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Hydrogen Splitting

Intramolecular Frustrated Lewis Pair with the Smallest Boryl Site: Reversible H_2 Addition and Kinetic Analysis**

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Abstract: *Ansa-aminoborane **1** (ortho-TMP–C_6H_4–BH_2; TMP = 2,2,6,6-tetramethylpiperid-1-yl), a frustrated Lewis pair with the smallest possible Lewis acidic boryl site (–BH_2), is prepared. Although it is present in quenched forms in solution, and BH_2 represents an acidic site with reduced hydride affinity, **1** reacts with H_2 under mild conditions producing ansa-ammonium trihydroborate **2**. The thermodynamic and kinetic features as well as the mechanism of this reaction are studied by variable-temperature NMR spectroscopy, spin-saturation transfer experiments, and DFT calculations, which provide comprehensive insight into the nature of **1**.*

A bifunctional approach using sterically hindered Lewis acid/base partners, so-called “frustrated Lewis pairs” (FLPs), has recently been employed to the activation of small molecules by heterolytic cleavage of σ- or π-bonds.[1] Hydrogen activation has been of particular interest in these studies as a number of inter- and intramolecular FLPs were shown to act as efficient metal-free catalysts for the hydrogenation of unsaturated bonds.[2] Heterolytic splitting of molecular hydrogen into the H^+/H^- pair is a highly endergonic process and requires the involvement of powerful Lewis donors and acceptors. To accomplish this reactivity, the active centers of an FLP have to be prevented from forming strong dative bonds, which would result in conventional Lewis adducts. This is usually achieved by means of steric encumbrance.

Originally, FLPs consisted of pentafluorophenyl boranes in combination with sterically crowded phosphines or amines or other strong, bulky bases.[3] However, soon after the first discoveries, variations of the nature of the Lewis acids and bases expanded the borders of FLP chemistry and improved comprehension. For example, the use of weaker bases was shown to accelerate the reduction of polar substrates[4] and enabled the hydrogenation of non-polar unsaturated bonds.[5] The use of moderately Lewis acidic[6] or highly sterically hindered boranes[7] resulted in pronounced functional-group tolerance. Furthermore, the asymmetric hydrogenation of imines could be induced by chiral boranes.[4,8] FLPs with cationic metallic[9] or borenium[10] Lewis acids are conceptual derivatives of the original idea as well.

Recently, we have been pursuing the development of intramolecular nitrogen/boron FLPs (so-called *ansa*-aminoboranes with the N and B centers in close vicinity), with a main emphasis on their application in catalytic hydrogenation processes (Figure 1).[11] In continuation of our efforts, we are currently targeting easily accessible *ansa*-aminoboranes with elementary substituents on the acidic site.[12] The acid–base strength of the active sites is of primary focus in designing new FLPs. According to the Gutmann–Beckett and Childs acidity scales, the Lewis acidity of inorganic boranes BX_3 (X = H or halogen) is comparable to that of the commonly used borane $B(C_6F_5)_3$.[13] However, computations suggest that BX_3 molecules are weaker acids in terms of their solution-phase hydride affinities; therefore, the $C_6F_5 \rightarrow X$ replacement and the use of BX_2 boryl groups cannot be justified a priori.[14,15] Another critical issue in our approach is the reduced size of the BX_2 unit, which may restrict the reactivity by different quenching modes. However, we anticipated that the rigid framework of *ortho*-phenylene-bridged aminoboranes, especially with bulky amines, can notably hinder the formation of strong intra- and intermolecular dative bonds. Moreover, the short *ortho*-phenylene linker appears to enhance the acid–base cooperativity in dihydrogen activation, giving rise to favorable thermodynamics for heterolytic H_2 splitting.[16]

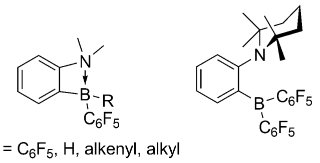

Figure 1. Previously studied *ortho*-phenylene-linked aminoboranes with sterically less (NMe_2) and more (2,2,6,6-tetramethylpiperidyl) demanding amino components.

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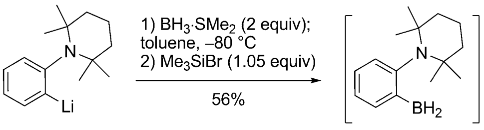
We have previously shown that the aminoborane *ortho*-TMP–C_6H_4–$B(C_6F_5)_2$ (TMP = 2,2,6,6-tetramethylpiperidyl) reacts instantly with H_2 producing thermally stable ammonium borate species.[11b] Herein, we report the synthesis and structural characterization of the BH_2 analogue of this compound, that is, aminoborane *ortho*-TMP–C_6H_4–BH_2 (**1**). In comparison to previously reported FLPs, **1** has several exceptional properties, such as a lower molecular weight, reduced Lewis acidity, and a small acidic boryl site, rendering this compound unique among the FLPs that have been characterized thus far. We demonstrate that **1** reversibly activates dihydrogen under mild conditions. The thermodynamics and kinetics of this reaction are examined in detail in a combined experimental/computational study. The thermodynamic equilibrium of H_2 addition allows the application of spin-saturation transfer NMR techniques to measure the reaction rate and to obtain accurate kinetic data for FLP-mediated H_2 activation.

Ansa-aminoborane **1** was prepared by sequential treatment of *ortho*-TMP-phenyllithium with $BH_3 \cdot SMe_2$ and Me_3SiBr in a one-pot fashion and was isolated as white crystals (pure by elemental analysis) in 56% yield (Scheme 1). In the solid state, **1** exists as a *trans* dimer (*trans*-(**1**)$_2$) as confirmed by single-crystal X-ray diffraction (Figure 2).



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Scheme 1. Preparation of aminoborane **1**. The bracket refers to a set of structural forms as discussed below.

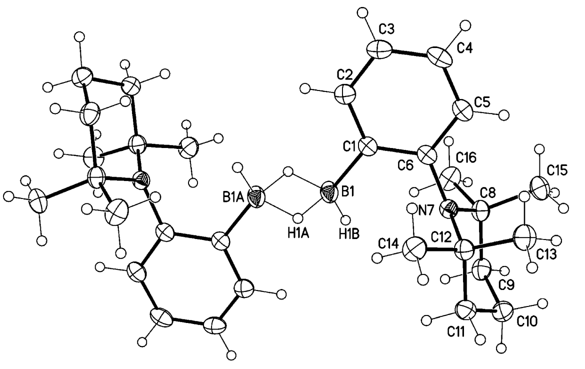


Figure 2. Structure of *trans*-(**1**)$_2$; crystallographic C_i symmetry, displacement parameters set at the 50% probability level. Selected bond distances [Å] and angles [°]: B1–B1A 1.782(3), B1–H1B 1.068(19), B1–H1A 1.253(16), B1A–H1A 1.243(17); B1-H1A-B1A 91.08(11).

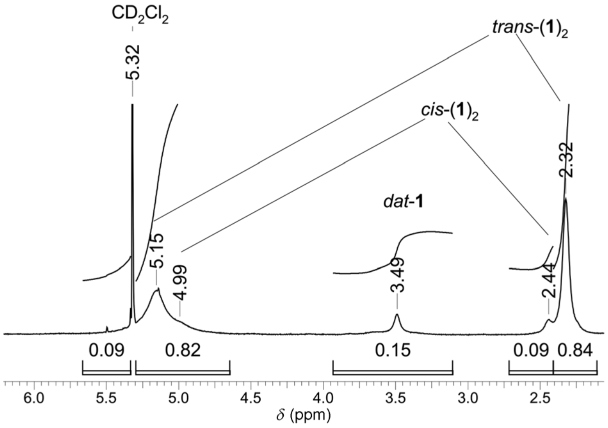


Figure 3. ^{11}B-decoupled ^{1}H NMR spectrum of **1** in CD_2Cl_2 (–15 °C, 500 MHz), showing various forms of aminoborane **1**. The region with the B*H* signals is depicted, together with their assignments and integral values.

NMR studies point to the coexistence of various forms of **1** in solution. In the ^{11}B NMR spectrum, only one very broad signal at 20.0 ppm is observed regardless of the temperature. ^{1}H NMR measurements in CD_2Cl_2 solution revealed several broad signals at room temperature. Some of them are B*H* signals that arise from coupling to ^{11}B and ^{10}B nuclei, while the rest of the signals are broad owing to rapid interchange between isomers of **1** on the NMR time scale. Cooling to –15 °C and using the ^{11}B decoupling technique enabled the identification of three distinct species, which were tentatively assigned to *trans*/*cis* dimeric structures and the datively bound monomeric form *dat*-**1** (see Figure 3).[17] The relative concentration of *dat*-**1** increases upon dilution of the solution as expected from the $^1/_2$ (**1**)$_2$⇌*dat*-**1** equilibrium. Variable temperature (VT) NMR studies indicated that *dat*-**1** is less stable than $^1/_2$ (**1**)$_2$ by 1.7–2.1 kcal mol^{-1}, depending on the temperature.

DFT calculations were carried out for these species to provide support for the above assignment (see the Experimental Section and the Supporting Information). The *trans*-(**1**)$_2$ form is predicted to be the most stable isomer in both dichloromethane (CH_2Cl_2) and toluene (Figure 4, left). The optimized geometry of this species compares well with that from the X-ray analysis.[18] The other two experimentally observed isomers, dimer *cis*-(**1**)$_2$ and monomer *dat*-**1**, were found to be only slightly less stable than *trans*-(**1**)$_2$ (e.g., in CH_2Cl_2, by 2.2 and 3.3 kcal mol^{-1} per monomer unit, respectively). In addition to these isomers, the open monomeric form with non-interacting B/N sites was also identified computationally (see *open*-**1** in Figure 4). This species is a well-defined local minimum on the potential energy surface, but it is thermodynamically less favorable than the quenched isomers.[19]

1,2-Linked (vicinal) FLPs that do not form intramolecular dative bonds are rare, but known.[11b,20] Such systems feature a linker with enhanced structural rigidity (such as the norbornene framework or the *ortho*-phenylene linker) combined with sterically encumbered acidic ($B(C_6F_5)_2$) and basic units (TMP or $PMes_2$). On the other hand, fairly stable four-membered heterocycles are already observed when the steric hindrance is slightly decreased. The upper limit of the dissociation energy of the dative bond was previously measured for such FLPs, and it ranges from 12.1 to 13.8 kcal mol^{-1}.[21] The computed free-energy difference between the *open*-**1** and *dat*-**1** forms (4.2–5.4 kcal mol^{-1}, depending on the solvent) suggests a situation somewhere

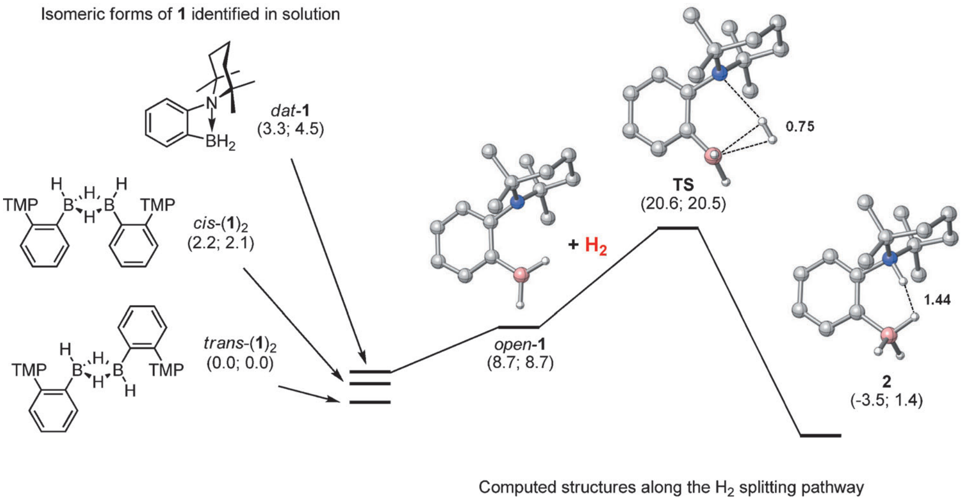


Figure 4. Computed energetics for various forms of aminoborane **1** and for the H_2 splitting by **1**. Relative standard Gibbs free energies (for $T=298$ K) are given in parentheses (in kcal mol^{-1}, with respect to $\frac{1}{2}$ *trans*-(**1**)$_2$ or $\frac{1}{2}$ *trans*-(**1**)$_2$ + H_2 for CH_2Cl_2 and toluene, respectively). Selected H–H bond lengths are given in Å (the bond length of free H_2 is 0.74 Å). H atoms attached to C atoms were omitted for clarity.

in between, resulting from the combination of the small BH_2 group with the very bulky TMP substituent and the rigid *ortho*-phenylene linker. The strain in the four-membered ring is still clearly borne out by the elongated B–N bond in *dat*-**1** (1.77 Å).

Similarly to the energy of Lewis adduct formation, the dimerization energy depends largely on the Lewis acidity of the borane and its steric congestion. For example, $(C_6F_5)_2BH$ is known to exist as a mixture of the monomer and dimer in solution,[22] whereas $C_6F_5BH_2$ or BH_3 are known to be only present in their dimeric forms.[15,23] Our results indicate that dimerization by B(μ-H)$_2$B bridges leads to a stable species for aminoborane **1** as well, for which *trans*-(**1**)$_2$ was found to be the prevailing form both in the solid state and in solution.

In light of the coexistence of various quenched forms of aminoborane **1**, the heterolytic H_2 splitting seems rather challenging. Indeed, we did not observe any reactivity in toluene at room temperature and atmospheric H_2 pressure, and we found only a very low conversion (1.8%) at −15 °C and 10 bar of initial H_2 pressure. Upon exposure of **1** to H_2 atmosphere in CD_2Cl_2 solution, however, the adduct **2** (see Table 1) was produced in significantly higher amounts, as evidenced by the large quadruplet signal at −28.4 ppm in the ^{11}B NMR spectrum (Figure 5).

The H_2 splitting product was found to be in dynamic equilibrium with the starting materials. The equilibrium can be shifted to **2** at higher H_2 pressures and lower temperatures. In CD_2Cl_2, at room temperature, and at 2.2 bar H_2 pressure, 5% conversion into **2** could be observed, whereas at −15 °C and 10 bar of initial H_2 pressure, conversion into **2** reached 72%. From VT ^{1}H NMR measurements for the reaction $\frac{1}{2}$ (**1**)$_2$ + $H_2 \rightleftharpoons$ **2**,[24] the following thermodynamic equilibrium parameters were determined for CD_2Cl_2: $\Delta H = -7.9 \pm 0.2$ kcal mol^{-1} and $\Delta S = -22.9 \pm 0.7$ cal mol^{-1} K^{-1}, which yield $\Delta G_{298} = -1.1$ kcal mol^{-1} and $\Delta G_{258} = -2.0$ kcal mol^{-1}. The latter value can be compared with the results obtained in [D$_8$]toluene, for which the experimental value of ΔG_{258} was found to be 0.7 kcal mol^{-1}.

To interpret these findings, we examined the thermodynamics and the mechanism of the heterolytic H_2 splitting by **1** by computations. The results are summarized in Figure 4 (right part). The reaction in CH_2Cl_2 was found to be clearly favored thermodynamically even though the reactant state corresponds to a stable dimeric species, and the reactive form of the present FLP (*open*-**1**) is fairly high in free energy. On the other hand, the reaction is predicted to be slightly endergonic in toluene, which is consistent with experimental observations.[25] Our results thus point to significant solvent effects on the reaction free energy of H_2 splitting. This can be related to the zwitterionic structure of the product molecule, which is stabilized more in a polar medium (such as CH_2Cl_2).[26] The hydride affinity of

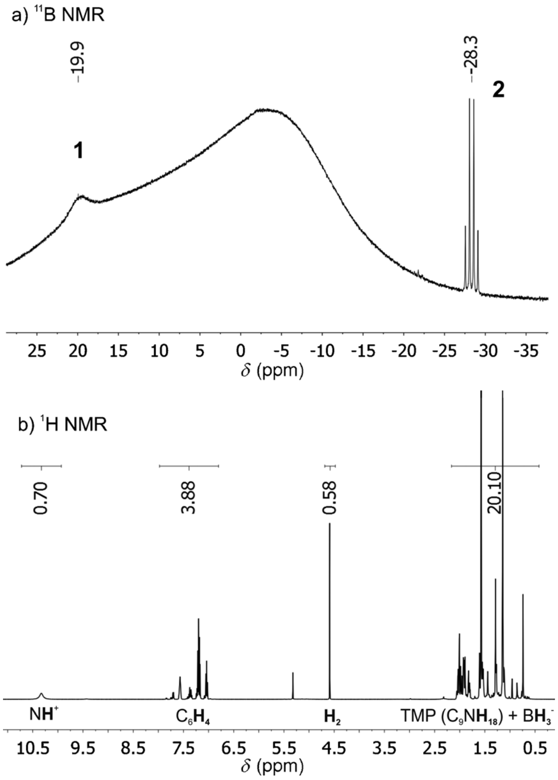


Figure 5. NMR studies of the equilibrium **1** + $H_2 \rightleftharpoons$ **2** at 10 bar initial H_2 pressure and in CD_2Cl_2. a) ^{11}B NMR spectrum at −15 °C. The broad singlet belongs to **1** (19.9 ppm) and the quadruplet to **2** (−28.4 ppm). b) ^{1}H NMR spectrum at −15 °C of **1** under the same conditions. Integration of the signals confirms 70% conversion into **2**.

1 is smaller than that of the analogous *ortho*-TMP−C_6H_4−$B(C_6F_5)_2$ molecule by 22 kcal mol^{-1}; nevertheless, the reaction $^1/_2$ $(\mathbf{1})_2 + H_2 \rightleftharpoons \mathbf{2}$ is still thermodynamically feasible.[27]

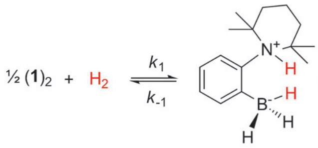
The structure of the transition state located along the H_2 splitting pathway (see TS in Figure 4) shares common features with those of previously investigated systems.[28] The elongated H−H bond, the pyramidalization of the borane unit, and the typical end-on N···H_2 and side-on H_2···B arrangement of the reacting partners are all in line with the electron-transfer reactivity model.[29] The activation barriers computed for the two solvents are practically identical (20.6 and 20.5 kcal mol^{-1} for CH_2Cl_2 and toluene), which stems from the early, and thus fairly nonpolar, nature of the transition state.

Although computational studies provide valuable insight into the mechanism of FLP-type hydrogen activation, kinetic measurements are highly desirable to test the mechanistic hypotheses.[30] Experimental kinetic studies using classical methods in this field are, however, challenging. The analysis of concentration/time profiles is usually interfered by hydrogen diffusion from gas to the liquid phase impeding the precise control over the concentration of the reactants. In the present reaction, the rapid and reversible addition of H_2 to aminoborane **1** implies a continuous exchange of dihydrogen between molecular H_2 and the adduct state (**2**), enabling the direct measurement of the exchange rate.

Herein, we used the spin-saturation transfer (SST) NMR method to monitor the rate of H_2 elimination from adduct **2**.[31,32] Based on our computational results, we assumed that this process occurs in a single step (via TS) resulting in *open*-**1** (involved in a rapid exchange with the other forms of **1**). This assumption is consistent with our recent report, where pairwise addition of H_2 to *ansa*-aminoboranes was demonstrated using parahydrogen-induced polarization.[33]

In the applied SST approach, the ^{1}H NMR signal of H_2 is totally saturated, which makes it NMR-silent. Under stationary conditions, the observed ^{1}H NMR signals of H_2-originating hydrogens in adduct **2** are due to the nuclear relaxation in **2**, as the saturation is continuously transferred by the dehydrogenation/hydrogenation events. A simple equation can be derived for the rate constant of H_2 release from **2** in this case.[18] The rate constants were determined for the temperature range of 27–57 °C using a 500 MHz ^{1}H NMR instrument, and kinetic parameters were derived accordingly (Table 1). A combination of these parameters with the thermodynamic data determined above for the equilibrium $^1/_2$ $(\mathbf{1})_2 + H_2 \rightleftharpoons \mathbf{2}$ formally provided kinetic parameters for the forward reaction as well ($^1/_2 (\mathbf{1})_2 + H_2 \rightarrow \mathbf{2}$): $\Delta H^{\ddagger} = 11.9 \pm 0.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = -21.6 \pm 2.9$ cal mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{298} = 18.3 \pm 0.9$ kcal mol^{-1}. The latter value is reasonably close to the computed activation barrier of H_2 activation (20.6 kcal mol^{-1}). The deviation is definitely within the error margin of the applied computational method. These results can be interpreted as solid support for the mechanistic picture envisioned for the present reaction.

Table 1: Rate constants and kinetic parameters derived from SST NMR measurements.[a]



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T [°C]	k_{-1} [s^{-1}]		$\mathbf{2} \rightarrow {}^1/_2\ (\mathbf{1})_2 + H_2$	$^1/_2\ (\mathbf{1})_2 + H_2 \rightarrow \mathbf{2}$
27	0.045787	$\Delta H^{\ddagger}$	19.8 ± 0.8	11.9 ± 0.8
35	0.119373	$\Delta S^{\ddagger}$	1.3 ± 2.9	−21.6 ± 2.9
42	0.213228	$\Delta G^{\ddagger}_{298}$	19.4 ± 0.9	18.3 ± 0.9
50	0.467992			
57	1.134892			

[a] $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$ in kcal mol^{-1}, $\Delta S^{\ddagger}$ in cal mol^{-1} K^{-1}.

In conclusion, we have developed the new *ansa*-aminoborane FLP **1**, which features a BH_2 group as the Lewis acidic component and 2,2,6,6-tetramethylpiperidine as the basic component. Although this sterically unbalanced intramolecular FLP is present in quenched forms in solution, and BH_2 represents an acidic site with reduced hydride affinity, the reactivity towards H_2 was clearly demonstrated. Solutions of **1** react instantly with H_2, producing adduct **2**, which appears to be in dynamic equilibrium with **1** and H_2 at moderate pressures and temperatures. Computations point to the advantage of using polar solvents to bias the reaction equilibrium towards the product side, which is in line with experimental observations. Additional NMR studies of the chemical equilibrium allowed us to establish accurate thermodynamic parameters for the H_2 splitting process and, for the first time in FLP chemistry, to provide activation parameters for this process. The kinetic analysis was carried out by measuring the rate for dehydrogenation of **2** using the spin-saturation transfer NMR technique. The reactivity of **1** with other small molecules and its potential application in catalytic hydrogenation are currently explored in our laboratories.

Experimental Section

Variable-temperature NMR studies: In a typical experiment, a solution of **1** (0.04–0.06 M, counted as a monomer) in CD_2Cl_2 or [D_8]toluene was placed in a heavy-wall NMR tube and charged with 10 bar H_2 at room temperature. The ^{1}H and ^{11}B NMR spectra were recorded at various temperatures (−15 to 42 °C). ^{1}H signals were integrated, and the equilibrium constant was determined.

Kinetic measurements: The sample was prepared similarly as above. The ^{1}H NMR signal of H_2 was presaturated for 10 s, and the decrease in the integral of the NH^+ signal was measured.[18]

DFT calculations were carried out using the dispersion-corrected range-separated hybrid ωB97X-D functional along with the 6-311G-(d,p) basis set as implemented in *Gaussian 09*. The electronic energies were refined by single-point energy calculations using a larger basis set (6-311++G(3df,3pd)). The SMD continuum model was employed to describe solvation. The reported energies refer to solvent-phase Gibbs free energies.[18]

CCDC 952301 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[14] For instance, BH_3 is predicted to be significantly less acidic than $B(C_6F_5)_3$ in our calculations (for details, see the Supporting Information).

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[17] A very similar picture for the isomers of **1** could be observed by NMR spectroscopy in $[D_8]$toluene as the solvent.

[18] For details, see the Supporting Information.

[19] The datively bound "head-to-tail" dimer of **1** has been identified computationally as well, but it is predicted to be very high in free energy (30 $kcal\,mol^{-1}$ higher than *trans*-$(\mathbf{1})_2$).

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[24] At higher temperatures, the two dimeric forms of **1** are indistinguishable; therefore, we refer to the reactant state of H_2 activation as $^1/_2\,(\mathbf{1})_2 + H_2$.

[25] A comparison of the measured and calculated reaction Gibbs free energies indicates that the present computational approach overestimates the thermodynamic stability of product **2** by approximately 2–3 $kcal\,mol^{-1}$ (see the Supporting Information).

[26] Similar solvent effects have been previously reported for H_2 activation with a norbornane-linked phosphorus/boron pair; see: M. Sajid, A. Lawzer, W. Dong, C. Rosorius, W. Sander, B. Schirmer, S. Grimme, C. G. Daniliuc, G. Kehr, G. Erker, *J. Am. Chem. Soc.* **2013**, *135*, 18567–18574.

[27] The reduced hydride affinity of **1** is partially due to dimerization. A detailed energy decomposition analysis for the two reactions is provided in the Supporting Information.

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