Hydrogen Transfer

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A Concerted Transfer Hydrogenolysis: 1,3,2-Diazaphospholene-Catalyzed Hydrogenation of N=N Bond with Ammonia–Borane**

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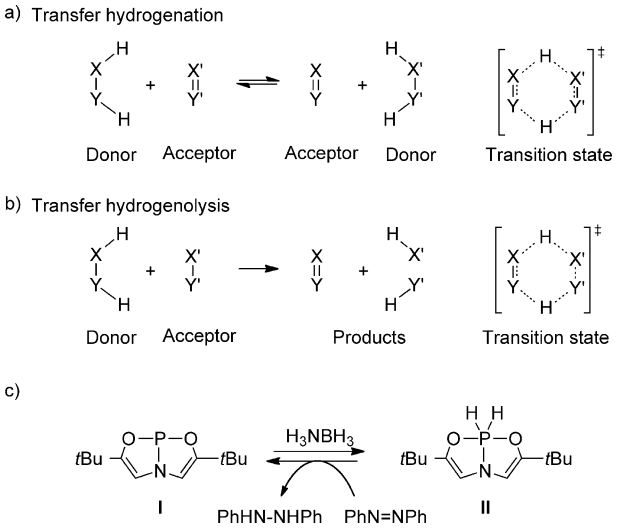
Abstract: *1,3,2-diazaphospholenes catalyze metal-free transfer hydrogenation of a N=N double bond using ammonia–borane under mild reaction conditions, thus allowing access to various hydrazine derivatives. Kinetic and computational studies revealed that the rate-determining step involves simultaneous breakage of the B–H and N–H bonds of ammonia–borane. The reaction is therefore viewed as a concerted type of hydrogenolysis.*

Ammonia–borane (**AB**; H_3NBH_3), an air-stable and non-flammable white solid, has a high gravimetric hydrogen density (19.6 wt%) and a small molecular weight (30.87 g mol^{-1}). In the past decade, not only the challenge of using **AB** as a H_2 storage material[1,2] but also the development of synthetic methodologies utilizing **AB** directly as a source of hydrogen has received considerable attention.[3] For the latter, transfer hydrogenation using a source in place of H_2 gas is considered to be greatly advantageous over the conventional methods for hydrogenation of unsaturated compounds in organic synthesis. Therefore, a deep mechanistic comprehension of elementary hydrogen-transfer steps involved therein is essential to establishing excellent transfer-hydrogenation systems.[4,5] Recently, Berke and co-workers reported the metal-free stoichiometic hydrogenation of organic molecules such as polar olefins, aldehydes, ketones, and imines, using **AB**.[6] Importantly, the hydrogen transfer from **AB** to imines was proven to follow a concerted mechanism involving a six-membered transition state (Scheme 1 a).[6d,7] An analogous mechanism was also predicted for the process of Meerwein–Pondorf–Verley reduction.[8] Similarly, Manners et al. demonstrated the hydrogen transfer between amine-boranes and aminoboranes also occurs bimolecularly in a single-step process.[9] A concerted pathway for a homopolar H_2 exchange process between ethane and ethylene was proposed to involve a very high barrier based on density functional theory (DFT) calculations.[10] These results indicate only hydrogen acceptors with polar π bonds, such as C=N or B=N, may lower the activation barrier to enable the facile, direct, double hydrogen transfer. To the best of our knowledge, hydrogenolysis, which involves a concerted hydrogen transfer to the single bond of a hydrogen acceptor has never been reported (Scheme 1 b).



Scheme 1. Concerted elementary processes for transfer hydrogenation (a) and transfer hydrogenolysis (b; X, Y, X′, and Y′: fragments of main group elements). c) **I**(P^{III})/**II**(P^{V}) redox catalysis for transfer hydrogenation of azobenzene with ammonia–borane.

Recent breakthroughs in using *p*-block elements as mimics for transition metals demonstrate that various main-group compounds featuring both strong electron-donor and electron-acceptor sites can activate small molecules.[11] There are a few reports on the activation of B–H and N–H bonds of **AB** by main-group compounds; however, their applications in catalysis still remain highly challenging.[12,13] Radosevich and co-workers showed that a catalytic amount of the phosphorus compounds **I** promotes a transfer hydrogenation of azobenzene using an excess amount of **AB** (Scheme 1 c).[14] Remarkably, the highly strained T-shape geometry of **I** allows the phosphorus center to possess both donating and accepting orbitals which interact effectively with protic and hydridic hydrogens from **AB**. As a result, the reaction of **I** and **AB** gave the dihydridophosphorane **II**, which was shown to be the resting state of the catalyst. Note that the unique **I**-(P^{III})↔**II**(P^{V}) redox mechanism is critical to building the catalytic cycle. All these pioneering studies encouraged us to investigate whether even a simple X′–Y′ single bond can activate **AB** when the bond is strongly polarized ($\chi X' \ll \chi Y'$). Thus, a negatively polarized Y′ may act as a donor to form

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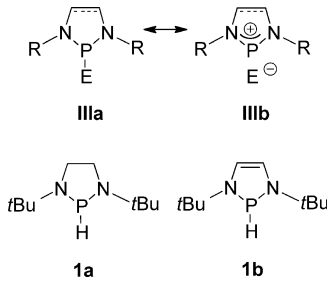
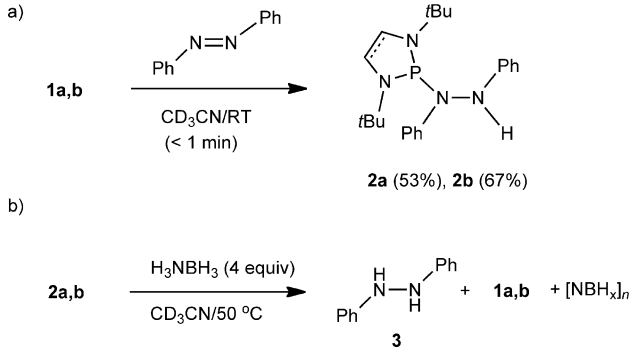
a bond with a proton, whereas a positively polarized X′ may accept a hydride from **AB** to achieve the unique hydrogenolysis (Scheme 1b). To examine our hypothesis, we chose the N-heterocyclic phosphanes **III** as hydrogen acceptors because they display substantial P–E bond polarity, which is attributed to a hyperconjugative interaction between lone-pair electrons on N and the σ*(P–E) orbital (Scheme 2).[15] Herein, we report a hydrogenolysis involving a concerted double hydrogen transfer between **AB** and N-heterocyclic phosphanes in the metal-free catalytic transfer hydrogenation of a N=N bond.



Scheme 2. A generic structure of the N-heterocyclic phosphanes **III** and 2-*H*-1,3,2-diazaphospholenes **1**.

The hydride-type reactivity of the P–H bond in the 2-*H*-1,3,2-diazaphospholenes **1a**,**b** (Scheme 2) has been extensively studied by Gudat et al., but the reaction of **1** with a compound having a N=N bond has not been described.[16] First, we synthesized the N-heterocyclic phosphinohydrazines **2a**,**b** from the reaction of **1a**,**b** and azobenzene (Scheme 3a).

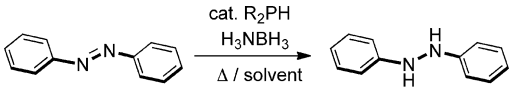


Scheme 3. a) Synthesis of the N-heterocyclic phosphinohydrazines **2a**,**b**. b) Reaction between **2a**,**b** and ammonia–borane.

The P–H addition to the N=N bond of azobenzene proceeded readily at room temperature, and the quantitative formation of **2a**,**b** was confirmed by ^{31}P NMR spectroscopy (**2a** in CD_3CN: $\delta = 101.9$ ppm, **2b**: $\delta = 90.0$ ppm). The compounds **2a**,**b** were isolated in moderate yield (**2a**: 53%, **2b**: 67%). A single crystal of **2a** was obtained by recrystallization from a benzene solution, and the molecular structure was unambiguously determined by a single-crystal X-ray diffraction.[17] Next, **2a**,**b** was reacted with excess **AB** (4 equiv) at 50°C in a deuterated acetonitrile solution. The reaction was monitored by ^{31}P NMR spectroscopy, and the formation of both diphenyl hydrazine (**3**) and **1a**,**b** was observed, thus demonstrating a hydrogenolysis of the exocyclic P–N bond by **AB** (Scheme 3b). Note that the initial hydrogenolysis occurred at only the exocyclic P–N bond in **2a**,**b**, probably because of the thermodynamic and kinetic stability of the endocyclic P–N bonds. In the reaction of **2a** with **AB**, however, further P–N bond cleavage in **1a** took place competitively, and the generation of PH_3 was confirmed.[18] Significantly, when H_3NBD_3 was employed for the same reaction with **2b**, only 2-*D*-1,3,2-diazaphospholene [D]-**1b**(**D**) was regenerated, thus showing the regiospecificity during the hydrogen transfer from **AB** to **2a**,**b** (see Figures S1-1-2 and S1-1–3 in the Supporting Information).

We attempted to apply the stoichiometric two-step transformation of azobenzene into **3** via **2** in a catalytic process. In the absence of catalysts, little production of **3** was observed (Table 1, entry 1). Diaryl- and dialkylphosphines did not promote the reaction, even when stoichiometric amounts were used (Table 1, entries 2 and 3). In contrast, with 5 mol% of **1a**, a small amount of **3** was detected (Table 1, entry 4). To our delight, **1b** showed considerable catalytic activity for the transfer hydrogenation. After 24 hours at 50°C, a clean conversion was observed with more than 90% yield (Table 1, entry 5). Under these reaction conditions, the rapid addition of **1** to the N=N bond of azobenzene formed the adduct **2**, and then the subsequent hydrogen transfer from ammonia–borane cleaved a P–N bond and reproduced **1** to complete a catalytic cycle. Indeed, during the reaction, ^{31}P NMR spectroscopy showed only a single peak corresponding to **2b**, the actual resting state of the catalyst in this cycle. Thus, the P^{III} oxidation state of the catalysts does not change during

Table 1: Optimization of the reaction conditions.[a]



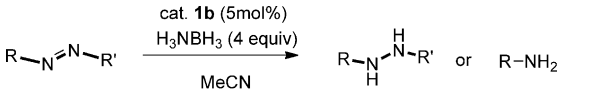
Entry	**cat.** [mol%]	**AB** [eq]	Solvent	*T* [°C]	*t* [h]	Yield [%][b]
1	none (0 mol%)	4	$CDCl_3$	80	48	< 5
2	Ph_2PH (100 mol%)	4	$CDCl_3$	50	24	0
3	tBu_2PH (100 mol%)	4	$CDCl_3$	50	24	0
4	**1a** (5 mol%)	4	$CDCl_3$	50	24	18
5	**1b** (5 mol%)	4	$CDCl_3$	50	24	94
6	**1b** (5 mol%)	4	$CDCl_3$	50	12	67
7	**1b** (5 mol%)	4	[D_8]THF	50	12	6
8	**1b** (5 mol%)	4	C_6D_6	50	12	21
9	**1b** (5 mol%)	4	CD_2Cl_2	50	12	> 99
10[c]	**1b** (5 mol%)	4	CD_3CN	50	12	> 99
11	**1b** (5 mol%)	4	CD_3CN	50	4	98
12	**1b** (2 mol%)	4	CD_3CN	50	4	36
13	**1b** (5 mol%)	1	CD_3CN	50	12	77
14	**1b** (5 mol%)	4	CD_3CN	RT	72	79

[a] Reaction conditions: azobenzene (0.30 mmol), **AB** (1.20 mmol), solvent (1.0 mL). Catalyst loading relative to azobenzene. [b] Yields are determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c] The reaction excluding light was also examined and gave the same result.

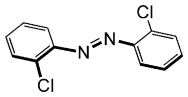
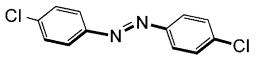
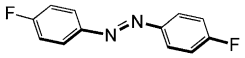
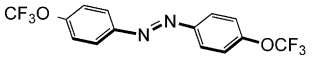
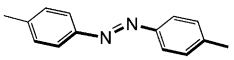
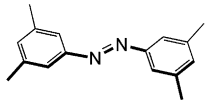
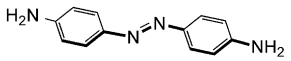
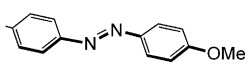
the catalytic process. A brief screening of solvents revealed that both dichloromethane and acetonitrile are suitable for the reaction (Table 1, entries 6–10). We also confirmed near completion of the reaction after only 4 hours (Table 1, entry 11). When the catalyst loading was decreased to 2 mol%, **3** was formed in 36% after 4 hours (Table 1, entry 12). Even with one equivalent of ammonia–borane, the yield of **3** reached 77% after 12 hours (Table 1, entry 13). It is noteworthy that the catalytic transfer hydrogenation is effective even at room temperature. Although a longer reaction time was required, **3** was obtained in 79% yield after 72 hours (Table 1, entry 14).

With the optimized reaction conditions in hand, the scope of the catalytic reaction was briefly examined with various (*E*)-azo-compounds (Table 2). Azoarenes bearing chloro, fluoro, and trifluoromethoxy groups (**4a–d**) afforded the corresponding hydrazine derivatives in good to excellent yields (**5a–d**). Electron-donating alkyl groups (**4e**,**f**) were also well tolerated (**5e**,**f**). For the analogous reactions with substrates including 4-amino (**4g**) or 4-methoxy phenyl groups (**4h**), transfer hydrogenation and subsequent N–N bond cleavage occurred, and only the corresponding aniline derivatives were obtained (**6g**,**h**).[19] Unsymmetrical hydrazine derivatives were also afforded in excellent yields (82–95%).

Table 2: Scope of the transfer hydrogenation of (*E*)-azo-compounds.[a]



4a-l 5 6

4		T [°C]	t [h]	Product	Yield [%][a]
4a		RT	< 1	5a	95 (83)
4b		50	3	5b	95 (89)
4c		50	18	5c	95 (61)
4d		50	3	5d	81 (53)
4e		50	6	5e	83 (61)
4f		50	9	5f	77 (67)
4g		50	6	6g	91 (60)
4h		50	10	6h	97 (62)

[a] Yields determined by NMR spectroscopy (yields of isolated products are given within parentheses). For complete results containing unsymmetrical azocompounds as substrates, TOFs for all reactions, and a Hammett plot (using **4b**,**d**,**e**), see the Supporting Information.

The pathway for the reaction between **2b** and **AB** was explored theoretically using DFT calculations at the M05-2X(SCRF)/6-311G(d,p) level of theory (Figure 1).[20] An energetically feasible pathway for the concerted double hydrogen transfer was obtained. The six-membered cyclic transition state (**TS**) involved hydrogen bonding between the

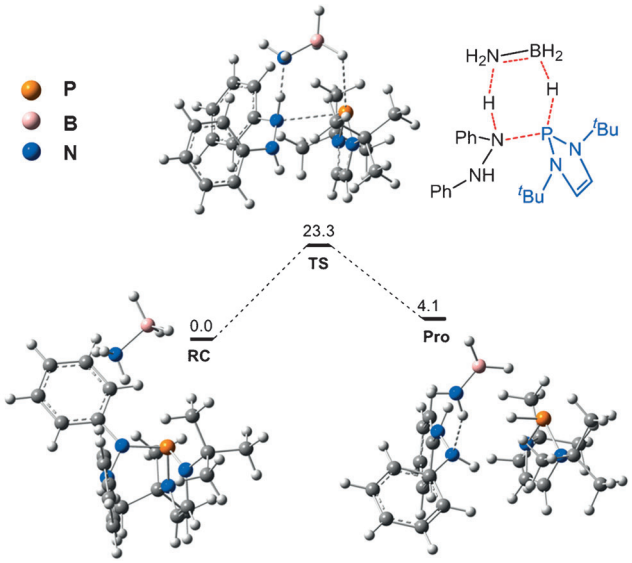


Figure 1. DFT-calculated free energy profiles (kcal mol^{-1}) for the proposed mechanism of the concerted double hydrogen transfer between ammonia–borane and **2b**. The optimized structures were obtained at the M05-2X/6-311G(d,p) level. The ΔG in CH_3CN at 298 K were obtained from the M05-2X/6-311G(d,p) gas-phase harmonic frequency and the energy in CH_3CN.

N and P of **2b** and the protic and hydridic, hydrogen atoms respectively, of **AB**, and is consistent with the polarized atomic charge distribution (P: +1.35, N: −0.62) on the exocyclic P–N bond in **2b**, as obtained with natural population analysis.[21] The computationally estimated activation parameters for the concerted process ($\Delta H^{\ddagger} = 20.1$ kcal mol^{-1}, $\Delta G^{\ddagger}_{(298)} = 23.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -10.9$ e.u.) agreed well with the experimental results ($\Delta H^{\ddagger} = 21.8 \pm 2.2$ kcal mol^{-1}, $\Delta G^{\ddagger}_{(298)} = 25.2 \pm 4.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -11.6 \pm 6.8$ e.u.). The free-energy diagram suggests that the reaction is slightly endergonic, but the free energy will be further lowered as the transient aminoborane [$H_2N=BH_2$] intermediate will react with **AB** immediately.[6d] To examine whether a stepwise hydrogen-transfer mechanism is plausible, relaxed energy scan calculations for the first hydrogen transfer were also carried out. Neither proton nor hydride transfers from **AB** to **2b** provided a stable transition state, thus indicating that these processes are not likely to occur (see Figure S4-4 in the Supporting Information).

To gain insight into the hydrogen-transfer mechanism, we carried out further analysis of the catalytic reactions using deuterated ammonia–boranes to examine deuterium kinetic isotope effects (DKIEs) on the reactions. A CD_3CN solution of azobenzene with 5 mol% of **1b** and excess deuterated ammonia–borane in a sealed NMR tube was heated at 50°C,

and the reaction was monitored by NMR spectroscopy at five minute intervals. The DKIE values were determined based on the rate constants simulated from the kinetic conversion chart (Figure 2). Normal DKIEs of 1.44 and 3.05 were observed for the reactions of azobenzene with H_3NBD_3 and D_3NBH_3, respectively. The double DKIE reaction with D_3NBD_3

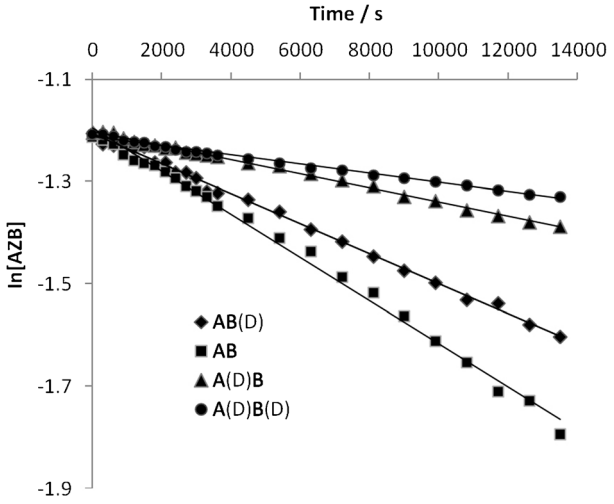


Figure 2. Kinetic conversion chart with logarithmic plot for the reaction of azobenzene with deuterated ammonia–boranes; H_3NBD_3=AB(D), D_3NBH_3=A(D)B, D_3NBD_3=A(D)B(D), catalyzed by 5 mol% of **2b** at 50°C.

showed the largest DKIE of 4.67, and demonstrates both B–H and N–H transfers are involved in the rate-determining step. A theoretical calculation employing deuterated ammonia–boranes provided a DKIE value of 1.35 (H_3NBD_3), which agrees fairly well with the experimental value. The estimated DKIE values of 2.31 (D_3NBH_3) and 3.11 (D_3NBD_3) were somewhat smaller than the experimental values. Nevertheless, the agreement between the experiments and theory was reasonably good, and importantly, the relative magnitudes of DKIEs were reproduced theoretically. Theory thus supports the proposed concerted mechanism in the double-hydrogen-transfer reaction.

In summary, we have developed metal-free transfer hydrogenation of a N=N bond with ammonia–borane, catalyzed by diazaphospholenes **1** under mild reaction conditions. Stoichiometic reactions revealed the catalytic cycle involves two key steps. Different from the $P^{III}\leftrightarrow P^{V}$ redox mechanism of Radosevich et al., the catalyst maintains the P^{III} oxidation state throughout the whole catalytic cycle. The initial step is the facile addition of the P–H bond of **1** to the N=N bond, thus leading to the phosphinohydrazines **2**. The second step involves the hydrogenolysis of the exocyclic P–N bond of **2** by hydrogen transfer from ammonia–borane. The DKIE study demonstrated both the B–H and N–H bonds of **AB** are cleaved in the rate-determining step, which is consistent with a concerted double-hydrogen-transfer mechanism. The concerted mechanism was also supported by DFT calculations. To further expand the scope of the reaction reported herein, we are currently investigating the reactions with substrates featuring other unsaturated bonds.

Experimental Section

For complete experimental details and computational results, see the Supporting Information.

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Keywords: ammonia-borane · azo compunds · hydrogen transfer · main group elements · phosphanes

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[17] CCDC 978856 (**2a**) 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.

[18] See Figure S1-1-1 in the Supporting Information.

[19] Although the mechanism is still not clear, presumably the π-electron donor substituents at *para* position increased the reactivity of N–N bond in the corresponding intermediate **5g**,**h**, and thus resulted in the cleavage of the N–N bond under the reaction conditions.

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