showed ^{11}B solid state MAS NMR peaks at -5.2 and -4.3 ppm,^{*} respectively, significantly different from the corresponding values in $\text{B}(\text{OCH}_3)_4^-$. However, for the solid state decomposition product **48** and its Na analogue, δ values of -3.9 and -6.4 ppm,^{*} respectively, were observed, in better agreement with the corresponding experimental value of -8.6 ppm in $\text{BH}(\text{OCH}_3)_3^-$. The only possibilities that can be ruled out unambiguously based on the available data are the presence of $\text{BH}_3(\text{OR})^-$ or BH_4^- in **48**, which would display distinctive chemical shifts around -26 or -50 ppm, respectively. The chemical shifts for the other alkoxyborohydride species are too close to each other for a safe conclusion to be drawn. It would be very difficult to distinguish, especially in the solid state, between a $\text{BH}(\text{OR})_3^-$ structure and the 1:1 mixture of $\text{BH}_2(\text{OR})_2^-$ and $\text{B}(\text{OR})_4^-$ that would result from disproportionation. An experiment that would possibly differentiate between the two possibilities is to decompose a sample of **47** that contains 50% deuterated borohydride. If any disproportionation occurred during decomposition, mixed $\text{BHD}(\text{OR})_2^-$ species would result, which should display IR bands significantly different from those of $\text{BH}_2(\text{OR})_2^-$ or $\text{BD}_2(\text{OR})_2^-$. Ab initio calculations at the RHF/6-31G* level predict the BH and BD stretching frequencies in $\text{BHD}(\text{OR})_2^-$ to be shifted by -10 and -53 cm^{-1} , respectively, relative to the corresponding values in dialkoxyborohydride or -borodeuteride, respectively. The reference $\text{LiBD}_4\cdot\text{TEA}$ (**47a**) was first synthesized. The solid-state decomposition product resulting from this material (**48a**) exhibits the ν_{BD} at 48 cm^{-1} lower than the starting compound **47a** (Table 3.2). This change is comparable with the corresponding shift of -43 cm^{-1} accompanying the transformation of **47** to **48**. The 50%

^{*} Corrected by +0.7 ppm for adjustment to the $\text{B}(\text{OCH}_3)_3$ reference.^{110a}

deuterated complex (**47b**) was then obtained, starting from a 1:1 mixture of LiBH_4 and LiBD_4 in THF, by precipitation with TEA. It exhibits ν_{BH} and ν_{BD} values that are very similar to the corresponding values in **47** and **47a** (Table 3.2). The IR spectrum of its solid-state decomposition product (**48b**) is virtually identical with the spectrum obtained by addition of the spectra corresponding to **48** and **48a** (Table 3.2). This result suggests that no disproportionation occurs during the solid-state decomposition of **47**, as a result of the isolation and reduced mobility of the borohydride units in **47** and **48**.

Table 3.2. IR data for $\text{LiBH}_4 \cdot \text{TEA}$ (**47**), $\text{LiBD}_4 \cdot \text{TEA}$ (**47a**), $\text{LiBH}_4(50\% \text{D}) \cdot \text{TEA}$ (**47b**), and their corresponding solid state decomposition products, **48**, **48a**, and **48b**. LiBH_4 is included for comparison.

	IR $\nu_{\text{BH(BD)}} (\text{cm}^{-1})$
47	2231, 2290, 2369
48 initial	2171, 2247, 2301
annealed	2340, 2368
47a	1652, 1704
48a initial	1656
annealed	1615 ^a
47b	1649, 1703, 1752
	2226, 2292, 2384
48b initial	1656
	2169, 2247, 2291
annealed	1613 ^a
	2340, 2369
LiBH₄	2219, 2301, 2378

^a uncertain value due to the low intensity of the absorption and overlap with other vibration modes.

Thus, the decomposition process in the solid-state differs significantly from that in solution, demonstrating again the ability of dihydrogen bonding to exert topochemical control in the OH...HB to O-B conversion.

Attempts to enhance the crystallinity of **48** by annealing at 120 °C under Ar resulted in a decrease of the XRD peaks' intensities, until they completely disappeared after approximately 2 weeks, or 4 days if heated as a DMSO suspension. While the hydridic content remained unchanged (one H⁻), the ¹¹B and ⁷Li MAS NMR chemical shifts moved 1.3 and 2.1 ppm downfield and upfield, respectively (Table 3.1). These changes point up the metastable nature of this topochemically controlled product. Moreover, the appearance of the BH stretching region in the IR spectrum changed considerably (Table 3.2) and apparently irreversibly, as the BH stretching absorptions did not revert to the original values even after 8 months at room temperature. A ν_{BH} shift to shorter wavelengths in metal borohydrides generally indicates a stronger BH⁻...M⁺ interaction,¹¹¹ and therefore a similar situation could be present in **48**. The observed shifts in the solid-state ¹¹B and ⁷Li MAS NMR spectra are in agreement with this supposition. On the other hand, no disproportionation seems to have occurred, since again the IR spectrum of annealed **48b** is basically a summation of the corresponding spectra for **48** and **48a** (Table 3.2). The result of a topochemical reaction, the structure of **48** was very likely controlled by kinetic factors, and its subsequent annealing presumably allowed structural relaxation into a thermodynamically more stable arrangement in which the oppositely charged BH(OR)₃⁻ and Li⁺ units are closer in space. The profound modifications in the IR spectrum of **48** and the relatively small downfield shift in its ¹¹B NMR spectrum are in good qualitative agreement with a BH(OCH₃)₃⁻...Li⁺ model, whose

optimized Cs symmetrical structure at the RHF/6-31G* level is shown in Figure 3.7. Its ν_{BH} frequency (scaled by 0.97 based on the ratio between the theoretical and experimental values of the strongest absorption in BH_4^-) is estimated at 2418 cm^{-1} , comparable with the 2368 cm^{-1} value found in **48** after annealing. The ^{11}B NMR δ value of -10.7 ppm calculated for this model structure is virtually identical with the corresponding value in $\text{BH}(\text{OCH}_3)_3^-$, predicting that the above mentioned interaction with Li^+ should have minimal influence over the ^{11}B NMR chemical shift.

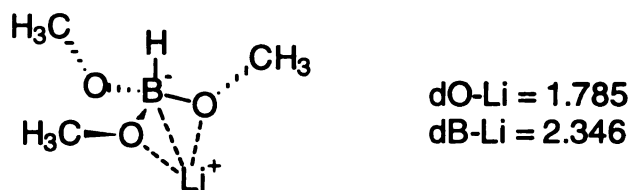


Figure 3.7. Calculated structure of $\text{LiBH}(\text{OCH}_3)_3$ with the interatomic distances in Å.

The fresh or annealed **48** is inert to ethanol, phenol, or acetone. However, it reacts with $\text{Pd}(\text{AcO})_2$ in THF at room temperature to yield an amorphous hygroscopic green powder, soluble in DMSO, and presumably containing Pd^0 , as indicated by deposition of Pd black upon H_2O hydrolysis. IR, ^1H and ^{11}B NMR spectroscopies showed the consumption of the BH, and attachment of the acetate group to the B (See Experimental). This material might be a very effective catalyst for various transformations, considering the presumable high dispersion of the Pd centers on the polymeric borate support.

Mechanistic Study of the Topochemical Dihydrogen to Covalent Bonding Transformation in $\text{LiBH}_4\cdot\text{TEA}$.¹¹² There are a few fundamental issues to be considered regarding the mechanism of the topochemical decomposition of **47** in particular, and of dihydrogen-bonded complexes in general. As for many other solid-state reactions,

conventional concepts like concentration, reaction order, or molecularity have little applicability here. More relevant in this context are the appearance and morphological evolution of the product phase, as well as its compatibility and "solubility" in the reactant phase (See Chapter 2). As thermally initiated solid state reactions that yield both solid and gaseous products, decompositions of **47** (and other dihydrogen-bonded systems), are complex processes involving not only chemical steps such as breaking and formation of bonds, but also physical transformations like destruction of the initial lattice, reactant/product solid solution formation (with possible separation of the product phase), diffusion and desorption of H₂, and heat transfer. The variations in the crystals' morphology are of particular interest as they can provide critical information about the mechanism of decomposition.¹¹³ The mechanism of this solid state decomposition at the molecular level is particularly relevant for the successful design of the next generation of dihydrogen-bonded systems, and also for a better understanding of such fundamental processes as proton transfer or covalent bond formation, extensively studied in the gas phase and solution, but considerably less in the solid state.

Figure 3.8 presents typical optical micrographs showing crystals of **47** at different stages of decomposition at 110 °C. The initial transparent crystals gradually become opaque as the reaction progresses toward completion, suggesting the separation of a new phase. There is no visible reaction front advancing through the crystal; instead, the process appears to start randomly and proceed uniformly in the crystal bulk. The size and morphology of the crystals remained virtually unchanged during decomposition, practically eliminating the possibility of melting.

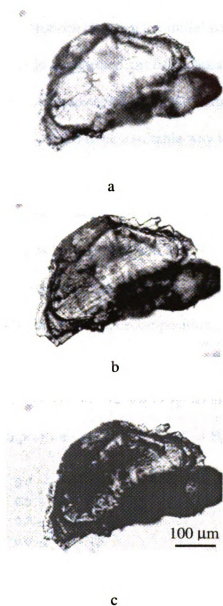


Figure 3.8. Typical microscopic view (transmitted light) of $\text{LiBH}_4\cdot\text{TEA}$ solid-state decomposition: (a) initial crystal, (b) 10 min at 110 °C, (c) final decomposed crystal; Scale bar: 100 μm .

When decomposition of **47** was monitored in situ by ^{11}B solid-state MAS NMR spectroscopy, no other boron species than the initial BH_4^- and the final trialkoxyborohydride could be detected, probably because of the increased reactivity and the short lifetime of the intermediate mono- and dialkoxyborohydrides. Integration of the two well-separated peaks proved to be a suitable way to measure the extent of the solid-state decomposition, and thus to study the kinetics of this topochemical reaction independent of other physical transformations that occur during the process. The reaction was studied at temperatures between 105 and 120 °C, using $\text{LiBH}_4\cdot\text{TEA}$ samples from the same batch for each experiment to eliminate any possible error introduced by sample variation, as significant differences in decomposition rates was noticed among various preparations, a feature characteristic of many solid-state reactions.⁹⁵ The resulting conversion-time curves (Figure 3.9) have the typical sigmoid shape characteristic for most solid-state decompositions of the type $\text{A}_{\text{solid}} \rightarrow \text{B}_{\text{solid}} + \text{C}_{\text{gas}}$ (See Section 2.3).⁹⁴

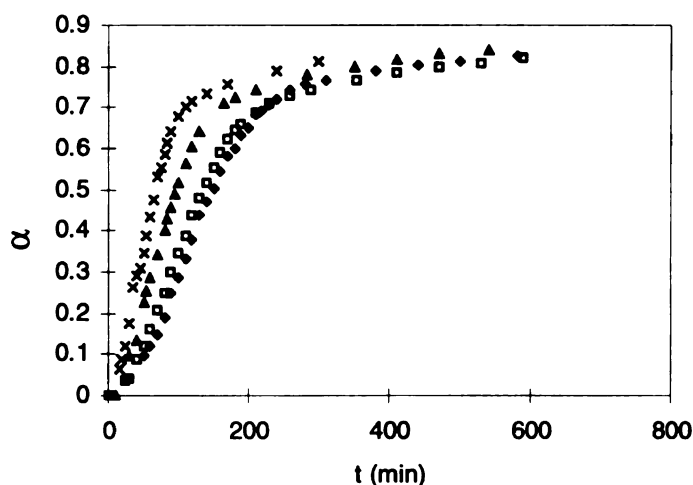


Figure 3.9. Conversion (α) vs. time curves for the solid-state decomposition of **47**: $\blacklozenge$ = 105 °C; $\square$ = 110 °C; $\blacktriangle$ = 115 °C; $\times$ = 120 °C.

The agreement of our data to various solid-state decomposition models (Section 2.3)⁹⁴ were compared, and the best match was found for a nucleation and two-dimensional growth mechanism. The corresponding plots of $[-\ln(1 - \alpha)]^{1/2}$ against time for different temperatures studied are presented (Figure 3.10), together with the obtained rate constants k , the correlation coefficients of the linear regression analysis R^2 , and the conversion ranges for which the Avrami-Erofeev law is obeyed (Table 3.3).

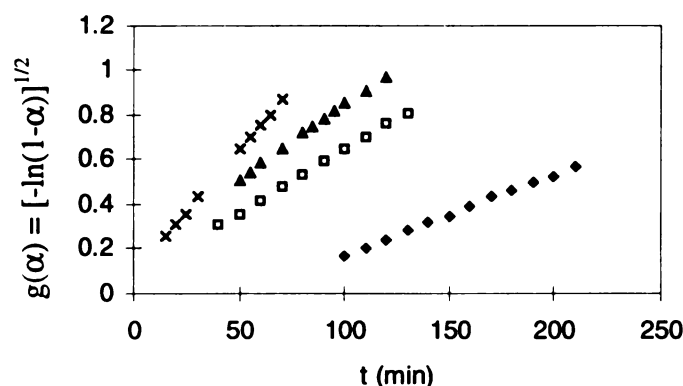


Figure 3.10. Plots of the Avrami-Erofeev law, $[-\ln(1-\alpha)]^{1/2}$ against time, for the solid state decomposition of **47**: ◆ = 105 °C; □ = 110 °C; ▲ = 115 °C; × = 120 °C.

It could be speculated that the two-dimensional expansion of nuclei might originate in the crystal structure of **47**, consisting of one-dimensional dihydrogen-bonded ribbons linked by conventional H-bonds in overall extended layers. Once decomposition has started, it is more likely it will propagate within the same layer, where the H-bonding network is disrupted, weakening thus the compactness of the crystalline environment. By comparison, a similar mechanism, but with a three-dimensional growth of nuclei ($n = 3$), gave a significantly worse match (av. $R^2 = 0.9852$ vs. 0.9984 for $n=2$).

Table 3.3. Rate constants k for the solid state decomposition of **47**, calculated from the Avrami-Erofeev law for nucleation and two-dimensional growth in the specified conversion ranges, together with the correlation coefficients of the linear regression analysis R^2 .

Temp (°C)	k (min ⁻¹) $\times 10^4$	Conversion Range	R^2
105	37 ± 1.4	0.284-0.681	0.9980
110	56 ± 2.6	0.090-0.480	0.9988
115	66 ± 2.8	0.224-0.606	0.9979
120	111 ± 0.9	0.064-0.531	0.9990

The measured rate constants for the solid-state decomposition of **47** at temperatures between 105 and 120 °C obey the Arrhenius equation ($R^2 = 0.9755$), as illustrated by the linear dependence of $\log k$ against $1/T$ (Figure 3.11). At temperatures above 120 °C, the solid-state decomposition of **47** becomes faster than predicted by the Arrhenius equation. A possible explanation is that the dissipation of the resulting heat becomes too slow compared to decomposition rate, eventually leading to the autoacceleration of reaction. An activation energy of 21.0 ± 2.4 kcal/mol for the solid-state decomposition of **47** can be estimated from our data. Similarly, using the Eyring equation, the activation parameters for decomposition, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, were calculated to be 20.1 ± 2.4 kcal/mol and -16.8 ± 6.2 e.u., respectively.

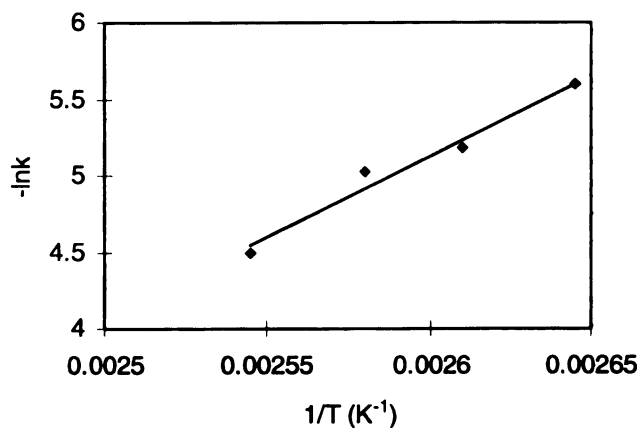


Figure 3.11. Arrhenius plot for the solid-state decomposition of **47** at 105-120 °C.

When the isoconversional method⁹⁸ (Eq. 5, Section 2.3) was used, comparable activation energies within experimental errors were obtained (Figure 3.12).

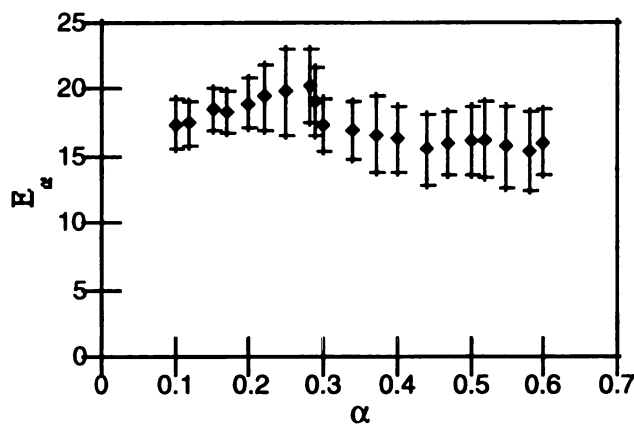


Figure 3.12. Variation of activation energy with conversion for the solid-state decomposition of **47**, obtained using the isoconversional method.

However, analyses starting with $t_{0,i}$ initial times set at various extents of reaction α , yielded different E_a values. For instance, when $t_{0,i}$ was set for $\alpha = 0.1$, the resulting

activation energies varied between 14.9 and 24.1 kcal/mol. In comparison, the Avrami-Erofeev ($n = 2$) model analysis did not show much variation.

Since the kinetic measurements were done by in situ ^{11}B NMR spectroscopy which allowed direct monitoring of the appearance of the final trialkoxyborohydride product, independent of other physical processes such as nucleation, phase separation, or diffusion and desorption of H_2 , and considering the fact that no phase transition occurred prior to decomposition, as shown by powder X-ray diffraction, it is reasonable to assume that the kinetic parameters found in this study are directly related to the chemical transformations responsible for decomposition.¹¹⁴ Moreover, the present activation parameters are comparable with the activation enthalpy of 20.6 ± 1 kcal/mol and activation entropy of -22.3 ± 3 e.u. found for the hydrolysis of BH_4^- in neutral water, and associated with the rate limiting proton transfer step.¹⁰⁰ However, the mechanism could be different in the solid-state, with the H_2 evolution slowed down by the crystal constraints, possibly becoming the rate-determining step. To address this question, we studied the solid state decomposition of $\text{LiBH}_4 \cdot \text{N}(\text{CH}_2\text{CH}_2\text{OD})_3$, the analogue of **47**, with the OH groups deuterated. H/D exchange between BH_4^- and OD groups of the TEA is expected for a scheme involving fast, reversible proton transfer followed by slow H_2 loss. However, no H/D exchange was observed at any stage of decomposition, under various conditions, as indicated by the IR or ^1H NMR of the partly or fully decomposed deuterated complex. This experiment suggests that as in solution, the proton transfer is slow compared to H_2 loss and B-O covalent bond formation (Figure 3.13). It should be stressed here that these results are interpreted using a stepwise mechanism for the solid state decomposition based on analogy with the aqueous hydrolysis of BH_4^- in neutral

water, and theoretical calculations supporting the existence of the BH_5 intermediate.¹⁰¹ In solution, a one step reaction with a four center transition state could be unambiguously eliminated based on kinetic isotope effects and hydrolysis experiments in the presence of trimethylammonium ion.¹¹⁵ In our solid-state system, on the other hand, the possibility of a concerted mechanism cannot be ruled out. However, considering the similarity of the reacting partners and the activation parameters found in this study and in solution, it appears the same mechanism seems likely to apply for both.

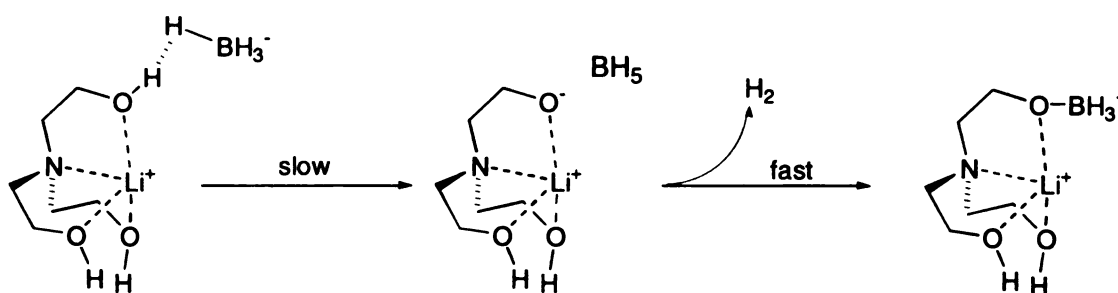
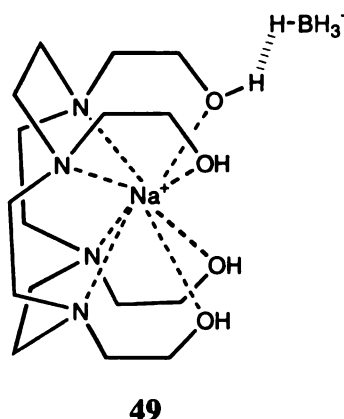


Figure 3.13. Proposed mechanism for the first $\text{O-H}\cdots\text{H-B}$ to O-B topochemical conversion in **47**.

To all appearances, the measured activation parameters in this study correspond to rate-limiting proton transfer at the interface between the crystalline dihydrogen-bonded system **47** and the newly formed covalent product **48**. The reacting partners in this region are presumably more flexible than in the perfectly ordered environment of the undisturbed crystal. The somewhat lower activation entropy found for the solid-state process, compared to the similar reaction in water, could be attributed to the preorganization imposed by the dihydrogen bonding network in the crystal. Despite the

heterogeneous nature of decomposition, the topochemical information is nonetheless transferred through the interface to the newly formed covalent product.

Toward Crystalline Covalent Solids: Crystal-to-Crystal Dihydrogen to Covalent Bonding Transformation in $\text{NaBH}_4\cdot\text{THEC}$ (49).¹¹⁶ The $\text{NaBH}_4\cdot\text{THEC}$ (THEC = *N,N',N'',N'''*-tetrakis-(2-hydroxyethyl)cyclen) complex exemplifies a system that combines both the closed loop and the globular cation strategies, leading as a result for the first time to a crystalline covalent product, in a crystal-to-crystal thermal decomposition.



The complex precipitates from a 1:1 mixture of NaBH_4 and THEC in 2-propanol, and its crystal structure is shown in Figure 3.14. The THEC ligand adopts a conformation with all hydroxyethyl arms oriented toward the same face of the azacrown ring, as observed in previously reported metal complexes containing this ligand.¹¹⁷ The nitrogen and oxygen atoms are thus organized in a pseudo-cubic geometry, encapsulating the octacoordinated Na cation. The Na^+THEC units have thus the appropriate geometry for the formation of the desired closed-looped dihydrogen-bonded assembly.

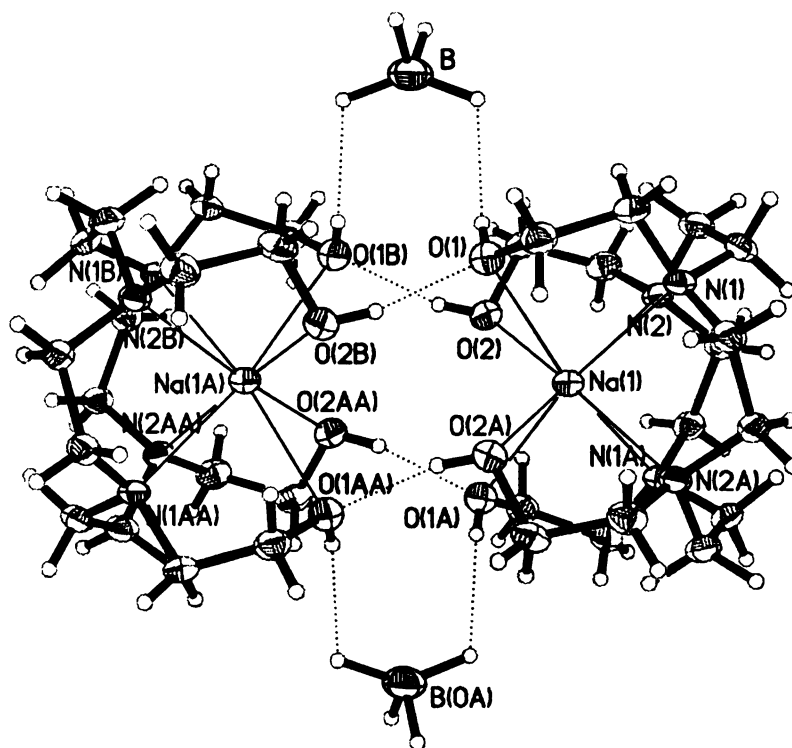


Figure 3.14. X-Ray crystal structure of $\text{NaBH}_4 \cdot \text{THEC}$ illustrating the self-assembly in dihydrogen-bonded dimers.

Indeed, these cations self assemble in D_2 symmetrical dimers, held together by four conventional $\text{O}(2)\text{-H}\cdots\text{O}(1)$ hydrogen bonds, complemented by four orthogonal $\text{O}(1)\text{-H}\cdots\text{H-B}$ proton-hydride interactions involving the borohydride anions (Figure 3.14). The observed $\text{H}\cdots\text{H}$ distance is 2.00 Å long, and the $\text{OH}\cdots\text{H-B}$ and $\text{O-H}\cdots\text{HB}$ angles display values of 115 and 151°, respectively. There is no hydrogen bonding interconnecting the dimers, which are packed in two-dimensional layers (Figure 3.15). The layers are stacked in a parallel fashion, creating thus one-dimensional channels along the a axis, in which the BH_4^- anions reside.

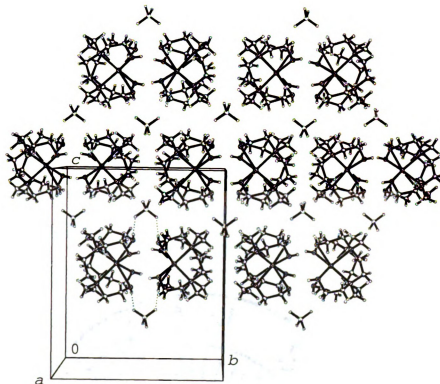


Figure 3.15. Crystal packing in NaBH₄·THEC.

The association in closed loops, as well as the packing mode of the large globular $\{\text{Na}_2(\text{THEC})_2\}^{+2}$ cations, appear to fulfill the two geometrical requirements that were predicted to favor the transfer of crystallinity from dihydrogen- to covalent-bonded networks. Solid-state decomposition of **49**, induced by heating under an inert atmosphere at 160 °C for 20 h, resulted in complete elimination of H₂, as indicated by the FT-IR and ¹¹B solid state MAS-NMR spectra of the resulting material. Thermogravimetric analysis showed a remarkably sharp 1.88 % weight loss between 168.0 and 168.8 °C, which corresponds to 3.63 mol H₂. The solid-state decomposition product exhibits high

crystallinity, as indicated by microscopic examination, which showed good transparency to polarized light for the decomposed crystals (Figure 3.16). The reaction appears to be crystallographically homogeneous, in direct contrast to the $\text{LiBH}_4\cdot\text{TEA}$ dihydrogen-bonded system, where the covalent product nucleated as a separate phase.

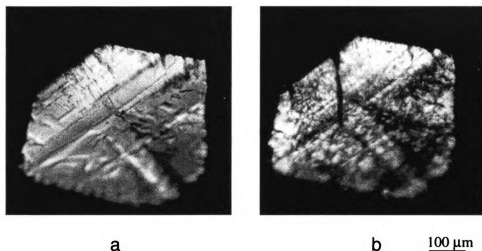


Figure 3.16. Polarizing microscopic view of $\text{NaBH}_4\cdot\text{THEC}$ crystal-to-crystal decomposition: a) initial crystal; b) after 20 h at 160 °C. Scale bar = 100 μm .

That the solid state decomposition of **49** is a single-phase transformation is also supported by powder XRD analysis, which shows a gradual shift of the diffraction pattern as the reaction progresses. As depicted in Figure 3.17, the final covalent product exhibits high crystallinity, in agreement with the microscopic observations. For comparison, an amorphous solid results when **49** is decomposed in the melt at 200 °C for 10 min (Figure 3.17c).

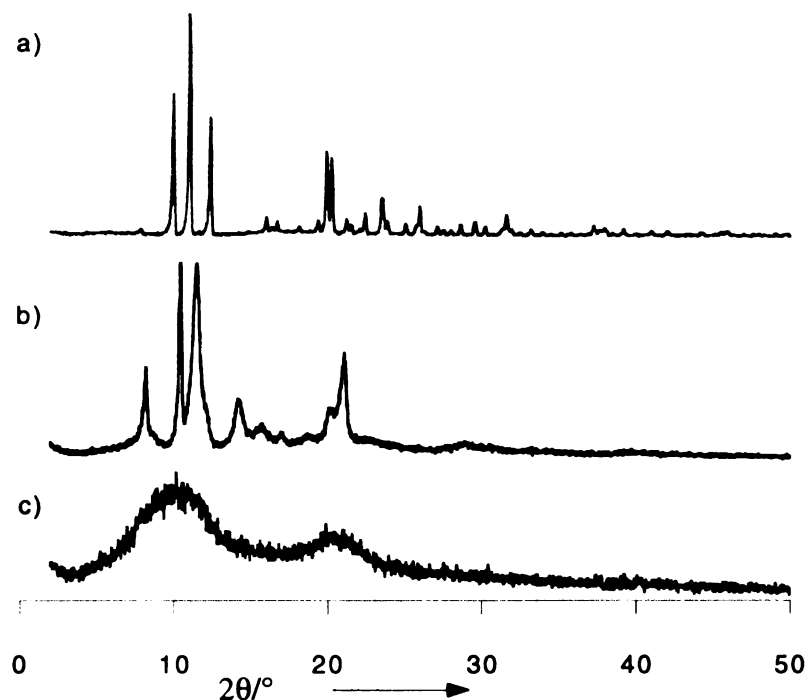


Figure 3.17. Powder XRD patterns for: a) dihydrogen-bonded complex **49**; b) solid-state decomposition product; c) product of decomposition in the melt.

The unit cell parameters for the decomposition product, calculated using the powder XRD data, are: $a = 8.600(34) \text{ \AA}$, $b = 13.864(74) \text{ \AA}$, $c = 16.895(27) \text{ \AA}$, and $V = 2014(11) \text{ \AA}^3$. They correspond to 3.3, 2.5, 3.5, and 9.0 % shrinkage, respectively, relative to **49**.

For this comparison, the following values derived from powder XRD at room temperature were used for **49**: $a = 8.894(7)$, $b = 14.214(13)$, $c = 17.509(17)$, $V = 2214(3)$.

The evolution of unit cell parameters during the solid-state decomposition of **49** at 120 °C could be monitored by powder XRD (Figure 3.18).

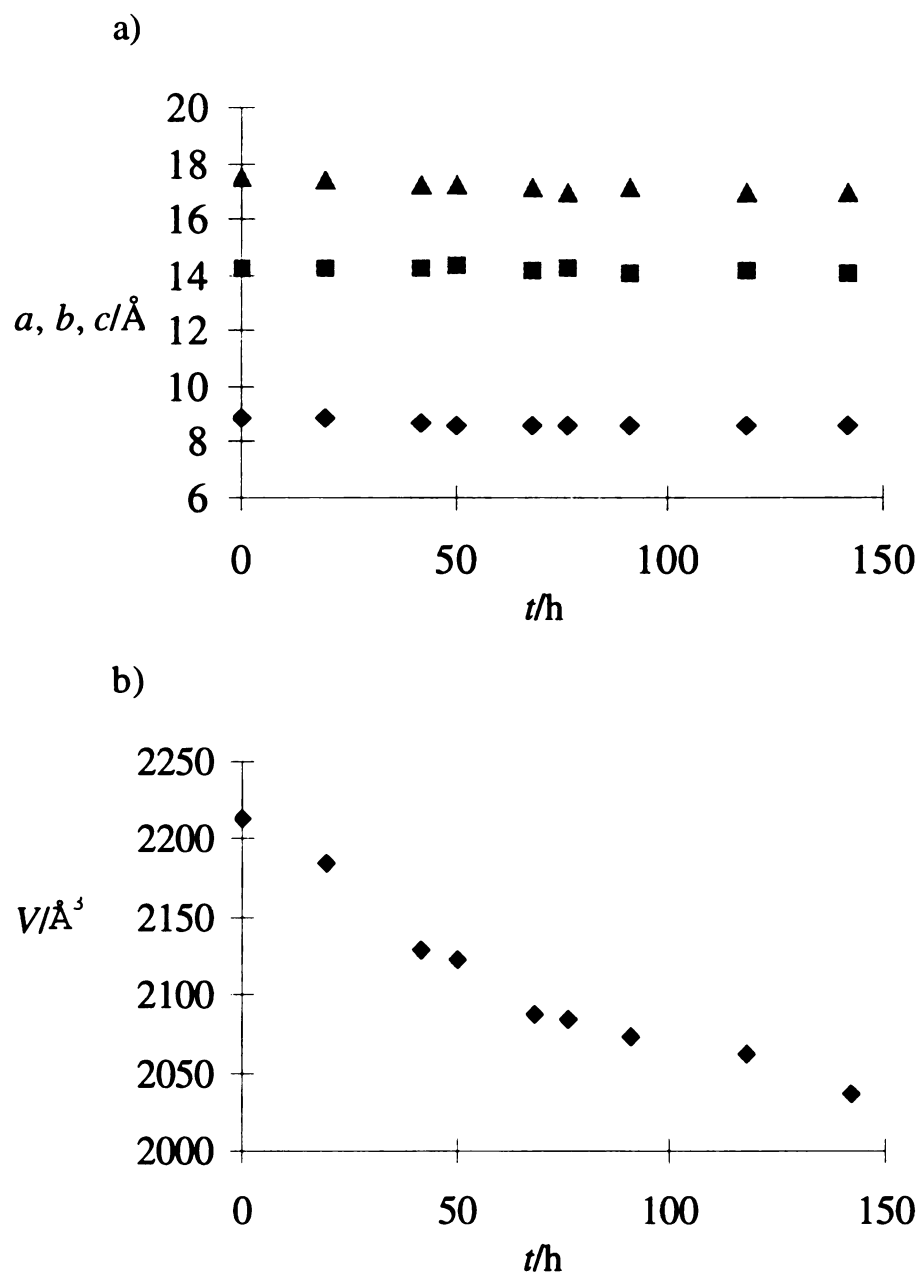


Figure 3.18. Evolution of unit cell axes (a) and volume (b) during the solid-state decomposition of $\text{NaBH}_4\cdot\text{THEC}$ at 120 °C, monitored by powder XRD.

As shown in Figure 3.18, the initial crystal lattice smoothly transforms into the corresponding lattice of the product, indicating a crystal-to-crystal process.

Despite sustained efforts, the detailed structure of the decomposed crystal has remained elusive to date. The relatively big change in the unit cell accompanying the solid-state decomposition ultimately results in deterioration of the single crystals' quality, precluding their X-ray structural investigation. Also, the unexpected insolubility of the product in common organic solvents does not allow its recrystallization. Considering the crystal packing of **49**, with no interdimer hydrogen bonding present, formation of discrete molecular cages is expected from the solid-state decomposition. Crosslinking between dimers would require substantial intermolecular rearrangements, which is highly unlikely in a crystallographically homogeneous, lattice-controlled transformation. Figure 3.19 presents a possible structure for the putative molecular cages, optimized with the DFT method at the B3LYP/6-31G* level.¹¹⁸ No unusual values for the bond lengths and angles were observed in the resulting C_2 symmetrical structure, suggesting minimal strain in these covalent dimers.

When **49** was decomposed in DMSO by heating at 120 °C for 48 h, a crystalline product precipitated in high yield. X-ray structural analysis of the resulting crystals revealed a centrosymmetric molecular cage very similar to that expected for the solid-state reaction (Figure 3.20). However, one of the hydroxyethyl arms in each of the two THEC ligands in the dimer does not bind the boron atom, nor does it complex the Na cation, being replaced by an OH group, presumably from water present in the solvent. Except for the Na, the four N atoms, and C(4) and C(6), all the atoms in the structure are disordered over two sites, with 90.1 and 9.9 % occupancies, respectively.

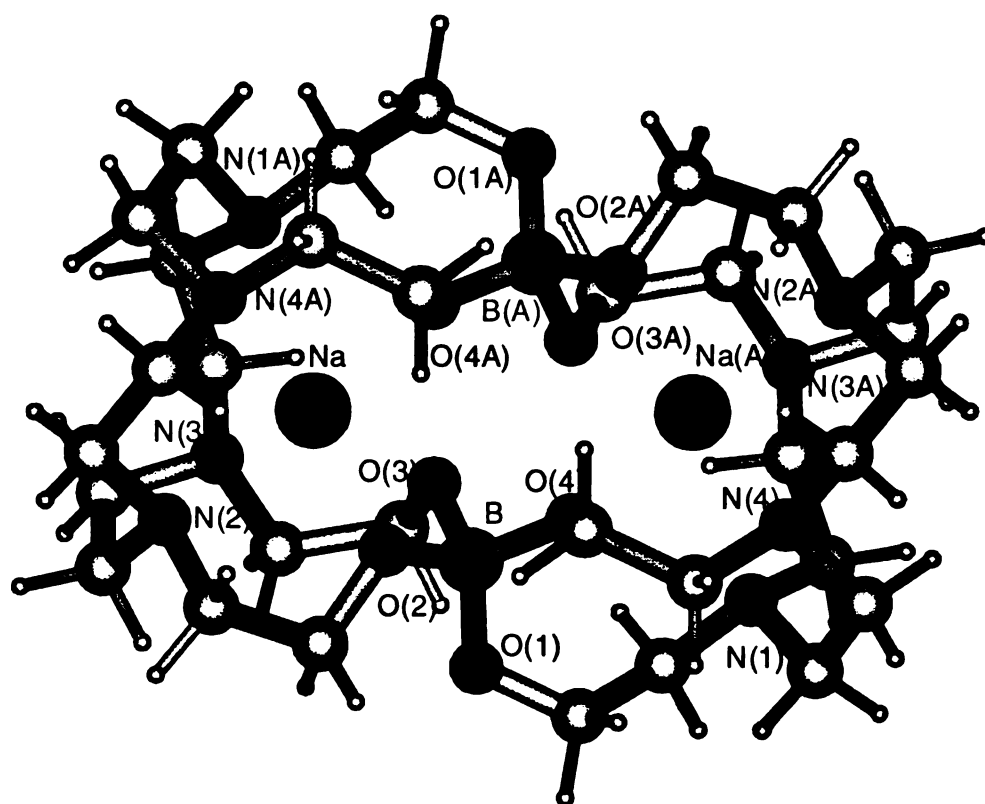


Figure 3.19. Molecular model of the product from the solid-state decomposition of **49**; selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: B-O(1) 1.458, B-O(2) 1.482, B-O(3) 1.497, B-O(4) 1.474, O(1)-B-O(2) 112.5, O(1)-B-O(3) 109.1, O(1)-B-O(4) 114.6, B-O(1)-C 123.7, B-O(2)-C 122.3, B-O(3)-C 125.9, B-O(4)-C 125.6, N(1)-Na 3.003, N(2)-Na 2.714, N(3)-Na 2.435, N(4)-Na 2.565, O(2)-Na 2.670, O(3)-Na 2.276, O(4)-Na 2.228.

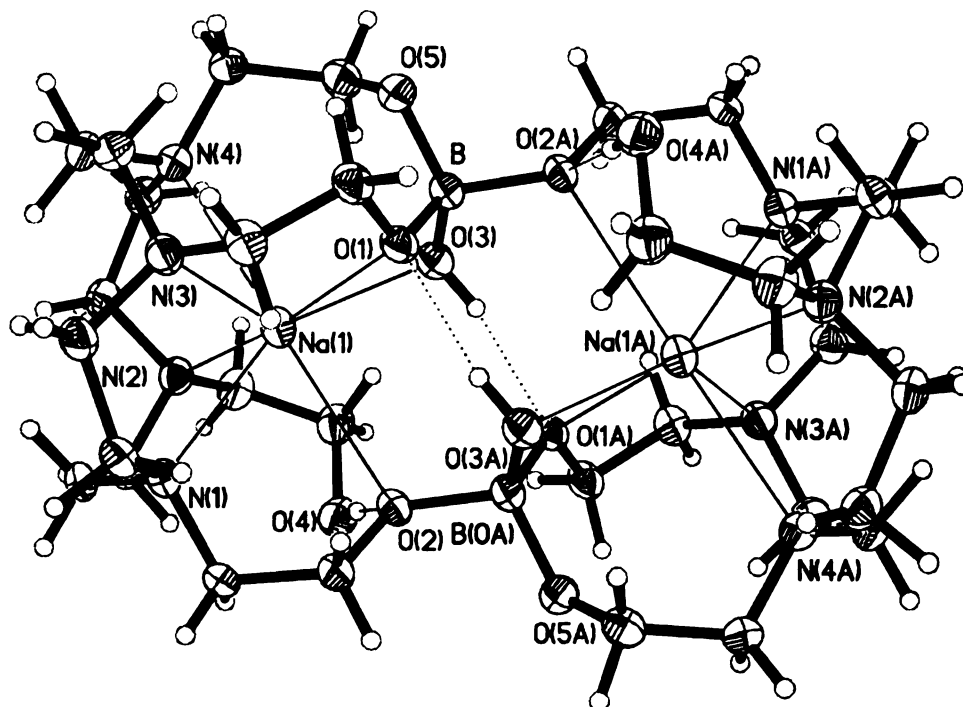


Figure 3.20. X-Ray crystal structure of the major conformation found in the covalent dimer obtained by decomposing **49** in DMSO; selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: B-O(1) 1.502(2), B-O(2) 1.511(2), B-O(3) 1.450(2), B-O(5) 1.457(2), O(1)-B-O(5) 111.6(1), O(2)-B-O(5) 109.8(1), O(3)-B-O(5) 111.6(1), B-O(1)-C 121.7(1), B-O(2)-C 113.2(1), B-O(5)-C 122.8(1), N(1)-Na 2.519(1), N(2)-Na 2.540(1), N(3)-Na 2.565(1), N(4)-Na 2.682(1), O(1)-Na 2.371(1), O(2)-Na 2.796(1), O(3)-Na 2.391(1), O(4)-H 0.82(2), O(4)H $\cdots$ O(2) 1.92(3), O(4) $\cdots$ O(2) 2.735(4), O(4)-H-O(2) 175.1(3).

Like the solid-state decomposition product, the compound obtained from DMSO is surprisingly insoluble in common organic solvents, despite its relatively small size, overall neutral charge, and lack of intermolecular hydrogen bonding.

In situ ^{11}B MAS NMR spectroscopy proved again to be a convenient method for monitoring the solid-state dihydrogen to covalent bonding transformation and measuring the kinetics of decomposition. As in the case of the heterogeneous transformation in $\text{LiBH}_4\cdot\text{TEA}$, no boron species other than the initial borohydride and the final borate could be observed. The extent of reaction at 160 °C could be easily measured by integration of the two peaks, and the conversion-time curve is depicted in Figure 3.21. After an initiation period, the reaction is accelerated up to approximately 75% conversion, after which time it is slowed down significantly. No common kinetic model for solid-state decompositions was found to fit the existing data. For comparison, the extent of lattice conversion vs time was plotted, using the data from the solid-state decomposition of **49** at 120 °C, monitored by powder XRD. As illustrated in Figure 3.22, the obtained curve is qualitatively comparable with the one obtained from the ^{11}B NMR measurements. The enhanced reaction rate at the intermediate stages of decomposition might originate in the increased strain caused by the enforced coexistence of the initial and final crystal lattices. On the other hand, powder XRD examinations at different extents of decomposition showed a gradual deterioration of crystallinity as the reaction progressed, followed by significant recovery of the diffraction pattern at the late stages of reaction. This increased lattice looseness at intermediate conversions appears to facilitate the chemical reaction relative to the initial and final stages, when the reacting molecules are constrained in a more rigid, unperturbed crystalline lattice.

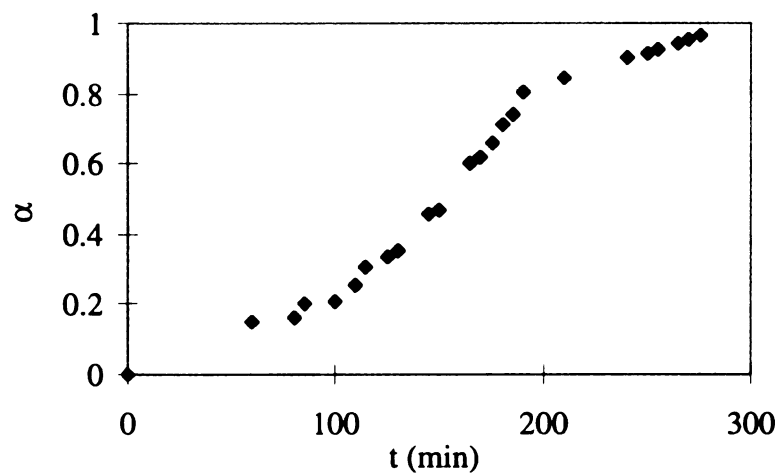


Figure 3.21. Conversion (α) vs time curve for the solid-state decomposition of $\text{NaBH}_4\cdot\text{THEC}$ at 160 °C, obtained using in situ ^{11}B MAS NMR.

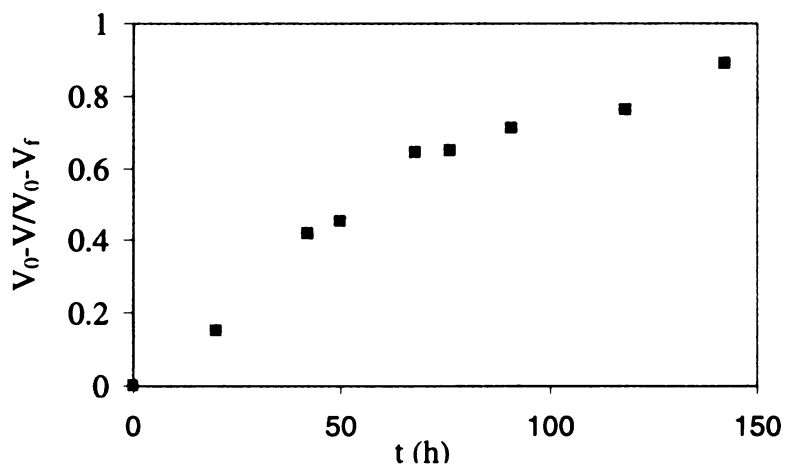


Figure 3.22. Lattice conversion ($V_0 - V / V_0 - V_f$) vs time curve for the solid-state decomposition of $\text{NaBH}_4\cdot\text{THEC}$ at 120 °C, obtained using powder XRD.

In summary, the first crystal-to-crystal dihydrogen to covalent bonding transformation was carried out. This outcome appears to be the result of the judicious engineering of the starting dihydrogen-bonded system, which was designed to satisfy both the closed loop and globular cation geometrical criteria.

Structural Variations from the $\text{NaBH}_4\cdot\text{THEC}$ System. The $\text{NaBH}_4\cdot\text{THEC}$ complex demonstrated that careful design of dihydrogen-bonded crystals permits transfer of crystallinity to the covalent products resulting from their solid-state decomposition. The next step is to extend this concept to the construction of higher-dimensional crystalline covalent systems, a class of compounds to which few purposeful synthetic paths exist. Further elaboration of the dihydrogen-bonded building blocks present in **49**, which proved to possess the required geometrical and solid-state reactivity prerequisites, appears to be the most potentially successful approach toward our objective. However, an important and necessary condition is that the dihydrogen-bonded dimeric motif observed in **49** be robust enough to survive substantial modifications in molecular structure. This section presents some preliminary results from the systematic investigation of the relationship between molecular structure and supramolecular organization in metal borohydride complexes with THEC-type ligands. We seek an understanding of the factors that govern the crystal packing in these dihydrogen-bonded systems, and possibly to control them for the crystal engineering of the desired extended dihydrogen-, and ultimately covalent-bonded networks.

We first explored the role of the metal borohydride in determining the self-assembly into dihydrogen-bonded dimers. The LiBH_4 and KBH_4 complexes with THEC were therefore synthesized to investigate the effect of changing the metal cation upon

crystal structure. Unfortunately, the modest crystallinity of the former, and the propensity of the latter to form polycrystalline aggregates instead of single-crystals, precluded their detailed structural elucidation. The $\text{NaCNBH}_3\cdot\text{THEC}$ (**50**) complex was then synthesized to explore the contribution of the hydridic partner in the formation of the closed-looped dimers. The white crystalline compound melts at 230-234 °C with decomposition and gas evolution. However, its crystal structure, which is depicted in Figure 3.23, reveals the absence of any $\text{O-H}\cdots\text{H-B}$ close contacts, the cyanoborohydride anion participating with the N atom via conventional H-bonding instead.

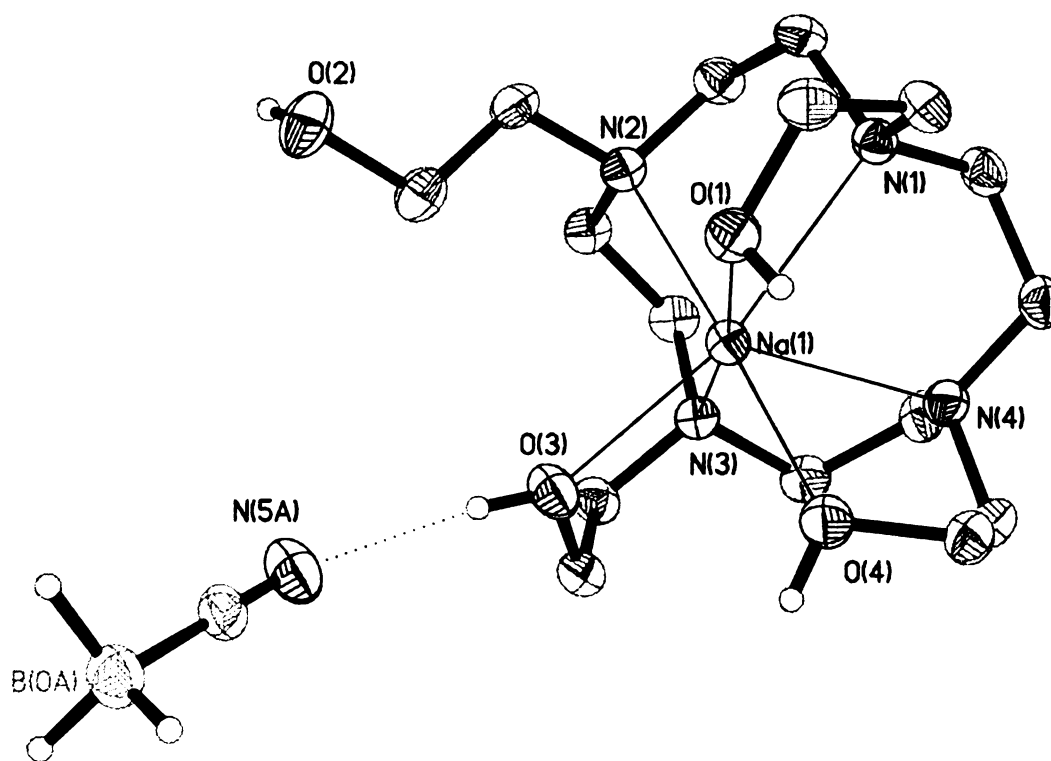


Figure 3.23. X-Ray crystal structure of $\text{NaNCBH}_3\cdot\text{THEC}$.

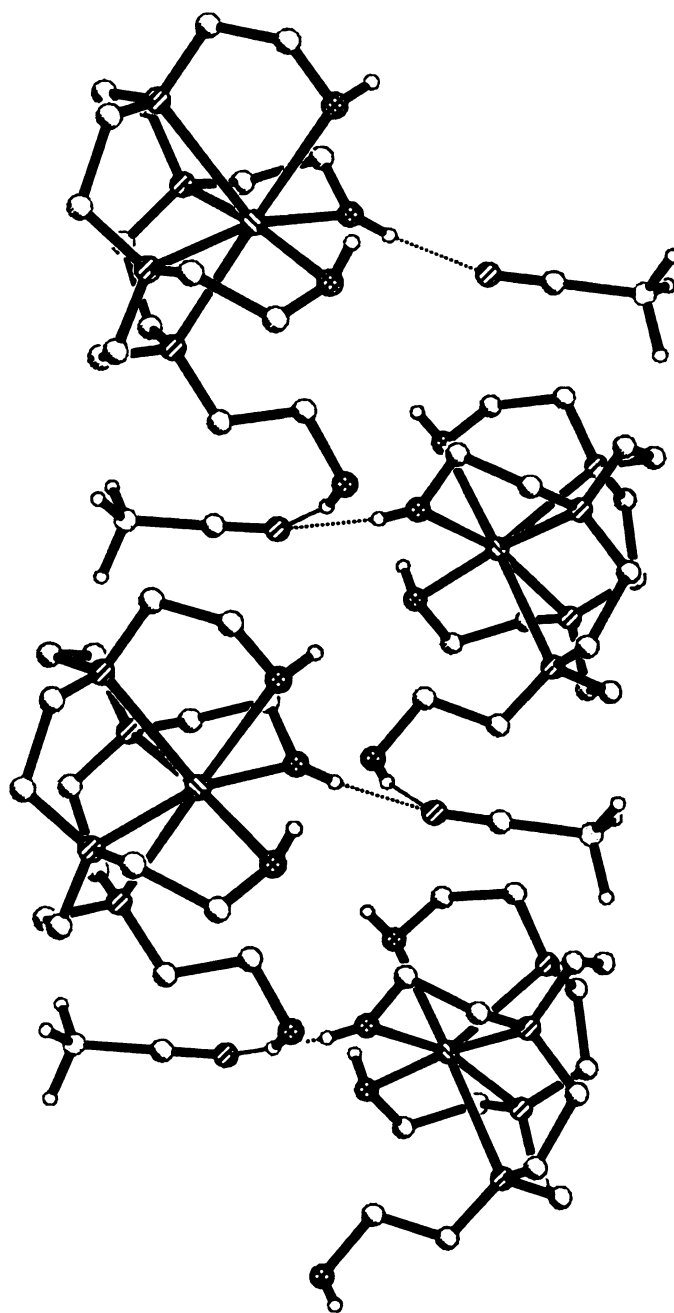
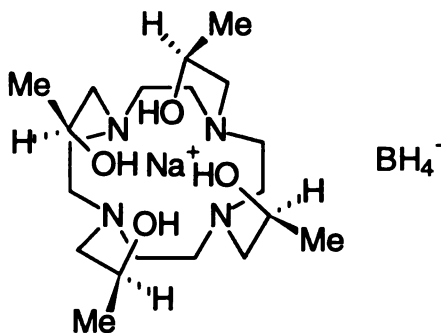


Figure 3.24. α -Helix formed by NaNCBH₃·THEC in the solid-state.

Notably, instead of forming dimers, in this case the Na-THEC units self-assemble into extended α -helices, via bifurcated O-H...N...H-O hydrogen bonds involving the CN groups (Figure 3.24). The helices are further associated in two-dimensional layers by O-H...O interactions. It thus appears that the O-H...H-B dihydrogen bonds in **49** are essential for the formation of the $\{\text{Na}_2(\text{THEC})_2\}^{+2}(\text{BH}_4^-)_2$ dimers, as their absence in **50** resulted in a completely different packing.

$\text{NaBH}_4 \cdot \text{THPC}$ (**51**) (THPC = 1,4,7,10-tetrakis((*S*)-2-hydroxypropyl)-1,4,7,10-tetraazacyclododecane) was synthesized to explore the effect of subtle molecular modifications in the ligand upon crystal packing. It was also hoped that the introduction of the Me groups would improve the solubility of the covalent dimers (if they are formed) in organic solvents.



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The complex precipitates as a white solid upon mixing NaBH_4 and THPC in 2-propanol. Its crystal structure is presented in Figure 3.25. The most notable feature is the formation of hydrogen-bonded dimers, which, however, display an S-shaped topology, as opposed to the O-shaped one in **49**. The most probable cause of this difference is the steric repulsion that would result between the Me groups, in an O-shaped configuration in **51**.

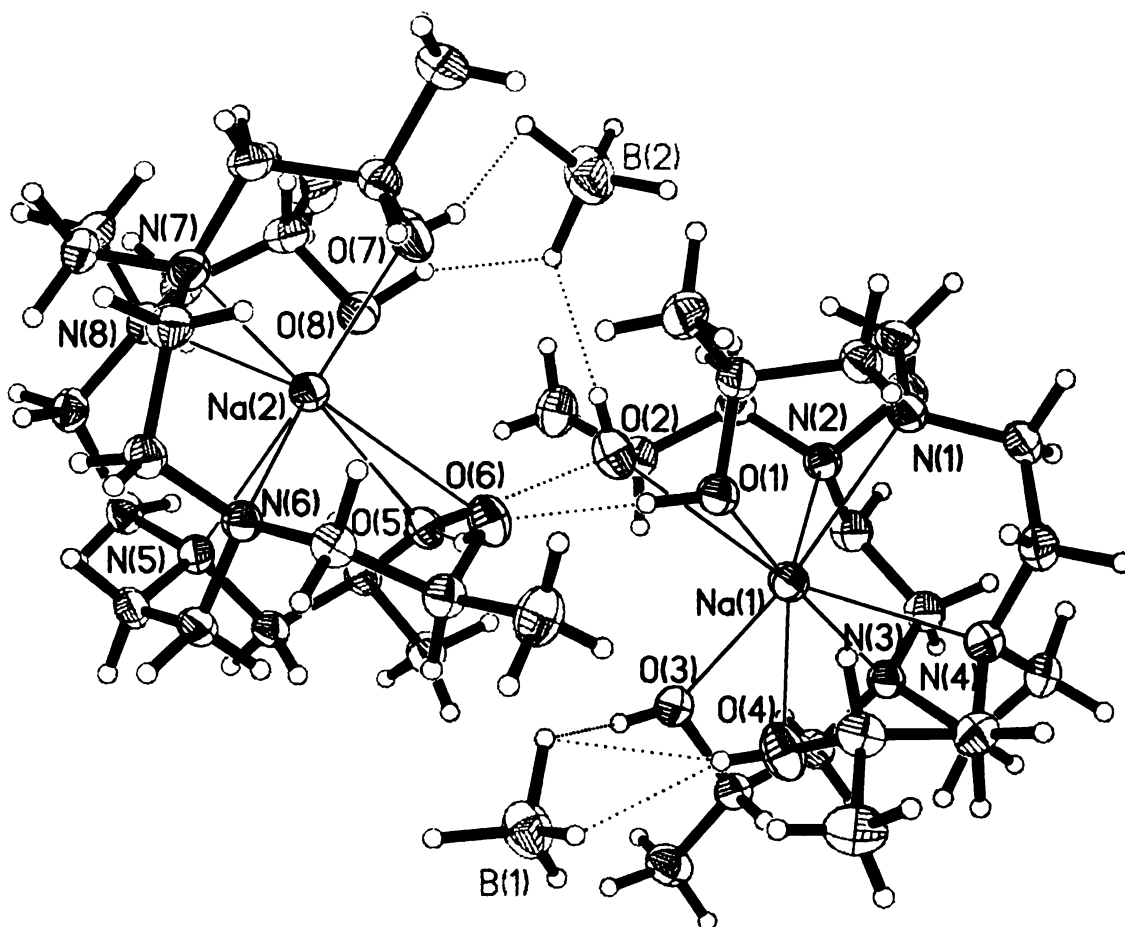


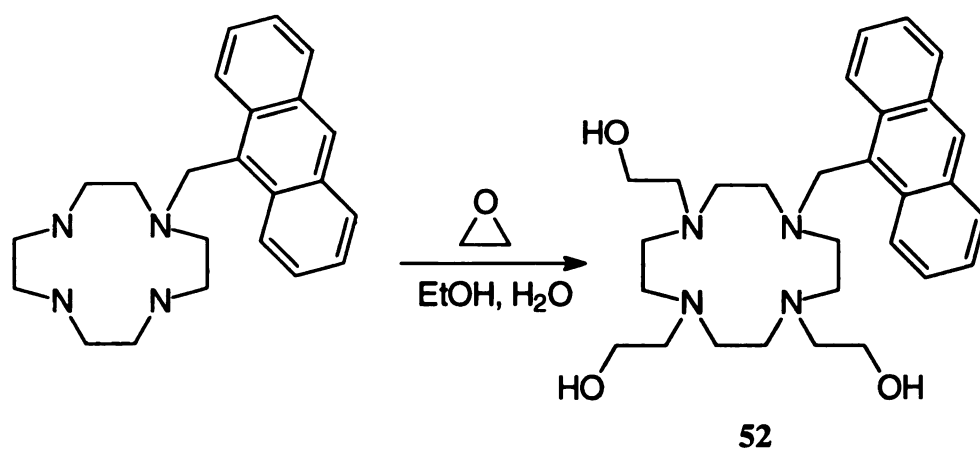
Figure 3.25. X-Ray crystal structure of $\text{NaBH}_4\cdot\text{THPC}$; dihydrogen bonding parameters ($\text{\AA}$, $^\circ$): $\text{O(4)H}\cdots\text{HB(1)}$ (lower) 2.106, $\text{O(4)H}\cdots\text{HB(1)}$ (upper) 2.266, $\text{O(3)H}\cdots\text{HB(1)}$ 2.005, $\text{O(7)H}\cdots\text{HB(2)}$ 1.927, $\text{O(8)H}\cdots\text{HB(2)}$ 1.676, $\text{O(2)H}\cdots\text{HB(2)}$ 1.904, O(4)H-H-B(1) (lower) 96.1, O(4)H-H-B(1) (upper) 88.7, O(3)H-H-B(1) 113.8, O(7)H-H-B(2) 110.7, O(8)H-H-B(2) 120.2, O(2)H-H-B(2) 133.3, O(4)-H-HB(1) (lower) 162.5, O(4)-H-HB(1) (upper) 143.9, O(3)-H-HB(1) 153.4, O(7)-H-HB(2) 155.4, O(8)-H-HB(2) 153.0, O(2)-H-HB(2) 169.3.

The two THPC units in the dimer are held together by O(1)H...O(6) and O(5)H...O(2) conventional hydrogen bonds, as well as by O(7)H...HB(2)H...HO(2) and O(8)H...HB(2)H...HO(2) dihydrogen bonds. The second borohydride anion interacts with the remaining O(3)H and O(4)H from one THPC ligand. As in **49**, no hydrogen bonding interconnects the dimers.

The solid-state decomposition of **51** was unfortunately precluded by partial liquefaction during heating, apparently due to the low melting point of the product(s).

More profound structural variations in the THEC supramolecular building block were brought about by replacing one of the hydroxyethyl arms with a 9-methylantracene group. The intention was to test the ability of the resulting tripodal ligand to maintain the association in dimers. Recurrence of this supramolecular motif could ultimately open the way to extended networks, by simple attachment of the tris-hydroxycyclen units to multidentate spacers, using the remaining N atoms. Furthermore, monitoring the orientation of the anthracene chromophores via fluorescence spectroscopy might offer an additional handle on the evolution of order during the solid-state decomposition.

The 9-(1',4',7'-tris-hydroxyethyl-cyclen)methylantracene (**52**) ligand was synthesized from 9-(1',4',7',10'-tetraazacyclododecyl)methylantracene¹¹⁹ and ethylene oxide (Scheme 3.6), and its structure was confirmed by X-ray crystallography (Figure 3.26). Upon mixing with NaBH₄ in 2-propanol, the NaBH₄·**52** complex (**53**) was formed, which precipitated as a white crystalline solid. Elemental analysis and ¹H NMR indicated the crystallization with 1 mol of solvent. The inclusion of 2-propanol was also supported by TGA, which showed a 10.35% weight loss, in good agreement with the 10.14% theoretical value. Single crystals, however, were grown from CH₃CN/Et₂O.



Scheme 3.6

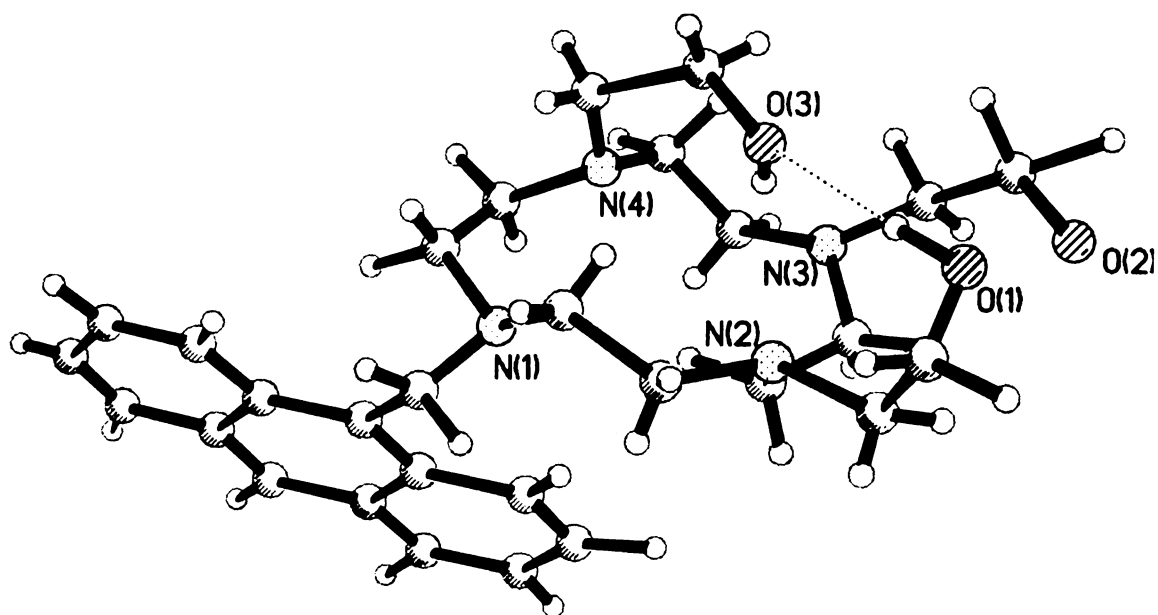


Figure 3.26. X-Ray crystal structure of 9-(1',4',7'-tris-hydroxyethyl-cyclen)methylanthracene.

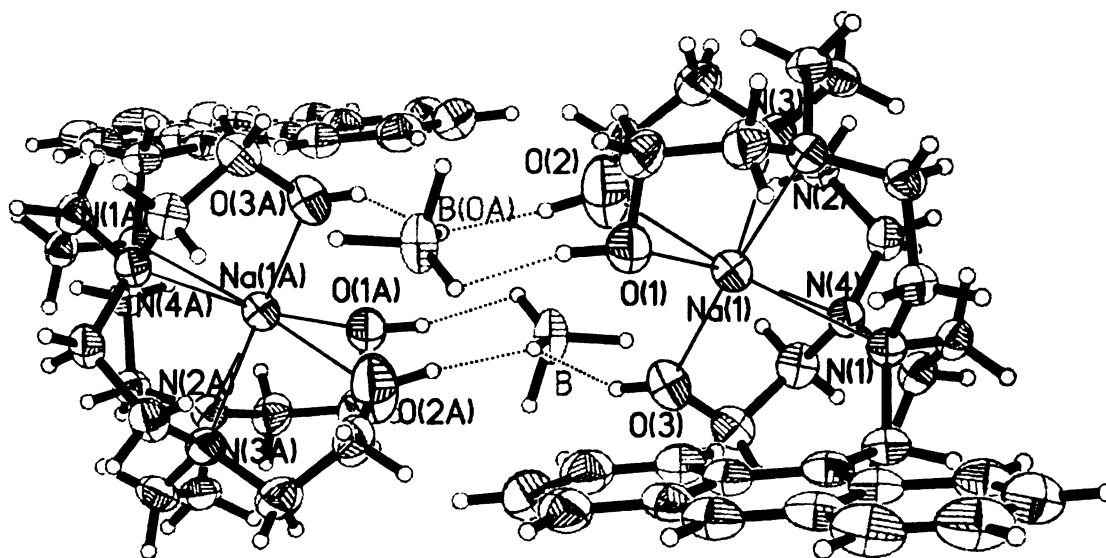


Figure 3.27. X-Ray crystal structure of **53**; normalized dihydrogen bonding parameters ($\text{\AA}$, $^\circ$): O(1)H $\cdots$ HB 1.692, O(2)H $\cdots$ HB 1.661, O(3)H $\cdots$ HB 1.730, O(1)H $\cdots$ H-B 114.5, O(2)H $\cdots$ H-B 117.8, O(3)H $\cdots$ H-B 116.1, O(1)-H $\cdots$ HB 166.8, O(2)-H $\cdots$ HB 155.1, O(3)-H $\cdots$ HB 154.6.

X-Ray structural examination of crystals of **53** obtained from acetonitrile-ether revealed the inclusion of 1 mol of disordered Et₂O. The crystal structure (Et₂O was omitted) is depicted in Figure 3.27, and shows the self-assembly in dihydrogen-bonded centrosymmetric dimers. However, compared with the previous structures, no O-H...O interaction is present in this case; instead, the BH₄⁻ anions are intercalated between the two ligands, forming three dihydrogen bonds with the OH groups. No conclusive results from the solid-state decomposition of **53** have been obtained to date, due to the insufficient quantity of its ether clathrate available.

In summary, NaBH₄ and various hydroxyethylcyclen ligands persistently self-assemble in dihydrogen-bonded dimers in the solid-state, as demonstrated by the crystal structures of **49**, **51**, and **53**. However, the exact topology of the dimers varies from one case to another, in response to structural modifications in the ligand. Nevertheless, this consistent recurrence of the general dimeric motif makes these dihydrogen-bonded units sufficiently reliable building blocks for supramolecular synthesis. Their incorporation into more elaborate structures, as suggested in Figure 3.28 would offer real prospects for the construction of extended dihydrogen-bonded, and ultimately covalent solids, with controlled architectures.

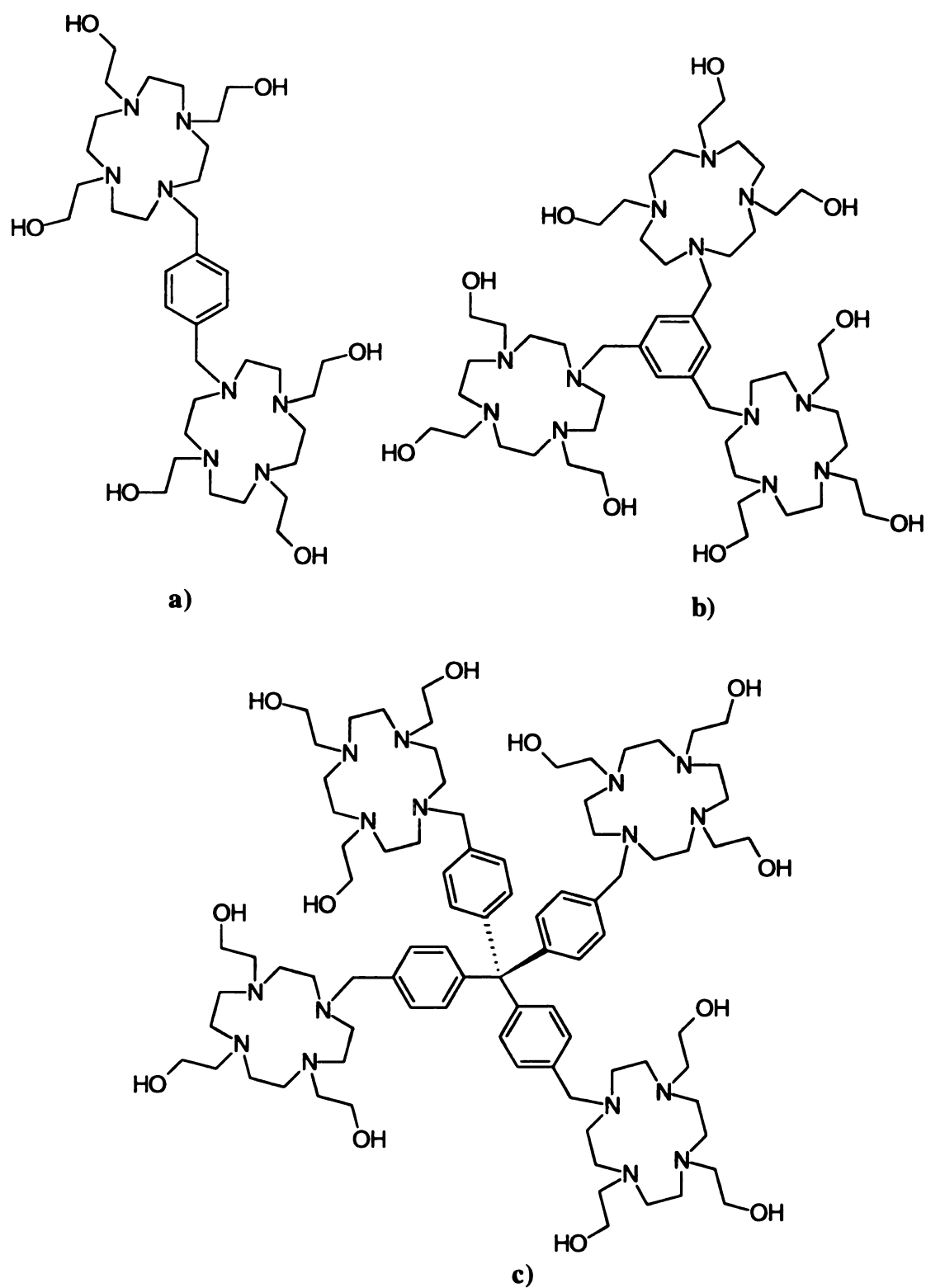


Figure 3.28. Prospective multidentate ligands for the construction of extended dihydrogen-bonded and covalent networks.

3.2. Conclusions

- Dihydrogen bonds can play an important role in defining solid-state supramolecular structures, comparable to conventional hydrogen bonds, as demonstrated by the crystal structures of all H...H bonded compounds studied, where this interaction significantly influenced the arrangement of molecules in crystals. Thus, with its capacity to control crystal packing, dihydrogen bonding, like traditional H-bonding, finds its place among the tools that chemists can use for supramolecular synthesis. The additional feature that makes this unconventional H-bonding particularly interesting is the ability to react, trading the weak H...H interactions for strong covalent bonds. As a direct consequence of this character, dihydrogen bonding has the potential to induce topochemical control, providing access to new materials otherwise not achievable.

- The NaBH₄·TEA complex has demonstrated the topochemical control concept. Its crystal structure shows multiple dihydrogen bonds between BH₄⁻ and the three OH groups from TEA. Loss of 3 moles of H₂ in the solid-state leads to a polymeric trialkoxyborohydride structure, whereas solution or melt decompositions yield NaBH₄ and a polymeric borate with no hydridic hydrogen left. Remarkably, more H₂ is lost in the solid-state decomposition than in the melt, despite the much higher reaction temperature in the latter (130 °C vs 82 °C). However, the product of the solid-state decomposition showed poor crystallinity and the reaction times were exasperatingly long due to the relatively low temperature required for decomposition in order to avoid melting.

- In addition to close H...H contacts, the relative acidity/basicity of the proton-hydride pairs significantly affect the solid-state reactivity of the dihydrogen-bonded systems. This was demonstrated by changing the H⁻ donor from BH₄⁻ to CNBH₃⁻ in the TEA complexes, which resulted in substantial decreases in dihydrogen bonding and solid-state reactivity.

- Fine-tuning of the dihydrogen bonds was possible in the TEA complexes by replacing the Li⁺ for Na⁺, which resulted in exceptionally short H...H contacts and enhanced solid-state reactivity. Decomposition of LiBH₄·TEA is also topochemical, apparently leading to a metastable one-dimensional polymeric trialkoxyborohydride structure, in direct contrast to decomposition in DMSO solution, which yielded a polymeric hydride free borate and unconverted LiBH₄, the disproportionation products. For comparison, no such disproportionation occurs during the solid-state decomposition, as demonstrated by H/D isotopic labeling experiments.

- The high solid-state reactivity of LiBH₄·TEA allowed the detailed study of the mechanism of H₂ loss and covalent bond formation in this dihydrogen-bonded complex, both at macroscopic and molecular level. Using in situ solid-state ¹¹B NMR and optical microscopy, it was found that, like most solid-state reactions, this decomposition is heterogeneous, with separation of the product phase from the parent crystal. Kinetic analysis and H/D exchange experiments established that proton transfer between the OH groups of the TEA and the BH₄⁻ anions, at the reactant/product interface, is the rate-limiting step, with activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 20.1 ± 2.4 kcal/mol and -16.8 ± 6.2 eu. These values are comparable with the analogous values found for the aqueous

hydrolysis of BH_4^- in neutral water, suggesting similar mechanisms for the solid and solution decompositions.

- Preservation of crystallinity was demonstrated to be possible in the topochemical dihydrogen to covalent bonding transformation of $\text{NaBH}_4\cdot\text{THEC}$, which was designed to satisfy both the closed loop and large globular cation geometrical criteria. Remarkably, its solid-state decomposition is a crystal-to-crystal process, as indicated by polarizing microscopy and powder XRD. However, the observed 9% shrinkage of the unit cell led to significant deterioration of the single crystals' quality, which in conjunction with the insolubility of the covalent product in organic solvents, precluded its detailed structural characterization. Nevertheless, this study is the first example to demonstrate that judicious engineering of dihydrogen-bonded crystals permits transfer of crystallinity to the covalent products resulting from their solid-state decomposition.

- Preliminary results suggest that NaBH_4 and various hydroxyethylcyclen ligands consistently self-assemble in dihydrogen-bonded dimers, as demonstrated by the crystal structure analysis of $\text{NaBH}_4\cdot\text{THEC}$, $\text{NaBH}_4\cdot\text{THPC}$, and $\text{NaBH}_4\cdot[9-(1',4',7'\text{-tris-hydroxyethyl-cyclen)methylanthracene}]\cdot\text{Et}_2\text{O}$. Consequently, incorporation of these dimeric building blocks in more elaborated systems may allow the rational construction of extended dihydrogen-bonded networks, and ultimately covalent solids, with controlled structures and functions.

3.3. Experimental Section

Materials. Common chemicals were purchased from commercial sources and used without further purification. *N*-[2-(6-Aminopyridyl)]-acetamidine hydrochloride was prepared by a literature procedure.¹²⁰ TEA-d₃ was obtained by repeated dissolution of TEA in D₂O (99.9% D) followed by removal of the water at 85 °C under vacuum, until the ¹H NMR (DMSO-d₆) signal for the OH protons completely disappeared. LiBD₄ was synthesized by metathesis,¹²¹ from NaBD₄ (98%D). THEC was prepared by a literature procedure.¹²² 1,4,7,10-Tetrakis((*S*)-2-hydroxypropyl)-1,4,7,10-tetraazacyclododecane (THPC) was synthesized from cyclen and *S*(-) propylene oxide.¹²³ 9-(1',4',7',10'-Tetraazacyclododecyl)methylanthracene was obtained by a literature procedure.¹¹⁹

Physical and Chemical Characterizations. Melting points were taken on a Thomas Hoover instrument and are uncorrected. FT-IR spectra were measured in KBr pellets on a Perkin Elmer Spectrum 2000 instrument. ¹H NMR (300.1 MHz) spectra were recorded on a Gemini-300 instrument. ¹³C NMR (75.4 MHz) and ¹¹B (96.23 MHz) NMR spectra were recorded on a Varian VXR-300 instrument. ¹¹B (128.33 MHz), ²³Na (105.81 MHz), and ⁷Li (155.44 MHz) solid-state MAS NMR spectra were measured on a Varian VXR-400 instrument. ¹¹B solution NMR chemical shifts were referenced to B(OCH₃)₃ in CDCl₃. ¹¹B solid state MAS NMR chemical shifts were referenced to solid boric acid; ²³Na and ⁷Li chemical shifts were referenced to solid NaCl and LiCl, respectively. A negative sign indicates chemical shifts upfield from references. X-ray powder diffraction measurements were conducted on a Rigaku-Denki RW400F2 diffractometer with monochromatic Cu K α radiation, operated at 45 kV and 100 mA. Optical micrographs

were obtained with a Nikon AFX-DX microscope equipped with a Mettler FP82HT hot stage. TGA was recorded on a CAHN TGSysystem 121 instrument at a heating rate of 5 °/min.

Hydridic Content Analyses. A 30-120 mg sample of the hydride-containing material was placed in a 50 mL side-armed round bottom flask, connected by a rubber tube to a 50 mL burette, half-filled with distilled water. About 10 mL of diluted HCl (1-2%) was rapidly added from a 25 mL addition funnel. The amount of the evolved H₂ was obtained by measuring the volume of the displaced water in the burette, after adjusting the gas pressure in the flask (by rising it to the corresponding height) to the atmospheric pressure. Typical uncertainty: ± 0.3 H⁻ equivalents.

In Situ ¹¹B MAS Solid State NMR. All spectra were recorded at a MAS frequency of 3.8 kHz, using 2.0 μ s $\pi/2$ pulses, with a recycle delay of 5 s, to allow full relaxation of all boron species.¹²⁴ For each experiment, 48 scans were acquired. The observed spectra were deconvoluted into Lorentzian lines, and the ratios of the resulting integrals, corresponding to product and starting material, respectively, were used to estimate the extent of decomposition.

Theoretical Calculations. All calculations were carried out with the GAUSSIAN 94 and 98 packages.¹²⁵ All structures were fully optimized and confirmed (except for the model of the decomposition product of **49**) by vibrational analysis to be minima on the potential energy surface.

Single Crystal X-Ray Structure Determination. X-Ray crystallographic measurements were carried out on a Siemens SMART CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), operated at 50 kV and 40 mA. The

structures were solved by direct methods and refined on F^2 using the SHELXTL software package.¹²⁶ Absorption corrections were applied using SADABS, part of the SHELXTL software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps and refined isotropically for all the structures. For the borohydride ions in **49**, however, only the hydridic hydrogens involved in dihydrogen bonding could be found, and the remaining H atoms from BH_4^- were calculated and placed in idealized positions. Similarly, for B(2)H_4^- in **51**, the two noninteracting hydridic hydrogens were calculated, and, in this case, the 4 H were subsequently constrained in an idealized tetrahedral geometry, with B-H distances of 1.21 Å.

Table 3.4. Crystal data and structure refinement for NAPA H₃BCN (44).

Empirical formula	C ₈ H ₁₄ BN ₅
Formula weight	191.05
Temperature	143(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.104(2)$ Å $b = 9.390(4)$ Å $c = 17.736(10)$ Å $\alpha = 99.38(4)^\circ$ $\beta = 95.99(4)^\circ$ $\gamma = 111.53(3)^\circ$
Volume	1068.3(9) Å ³
Z	4
Density (calculated)	1.188 g/cm ³
Absorption coefficient	0.077 mm ⁻¹
F(000)	408
Crystal size	0.6 x 0.3 x 0.15 mm
θ range for data collection	2.37 to 28.47°
Index ranges	$-8 \leq h \leq 8$, $-11 \leq k \leq 12$, $-10 \leq l \leq 23$
Reflections collected / unique	3118 / 3095 [R(int) = 0.0469]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3095 / 0 / 366
Goodness-of-fit on F ²	1.095
Final R indices [I>2 σ (I)]	R ₁ = 0.0455, wR ₂ = 0.1130
R indices (all data)	R ₁ = 0.0577, wR ₂ = 0.1238
Extinction coefficient	0.022(3)
Largest diff. peak and hole	0.262 and -0.163 eÅ ⁻³

Table 3.5. Crystal data and structure refinement for NaBH₄·TEA (45).

Empirical formula	C ₆ H ₁₉ BNNaO ₃
Formula weight	187.02
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 9.23510(10) Å b = 7.35120(10) Å c = 15.8083(2) Å α = 90° β = 103.6880(10)° γ = 90°
Volume	1042.73(2) Å ³
Z	4
Density (calculated)	1.191 g/cm ³
Absorption coefficient	0.123 mm ⁻¹
F(000)	408
Crystal size	0.52 x 0.38 x 0.31 mm
θ range for data collection	2.34 to 28.15°
Index ranges	-11 ≤ h ≤ 12, -9 ≤ k ≤ 9, -20 ≤ l ≤ 20
Reflections collected / unique	9787 / 2482 [R(int) = 0.0211]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2482 / 0 / 186
Goodness-of-fit on F ²	1.060
Final R indices [I > 2σ(I)]	R ₁ = 0.0250, wR ₂ = 0.0726
R indices (all data)	R ₁ = 0.0292, wR ₂ = 0.0743
Extinction coefficient	0.0102(31)
Largest diff. peak and hole	0.357 and -0.165 eÅ ⁻³

Table 3.6. Crystal data and structure refinement for NaNCBH₃·TEA (46).

Empirical formula	C ₇ H ₁₈ BN ₂ NaO ₃
Formula weight	212.03
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 7.55160(10) Å <i>b</i> = 15.1232(2) Å <i>c</i> = 10.57070(10) Å α = 90° β = 105.5380(10)° γ = 90°
Volume	1163.10(2) Å ³
Z	4
Density (calculated)	1.211 g/cm ³
Absorption coefficient	0.121 mm ⁻¹
F(000)	456
Crystal size	0.62 x 0.18 x 0.10 mm
θ range for data collection	2.41 to 28.17 deg.
Index ranges	-9 ≤ <i>h</i> ≤ 10, -19 ≤ <i>k</i> ≤ 20, -13 ≤ <i>l</i> ≤ 14
Reflections collected / unique	9974 / 2753 [<i>R</i> (int) = 0.0549]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	2753 / 0 / 199
Goodness-of-fit on <i>F</i> ²	1.053
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0352, <i>wR</i> ₂ = 0.0891
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0442, <i>wR</i> ₂ = 0.0945
Largest diff. peak and hole	0.232 and -0.219 eÅ ⁻³

Table 3.7. Crystal data and structure refinement for LiBH₄·TEA (47).

Empirical formula	C ₆ H ₁₉ BLiNO ₃
Formula weight	170.97
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁
Unit cell dimensions	<i>a</i> = 7.7156(5) Å <i>b</i> = 17.0039(11) Å <i>c</i> = 7.8656(5) Å α = 90° β = 98.1330(10)° γ = 90°
Volume	1021.55(11) Å ³
Z	4
Density (calculated)	1.112 g/cm ³
Absorption coefficient	0.081 mm ⁻¹
F(000)	376
Crystal size	0.44 x 0.23 x 0.21 mm
θ range for data collection	2.40 to 25.00°
Index ranges	-9 ≤ <i>h</i> ≤ 6, -17 ≤ <i>k</i> ≤ 20, -8 ≤ <i>l</i> ≤ 9
Reflections collected / unique	5330 / 3229 [R(int) = 0.0339]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3229 / 1 / 370
Goodness-of-fit on F ²	0.979
Final R indices [I > 2σ(I)]	R ₁ = 0.0417, wR ₂ = 0.0768
R indices (all data)	R ₁ = 0.0619, wR ₂ = 0.0839
Absolute structure parameter	1.7(10)
Extinction coefficient	0.015(3)
Largest diff. peak and hole	0.145 and -0.123 eÅ ⁻³

Table 3.8. Crystal data and structure refinement for NaBH₄·THEC (49).

Empirical formula	C ₁₆ H ₄₀ BN ₄ NaO ₄
Formula weight	386.32
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	I ₂₂₂
Unit cell dimensions	a = 8.8240(3) Å b = 14.1344(6) Å c = 17.3533(7) Å α = 90° β = 90° γ = 90°
Volume	2164.34(15) Å ³
Z	4
Density (calculated)	1.186 g/cm ³
Absorption coefficient	0.100 mm ⁻¹
F(000)	848
Crystal size	0.23 x 0.18 x 0.13 mm
θ range for data collection	1.86 to 28.20°
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -22 ≤ l ≤ 22
Reflections collected / unique	12854 / 2608 [R(int) = 0.0979]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2608 / 11 / 200
Goodness-of-fit on F ²	1.029
Final R indices [I > 2σ(I)]	R ₁ = 0.0487, wR ₂ = 0.1221
R indices (all data)	R ₁ = 0.0599, wR ₂ = 0.1399
Absolute structure parameter	0.7(5)
Extinction coefficient	0.0027(9)
Largest diff. peak and hole	0.488 and -0.250 eÅ ⁻³

Table 3.9. Crystal data and structure refinement for the decomposition product of NaBH₄·THEC in DMSO.

Empirical formula	C ₁₆ H ₃₄ BN ₄ NaO ₅
Formula weight	396.27
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 8.76960(10) Å <i>b</i> = 13.05710(10) Å <i>c</i> = 17.7724(2) Å α = 90° β = 96.36° γ = 90°
Volume	2022.50(4) Å ³
Z	4
Density (calculated)	1.301 g/cm ³
Absorption coefficient	0.112 mm ⁻¹
F(000)	856
Crystal size	0.47 x 0.39 x 0.29 mm
θ range for data collection	1.94 to 28.26°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -16 ≤ <i>k</i> ≤ 17, -23 ≤ <i>l</i> ≤ 22
Reflections collected / unique	20248 / 4840 [<i>R</i> (int) = 0.0261]
Absorption correction	None
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4840 / 0 / 462
Goodness-of-fit on <i>F</i> ²	1.043
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0352, <i>wR</i> ₂ = 0.0921
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0439, <i>wR</i> ₂ = 0.0966
Extinction coefficient	0.0000(9)
Largest diff. peak and hole	0.261 and -0.250 eÅ ⁻³

Table 3.10. Crystal data and structure refinement for NaNCBH₃·THEC (**50**).

Empirical formula	C ₁₇ H ₃₉ BN ₅ NaO ₄
Formula weight	411.33
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2 ₁
Unit cell dimensions	<i>a</i> = 25.2624(3) Å <i>b</i> = 9.4053(2) Å <i>c</i> = 9.4430(2) Å α = 90° β = 90° γ = 90°
Volume	2243.66(7) Å ³
Z	4
Density (calculated)	1.218 g/cm ³
Absorption coefficient	0.102 mm ⁻¹
F(000)	896
Crystal size	0.65 x 0.29 x 0.26 mm
θ range for data collection	1.61 to 28.20°
Index ranges	-32 ≤ <i>h</i> ≤ 32, -12 ≤ <i>k</i> ≤ 12, -12 ≤ <i>l</i> ≤ 12
Reflections collected / unique	22515 / 5336 [<i>R</i> (int) = 0.0187]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	5336 / 1 / 410
Goodness-of-fit on <i>F</i> ²	1.022
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0251, <i>wR</i> ₂ = 0.0637
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0276, <i>wR</i> ₂ = 0.0646
Absolute structure parameter	0.07(17)
Extinction coefficient	0.0058(9)
Largest diff. peak and hole	0.205 and -0.125 eÅ ⁻³

Table 3.11. Crystal data and structure refinement for NaBH₄·THPC (51).

Empirical formula	C ₂₀ H ₄₈ BN ₄ NaO ₄
Formula weight	442.42
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁
Unit cell dimensions	<i>a</i> = 9.7915(4) Å <i>b</i> = 18.1449(7) Å <i>c</i> = 14.6111(6) Å α = 90° β = 96.867(2)° γ = 90°
Volume	2577.27(18) Å ³
Z	4
Density (calculated)	1.140 g/cm ³
Absorption coefficient	0.092 mm ⁻¹
F(000)	976
Crystal size	0.49 x 0.41 x 0.18 mm
θ range for data collection	1.80 to 28.24°
Index ranges	-12 ≤ <i>h</i> ≤ 12, -24 ≤ <i>k</i> ≤ 24, -19 ≤ <i>l</i> ≤ 16
Reflections collected / unique	23846 / 11681 [<i>R</i> (int) = 0.0198]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	11681 / 20 / 923
Goodness-of-fit on <i>F</i> ²	0.789
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0358, <i>wR</i> ₂ = 0.0968
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0428, <i>wR</i> ₂ = 0.1023
Absolute structure parameter	0.09(18)
Largest diff. peak and hole	0.517 and -0.203 eÅ ⁻³

Table 3.12. Crystal data and structure refinement for 9-(1',4',7'-tris-hydroxyethyl-cyclen)methylantracene (**52**).

Empirical formula	C ₂₉ H ₄₂ N ₄ O ₃
Formula weight	494.67
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.7352(3) Å b = 12.2971(4) Å c = 13.7789(3) Å α = 69.152(2)° β = 79.456(2)° γ = 78.736(2)°
Volume	1346.11(7) Å ³
Z	2
Density (calculated)	1.220 g/cm ³
Absorption coefficient	0.080 mm ⁻¹
F(000)	536
Crystal size	0.39 x 0.18 x 0.08 mm
θ range for data collection	1.59 to 28.27°
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 15, -18 ≤ l ≤ 17
Reflections collected / unique	12550 / 6195 [R(int) = 0.0383]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6195 / 0 / 489
Goodness-of-fit on F ²	1.268
Final R indices [I > 2σ(I)]	R ₁ = 0.0825, wR ₂ = 0.2187
R indices (all data)	R ₁ = 0.1467, wR ₂ = 0.2369
Largest diff. peak and hole	1.571 and -0.708 eÅ ⁻³

Table 3.13. Crystal data and structure refinement for $\text{NaBH}_4 \cdot [9-(1',4',7'\text{-tris-hydroxyethyl-cyclen})\text{methylantracene}] \cdot \text{Et}_2\text{O}$ (**53**).

Empirical formula	$\text{C}_{33}\text{H}_{56}\text{BN}_4\text{NaO}_4$
Formula weight	590.62
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 12.7329(6)$ Å $b = 19.0589(2)$ Å $c = 13.7260(6)$ Å $\alpha = 90^\circ$ $\beta = 95.459(2)^\circ$ $\gamma = 90^\circ$
Volume	$3315.8(2)$ Å ³
Z	4
Density (calculated)	1.183 g/cm^3
Absorption coefficient	0.086 mm^{-1}
F(000)	1288
Crystal size	0.49 x 0.18 x 0.13 mm
θ range for data collection	1.83 to 28.25°
Index ranges	$-16 \leq h \leq 16$, $-25 \leq k \leq 25$, $-18 \leq l \leq 18$
Reflections collected / unique	30419 / 7907 [$R(\text{int}) = 0.0676$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7907 / 0 / 541
Goodness-of-fit on F^2	1.027
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0672$, $wR_2 = 0.1646$
R indices (all data)	$R_1 = 0.1547$, $wR_2 = 0.1969$
Largest diff. peak and hole	0.767 and -0.478 eÅ^{-3}

Syntheses:

***N*-[2-(6-Aminopyridyl)]-acetamidine cyanoborohydride (44).** 2.61 g (0.014 mol) of *N*-[2-(6-Aminopyridyl)]-acetamidine hydrochloride and 0.88 g (0.014 mol) of NaNCBH₃ were dissolved in 65 mL methanol and the resulting clear solution was left standing at rt for 12 h. After the removal of methanol *in vacuo*, 20 mL of THF were added and the solution was filtered. The filtrate was concentrated *in vacuo* and 100 mL of CH₂Cl₂ were added. The resultant precipitate was collected to yield 2 g (75%) of product as a white solid. X-Ray quality crystals were grown by diffusion of cyclohexane vapors into an isopropanol solution of **44**. Mp = 119-120 °C; IR (KBr): ν_{BH} = 2338, 2219 cm⁻¹, ν_{CN} = 2168 cm⁻¹; ¹H NMR (DMSO-d₆): δ 7.47 (t, *J* = 8 Hz, 1H, py), 6.52 (s, 2H, py), 6.26 (t, *J* = 8 Hz, 2H, py), 2.31 (s, 3H, CH₃), 0.21 (q, *J*_{BH} = 88.5 Hz, 3H, NCBH₃); ¹¹B NMR (DMSO-d₆): δ - 55.95 (q, *J*_{BH} = 88.8 Hz, NCBH₃); ¹³C NMR (DMSO-d₆): δ 164.0, 158.1, 150.6, 140.1, 104.4, 100.1, 20.0. Anal. Calcd for C₈H₁₄N₃B: C, 50.26; H, 7.33; N, 36.65. Found: C, 49.64; H, 7.57; N, 36.11.

NaBH₄·TEA (45). A mixture of 0.38 g (0.01 mol) NaBH₄ and 2.8 mL (0.02 mol) triethanolamine in 25 mL THF was stirred at rt for 2 h. Filtration of the precipitate obtained and washing with THF yielded 0.95 g (51%) of **45**. Crystals suitable for X-Ray crystallography were obtained by slow cooling of a solution of **45** in isobutanol from rt to -25 °C. Mp = 107-108 °C (dec.); IR (KBr): ν_{BH} = 2288 cm⁻¹; ¹H NMR (pyridine-d₅): δ 6.68 (br, 3H, OH), 3.87 (t, *J* = 5.1 Hz, 6H, OCH₂), 2.67 (t, *J* = 5.1 Hz, 6H, NCH₂), 1.30 (q, *J*_{BH} = 81.3 Hz, 4H, BH₄); ¹¹B NMR (DMSO-d₆): δ -49.28 (quintet, *J*_{BH} = 81.4 Hz, BH₄); ¹¹B MAS NMR (6000 Hz): δ - 47.9 ($\Delta\nu_{1/2}$ = 1826 Hz); ¹³C NMR (DMSO-d₆): δ

58.9 (OCH₂), 56.9 (NCH₂); ²³Na MAS NMR (6029 Hz): δ -9.9 (Δν_{1/2} = 1649 Hz). Anal. Calcd for C₆H₁₉NO₃BNa: C, 38.50; H, 10.16; N, 7.49. Found: C, 38.09; H, 10.47; N, 7.39; H⁺ content: 4.11.

NaNCBH₃·TEA (46). A mixture of 0.63 g (0.01 mol) of NaCNBH₃ and 1.4 mL (0.01 mol) of triethanolamine in 30 mL isopropanol was stirred at rt for 2 h. The undissolved material was filtered out and the isopropanol was slowly evaporated from the filtrate using a gentle stream of nitrogen. When it was almost dry, 50 mL of CH₂Cl₂ were added and the white solid was collected. Yield 1.1 g (52%). X-Ray quality crystals were grown by slow evaporation of a solution of **46** in isopropanol. Mp = 85-86 °C; IR (KBr): ν_{BH} = 2341 cm⁻¹, ν_{CN} = 2180 cm⁻¹; ¹H NMR (CH₃CN-d₃): δ 3.55 (t, *J* = 5.4 Hz, 6H, OCH₂), 3.46 (s, 3H, OH), 2.52 (t, *J* = 5.4 Hz, 6H, NCH₂), 0.26 (q, *J*_{BH} = 88.6, 3H, NCBH₃); ¹¹B NMR (DMSO-d₆): δ -55.9 (q, *J*_{BH} = 88.6, NCBH₃); ¹³C NMR (DMSO-d₆): δ 59.0 (OCH₂), 56.9 (NCH₂). Anal. Calcd for C₇H₁₈N₂O₃BNa: C, 39.62; H, 8.49; N, 13.21. Found: C, 38.73; H, 9.23; N, 13.21.

LiBH₄·TEA (47). 0.22 g (10 mmol) LiBH₄ and 1.4 mL (10 mmol) TEA were dissolved in 20 mL 2-propanol. Slow evaporation of most of the solvent under Ar followed by addition of 20 mL CH₂Cl₂ afforded 0.95 g (56 %) complex. X-Ray quality crystals were grown by diffusion of a diethyl ether layer into a solution of **47** in 2-propanol. ¹H NMR (CH₃CN-d₃): δ = 4.21 (s, 3H; OH), 3.60 (t, *J* = 5.1 Hz, 6H; OCH₂), 2.58 (t, *J* = 5.1 Hz, 6H; NCH₂), -0.23 (q, *J*_{BH} = 81.0 Hz, 4H; BH₄); ¹³C NMR (CH₃CN-d₃): δ 53.5 (NCH₂), 58.4 (OCH₂); ¹¹B NMR (CH₃CN-d₃): δ -55.98 (quintet, *J*_{BH} = 80.9 Hz; BH₄); ¹¹B MAS NMR (5997 Hz): δ -48.7 (Δν_{1/2} = 1586 Hz); ⁷Li MAS NMR (6000

Hz): δ 2.8 ($\Delta\nu_{1/2}$ = 1735 Hz); IR (KBr): ν_{BH} = 2290 cm^{-1} ; Anal. Calcd for $\text{C}_6\text{H}_{19}\text{O}_3\text{NBLi}$: C, 42.15; H, 11.11; N, 8.19. Found: C, 42.39; H, 11.56; N, 8.17.

$\text{LiBH}_4\cdot\text{TEA-d}_3$. A mixture of 0.22 g (10 mmol) of LiBH_4 and 1.4 mL (10.3 mmol) of TEA-d_3 in 30 mL THF was stirred under Ar at rt for 1 h. The resulting precipitate was filtered and washed with THF. Yield quantitative. ^1H NMR ($\text{CH}_3\text{CN-d}_3$): no OH signal; IR (KBr): ν_{OD} = 2516 cm^{-1} ; Anal. hydridic content: 4.06.

$\text{LiBD}_4\cdot\text{TEA}$ (47a). A mixture of 0.065 g (2.5 mmol) of LiBD_4 and 0.4 g (2.7 mmol) TEA in 8 mL THF was stirred under Ar at rt for 2h. The resulting precipitate was filtered and washed with THF. IR (KBr): ν_{BD} = 1704, 1652 cm^{-1} ; Anal. hydridic content: 3.90, 90% D based on ^1H NMR (DMSO-d_6).

LiBH_4 (50% D) $\cdot\text{TEA}$ (47b). A mixture of 0.044 g (2 mmol) of LiBH_4 and 0.052 g (2 mmol) of LiBD_4 was dissolved in 12 mL THF. An amount of 0.64 g (4.3 mmol) of TEA was subsequently added and the mixture was stirred under Ar at rt for 2h. The resulting precipitate was collected and washed with THF. IR (KBr): ν_{BD} = 1752, 1703, 1649 cm^{-1} , ν_{BH} = 2384, 2292, 2226 cm^{-1} ; Anal. hydridic content: 3.80, 54% D based on ^1H NMR (DMSO-d_6).

$\text{NaBH}_4\cdot\text{THEC}$ (49). 0.038 g (1 mmol) of NaBH_4 were dissolved in 10 mL 2-propanol and an amount of 0.366 g (1 mmol) of $\text{THEC}\cdot\text{H}_2\text{O}$ was subsequently added. After approximately 1 min a white precipitate was formed. The mixture was stirred for 1 h at rt under an Ar atmosphere. Filtration of the mixture yielded 0.3 g (78%) of **49**. Single crystals suitable for X-ray crystallography were grown by diffusion of Et_2O in a solution of **49** in CH_3CN . Mp = 180-181 $^\circ\text{C}$ (dec.); IR (KBr): ν_{BH} = 2298, 2225 cm^{-1} ; ^1H NMR (pyridine-d_5): δ 6.03 (br s, 4H, OH), 3.85 (t, J = 4.5 Hz, 8H, OCH_2), 2.49-2.41 (br, 24H,

NCH₂), 1.51 (q, $J_{\text{BH}} = 81.3$ Hz, 4H, BH₄); ¹³C NMR (CH₃CN-d₃): δ 51.17 (NCH₂), 56.45 (NCH₂), 58.96 (OCH₂); ¹¹B NMR (CH₃CN-d₃): δ -54.21 (quintet, $J_{\text{BH}} = 81.4$ Hz, BH₄); ¹¹B MAS NMR (4013 Hz): δ -45.4 ($\Delta\nu_{1/2} = 2198$ Hz); ²³Na MAS NMR (6028 Hz): δ -12.3 ($\Delta\nu_{1/2} = 1440$ Hz). Anal. Calcd for C₁₆H₄₀N₄O₄BNa: C, 49.74; H, 10.36; N, 14.51. Found: C, 49.37; H, 10.87; N, 14.80.

NaNCBH₃·THEC (50). A solution of 0.032 g (0.5 mmol) of NaNCBH₃ in 3 mL THF was added to 0.183 g (0.5 mmol) THEC·H₂O in THF. A white precipitate was formed immediately. The mixture was stirred 1 h at rt under an Ar atmosphere. The solid was subsequently filtered and washed with THF to yield 0.17 g (83%) of **50**. Single crystals suitable for X-ray crystallography were grown by diffusion of Et₂O in a solution of **50** in CH₃CN. Mp = 230-234 °C (dec.); IR (KBr): $\nu_{\text{BH}} = 2348$ cm⁻¹, $\nu_{\text{CN}} = 2162$ cm⁻¹; ¹H NMR (CH₃CN-d₃): δ 3.61 (t, $J = 4.8$ Hz, 8H, OCH₂), 3.25 (br s, 4H, OH), 2.47 (br, 24H, NCH₂), 0.25 (q, 3H, NCBH₃); ¹³C NMR (CH₃CN-d₃): δ 51.17 (NCH₂), 56.50 (NCH₂), 59.06 (OCH₂); ¹¹B NMR (CH₃CN-d₃): δ -56.60 (q, $J_{\text{BH}} = 88.3$ Hz, NCBH₃).

NaBH₄·THPC (51). 0.285 g (0.7 mmol) of THPC were added to a solution of 0.027 g (0.7 mmol) in 8 ml 2-propanol. In approximately 2 min a white precipitate was formed. The mixture was left standing for 1 h at rt, then the solid was filtered. Yield 0.085 g (27%). No melting occurs when the solid is heated up to 200 °C, at which temperature it turns brown, and eventually starts to melt at approximately 210 °C. Single crystals suitable for X-ray crystallography were grown by slow evaporation from 2-propanol. IR (KBr): $\nu_{\text{BH}} = 2290$ cm⁻¹; ¹H NMR (H₂O-d₂): δ 3.89 (br m, 4H, OCH), 2.90-2.87 (br d, 8H, NCH₂), 2.42-2.34 (br t, 4H, NCH₂), 2.09 (br s, 12 H, NCH₂) -0.27 (q, $J_{\text{BH}} = 80.72$ Hz, 4H, BH₄); ¹³C NMR (DMSO-d₆): δ 21.79 (CH₃), 49.17 (br, NCH₂), 51.03

(br, NCH₂), 61.58 (NCH₂), 62.31 (OCH₂); ¹¹B NMR (DMSO-d₆): δ -52.55 (quintet, *J*_{BH} = 82.8 Hz, BH₄); Anal. Calcd for C₂₀H₄₈N₄O₄BNa: C, 54.30; H, 10.86; N, 12.67. Found: C, 54.66; H, 11.39; N, 12.41.

9-(1',4',7'-tris-hydroxyethyl-cyclen)methylantracene (52). Warning: Ethylene oxide is a volatile (Bp = 11 °C), extremely toxic, carcinogenic substance. 0.2 g (0.57 mmol) of 9-(1',4',7',10'-tetraazacyclododecyl)methylantracene were dissolved in 3 mL absolute ethanol. 2 mL of water were added, and the solution was cooled to 0 °C. To this solution, 0.158 g (3.6 mmol) of ethylene oxide (cooled to 0 °C) were added, and the mixture was stirred at 0 °C for 2 h, and then another hour at rt. Solvent evaporation under vacuum at 35 °C yielded a yellow oil. A few mL of water were subsequently added, and the resulting aqueous solution was extracted with chloroform. Evaporation of CHCl₃ yielded a yellow oil, which was dissolved in minimal amount of 2-propanol, and a large excess of ether was added. Upon standing in the freezer over night, a yellow crystalline solid precipitated, which was filtered and washed with ether, to yield 0.12 g (42%) of **52**. Single crystals suitable for X-ray crystallography were grown by diffusion of Et₂O in a solution of **52** in 2-propanol. Mp = 131-133 °C; ¹H NMR (CH₃Cl-d₃): δ 8.36 (d, 2H, ArH), 8.29 (s, 1H, ArH), 7.87 (d, 2H, ArH), 7.38 (m, 4H, ArH), 4.8 (br, OH), 4.39 (s, 2H, CH₂-Ar), 3.47 (t, *J* = 4.5 Hz, 2H, OCH₂), 3.40 (t, *J* = 4.5 Hz, 4H, OCH₂), 2.73 (t, *J* = 4.5 Hz, 6H, NCH₂), 2.43-2.32 (br, 16H, NCH₂); ¹³C NMR (CH₃Cl-d₃): δ 130.83, 128.51, 127.11, 125.32, 124.50, 58.35, 58.01, 57.73, 55.65, 52.37, 52.11, 51.90, 50.88, 50.56; Anal. Calcd for C₂₉H₄₂N₄O₃: C, 70.45; H, 8.50; N, 11.34. Found: C, 70.23; H, 8.83; N, 11.04.

NaBH₄·[9-(1',4',7'-tris-hydroxyethyl-cyclen)methylanthracene]·iPrOH (53).

0.1 g (0.2 mmol) of 9-(1',4',7'-tris-hydroxyethyl-cyclen)methylanthracene were added to a solution of 0.008 g (0.21 mmol) of NaBH₄ in 4 mL 2-propanol. In approximately 4 min a white precipitate was formed. The mixture was stirred 2 h at rt under an Ar atmosphere, and subsequently filtered to yield 0.09 g (53%) of **53**. The solid turns red when heated, and partly melts at 190 °C. Single crystals suitable for X-ray crystallography were grown by diffusion of Et₂O in a solution of **53** in CH₃CN. IR (KBr): ν_{BH} = 2384, 2293, 2228 cm⁻¹; ¹H NMR (CH₃CN-d₃): δ 8.54 (s, 1H, ArH), 8.43 (d, 2H, ArH), 8.06 (d, 2H, ArH), 7.60 (m, 2H, ArH), 7.49 (m, 2H, ArH), 4.61 (s, 2H, CH₂-Ar), 3.72 (septet, 1H, iPrOH), 3.6-1.9 (br), 1.08 (d, 6H, iPrOH); ¹³C NMR (CH₃CN-d₃): δ 132.47, 130.23, 128.98, 127.77, 126.22, 125.46, 58.54, 57.98, 56.54, 56.15, 54.51, 52.65, 51.59, 51.26, 50.74; ¹¹B NMR (CH₃CN-d₃): δ -53.75 (quintet, J_{BH} = 80.4 Hz, BH₄); Anal. Calcd for C₃₂H₅₄N₄O₄NaB: C, 64.87; H, 9.12; N, 9.46. Found: C, 64.20; H, 9.06; N, 9.33.

Decomposition Studies:

Solid-State Decomposition of NaBH₄·TEA. 0.5-0.7 g of NaBH₄·TEA were heated at 82 °C under Ar or open atmosphere in a 7 × 27 mm glass tube immersed in refluxing acetonitrile, for 30-58 days. The resulting white solid is insoluble in common organic solvents and it does not melt up to 300 °C. The powder XRD shows a single phase with a broad peak at $2\theta = 9.4^\circ$ but no NaBH₄ or initial complex. IR (KBr): ν_{BH} = 2387, 2293, 2226 cm⁻¹; ¹¹B MAS NMR (6058 Hz): δ -7.1 ($\Delta\nu_{1/2}$ = 1390 Hz); ²³Na MAS

NMR (6004 Hz): δ -14.6 ($\Delta\nu_{1/2}$ = 2769 Hz). Anal. N/B/Na = 1/1/0.96; H⁻ content: 1.05-1.38.

Decomposition of NaBH₄·TEA in DMSO. A solution of 0.5 g of NaBH₄·TEA in 10 mL DMSO was heated at 110 °C under Ar for 55 h. The resulting precipitate was collected and washed with CH₂Cl₂ to yield 0.17 g of white solid insoluble in common organic solvents. Mp > 300 °C; IR (KBr): no B-H stretching vibration; ¹¹B MAS NMR (6000 Hz): δ -5.0 ($\Delta\nu_{1/2}$ = 1559 Hz); ²³Na MAS NMR (6011 Hz): δ -13.5 ($\Delta\nu_{1/2}$ = 2665 Hz). Anal. H⁻ content: 0.22.

Decomposition of NaBH₄·TEA in the Melt. 0.5 g of NaBH₄·TEA were placed in a 21 × 50 mm vial and heated under Ar at 130 °C in an oil bath for two hours. In about 1 min the solid melted with effervescence. After approximately another 10 min the melt solidified. The powder XRD confirmed the presence of NaBH₄. ¹¹B MAS NMR (5998 Hz): δ -2.3 ($\Delta\nu_{1/2}$ = 1394 Hz, 1 B), δ -50.4 ($\Delta\nu_{1/2}$ = 1017 Hz 1.2 B). Anal. H⁻ content: 2.03.

Solid-State Decomposition of LiBH₄·TEA. Aliquots of 0.1-0.5 g of LiBH₄·TEA were placed in a 21 × 50 mm vial and were preheated under Ar at 80-100 °C for 10-15 min. The temperature was subsequently raised to 120-130 °C, and heating was continued for about 2 h. The resulting white solid is insoluble in common organic solvents and it does not melt up to 300 °C. IR (KBr): ν_{BH} = 2301, 2247, 2171 cm⁻¹; ¹¹B MAS NMR (6000 Hz): δ -4.6 ($\Delta\nu_{1/2}$ = 1693 Hz); ⁷Li MAS NMR (6000 Hz): δ 3.1 ($\Delta\nu_{1/2}$ = 1611 Hz). Anal. H⁻ content: 0.97-1.08.

Annealing of the LiBH₄·TEA Solid-State Decomposition Product. A

suspension of 0.07 g of the solid-state decomposition product **48** ($H^- = 1.05$) in 5 mL of freshly distilled DMSO was heated at 120 °C under an Ar atmosphere for 4 days, then filtered and the resulting solid was washed with CH₂Cl₂. IR (KBr): $\nu_{BH} = 2368, 2340$ cm⁻¹; ¹¹B MAS NMR (6000 Hz): δ -3.3 ($\Delta\nu_{1/2} = 1677$ Hz); ⁷Li MAS NMR (3540 Hz): δ 1.0 ($\Delta\nu_{1/2} = 2496$ Hz). Anal. H^- content: 1.05.

Decomposition of LiBH₄·TEA in DMSO. A solution of 0.5 g of LiBH₄·TEA in 10 mL DMSO was heated at 120 °C under Ar for 4 days. The resulting precipitate was collected and washed with CH₂Cl₂. Yield 0.2 g. Mp > 300 °C; IR (KBr): no B-H; ¹¹B MAS NMR (6000 Hz): δ -5.9 ($\Delta\nu_{1/2} = 1726$ Hz). Anal. H^- content: 0.26.

H/D Isotope Exchange Experiments. Aliquots of 0.1-0.3 g of LiBH₄·TEA-d₃ were heated under Ar at 85-110 °C, monitoring the decompositions by H^- analysis. The partly or fully decomposed samples were analyzed by IR (KBr) and ¹H NMR (CH₃CN-d₃). No signals for the ν_{BD} in the IR or for OH in the ¹H NMR spectra were observed throughout the reaction.

Reaction of the LiBH₄·TEA Solid-State Decomposition Product (48**) with Pd(AcO)₂.** A sample of 0.1 g (≈ 0.61 miliequivalents of H^-) of the solid-state decomposition product **48** was suspended in 10 mL freshly distilled THF containing 0.136 g (0.61 mmol) Pd(AcO)₂. The mixture was stirred at rt under an Ar atmosphere for 24 h. After filtering and washing with THF, a green hygroscopic powder was obtained, which turned into a black paste if left in open atmosphere. Powder XRD analysis showed that this compound was completely amorphous, and no Pd black, or unconverted Pd(AcO)₂ was present. IR (KBr): $\nu_{AcO} = 1580$ cm⁻¹; no B-H; ¹H NMR (DMSO-d₆): very

complex, and indicates the presence of at least three different AcO groups: δ 1.72, 1.69, 1.63. ^{13}C NMR (DMSO- d_6): δ 22.94, 24.02, 25.17, 59.20, 61.64, 64.43, 66.26, 67.08; ^{11}B NMR (DMSO- d_6): δ -14.61.

Solid-State Decomposition of $\text{NaBH}_4\cdot\text{THEC}$. A sample of 0.07 g of $\text{NaBH}_4\cdot\text{THEC}$ was heated at 160 °C under an Ar atmosphere for 20 h. The resulting white solid is insoluble in common organic solvents and it does not melt up to 300 °C. IR (KBr): no B-H; ^{11}B MAS NMR (4038 Hz): δ -8.0 ($\Delta\nu_{1/2}$ = 2462 Hz); ^{23}Na MAS NMR (6001 Hz): δ -15.6 ($\Delta\nu_{1/2}$ = 3421 Hz).

Decomposition of $\text{NaBH}_4\cdot\text{THEC}$ in the Melt. A sample of 0.04 g of $\text{NaBH}_4\cdot\text{THEC}$ was rapidly heated to 200 °C under Ar. Melting occurred under these conditions, followed by immediate solidification. Heating was continued for 10 min. The IR spectrum of the resulting solid is virtually identical with the corresponding spectrum of the solid-state decomposition product. Powder XRD indicates an amorphous phase, and annealing at 160 °C for 24 h did not improve its crystallinity. ^{11}B MAS NMR (6000 Hz): δ -6.9 ($\Delta\nu_{1/2}$ = 1745 Hz); ^{23}Na MAS NMR (6000 Hz): δ -8.9 ($\Delta\nu_{1/2}$ = 2704 Hz).

Decomposition of $\text{NaBH}_4\cdot\text{THEC}$ in DMSO. A solution of 0.15 g of $\text{NaBH}_4\cdot\text{THEC}$ in 5 mL DMSO was heated at 120 °C under Ar for 48 h. A crystalline solid precipitated, which was filtered and washed with CH_2Cl_2 . Yield 0.13 g. ^{11}B MAS NMR (6060 Hz): δ -7.5 ($\Delta\nu_{1/2}$ = 1880 Hz); ^{23}Na MAS NMR (6058 Hz): δ -9.0 ($\Delta\nu_{1/2}$ = 2476 Hz).

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