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# Amine-Borane Dehydrogenation and Transfer Hydrogenation Catalyzed by α-Diimine Cobaltates

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**Abstract:** Anionic  $\alpha$ -diimine cobalt complexes such as  $[K(thf)_{1.5}\{(^{Dipp}BIAN)Co(\eta^4-cod)\}]$  (1, cod = 1,5-cyclooctadiene) catalyze the dehydrogenation of several amine-boranes. Based on the excellent catalytic properties, an especially effective transfer hydrogenation protocol for challenging olefins, imines, and *N*-heteroarenes has been developed. NH<sub>3</sub>BH<sub>3</sub> was used as dihydrogen surrogate, which transferred up to two equiv. H<sub>2</sub> per NH<sub>3</sub>BH<sub>3</sub>. Detailed spectroscopic and mechanistic studies are presented, which document the rate determination by acidic protons in the amine-borane.

#### Introduction

[a]

Transition metal-catalyzed dehydrogenations of amine-boranes have attracted great attention as a potentially versatile method of hydrogen storage and B-N materials synthesis.<sup>[1]–[3]</sup> Amineboranes can serve as solid hydrogen surrogates in transfer hydrogenations.<sup>[4]</sup> Various dehydrogenation and transfer hydrogenation protocols have been developed with precious metal catalysts, and the underlying mechanisms have been thoroughly studied.<sup>[5]</sup> By contrast, dehydrogenations are far less

hydrogenation of styrene. Waterman and co-workers reported that the cyclopentadienylcobalt complexes CpRCo(CO)<sub>2</sub>I (R= H, Me, Figure 1) catalyze ammonia borane (AB) dehydrogenation at elevated temperatures (65°C).<sup>[10]</sup> The authors performed catalytic transfer hydrogenations with styrenes, alkynes, and olefins with an excess (8 equiv.) of AB at 65°C within 6 h. Tripodal polyphosphine cobalt(I) hydrides (Figure 1) recently reported by Shubina and co-workers exhibited similar activity in the ABdehydrogenation.[11] A mechanism was proposed based on DFT calculations. <sup>t</sup>Bu<sub>2</sub>F P<sup>t</sup>Bu₂  $P = PPh_2$ R = H, Me E = N, PPeters 2013 Waterman 2015 Shubina 2017 N-Ar [K(thf)<sub>x</sub>]<sup>4</sup> N–Ar Ar-

THF, 2 h, 25°C

- cod

**Figure 1.** Homogeneous cobalt catalysts for amine-borane dehydrogenation (Dipp = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl, cod = 1,5-cyclo-

Ar = Dipp (1), Mes (2)

this work

advanced with the abundant and cheaper late 3d metals, despite

While a number of iron catalysts for amine-borane

dehydrogenations have been studied recently,<sup>[8]</sup> effective cobalt catalysts are scarce. <sup>[9]</sup><sup>[11]</sup> To our knowledge, only three well-

defined molecular cobalt catalysts have been reported to date

(Figure 1). Peters and co-workers reported bis(phosphino)boryl

(PBP) cobalt catalysts (Figure 1) for the dehydrogenation of dimethylamine-borane (DMAB)<sup>[9]</sup> and applications to the transfer

the recent progress with Ti, Mn, Fe, Co, and Ni catalysts.<sup>[7]-[12]</sup>

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octadiene).

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The paucity of cobalt-based amine-borane dehydrogenation and transfer hydrogenation catalysts<sup>[9]-[11]</sup> prompted us to investigate of complexes containing the efficacy redox-active bis(iminoacenaphthene)diimine (BIAN) ligands.[13] This ligand class was deemed particularly suitable because it offers a convenient synthesis from commercial precursors (>60 g scales), redox-activity, modular structure, and a persistent ligand backbone.<sup>[13]</sup> BIANs have mainly been exploited in noble metal catalysis so far,<sup>[14]</sup> while applications to 3d metal catalysis have only been reported very sporadically; systematic investigations are still in their infancy.<sup>[15]</sup>

#### **Results and Discussion**

Key discoveries and model reactions. We previously investigated the catalytic properties of low-valent ferrate and cobaltate anions in the hydrogenation of olefins, ketones, and imines.<sup>[16]</sup> The pre-catalysts  $[K([18]crown-6)(thf)_2][M(n^4$ anthracene)<sub>2</sub>] (M = Fe, Co)<sup>[17]</sup> and [K(thf)<sub>x</sub>][Co( $\eta^4$ -cod)<sub>2</sub>]<sup>[18],[19]</sup> (cod = 1,5-cyclooctadiene) enabled the hydrogenation of disubstituted alkenes, ketones and imines. Poor activities were observed for hydrogenation of tri-substituted alkenes and the dehydrogenations of amine-boranes.<sup>[19]</sup> We therefore set out to manipulate the stereoelectronic properties of the catalysts by incorporation of redox-active bis(imino)acenaphthene ligands. The synthesis of  $[K(thf)_{1.5}{(DippBIAN)Co(\eta^4-cod)}]$  (1) (Dipp = 2,6-diisopropylphenyl; cod = 1,5-cyclooctadiene BIAN = bisaryl-(imino)acenaphthene, Figure 1) was recently reported.<sup>[20]</sup> 1 and the closely related mesityl-derivative [K(thf){(MesBIAN)Co(n4-cod)] (2) (Mes = 2,4,6-trimethylphenyl, see the SI for details) were readily accessible in high yields from a straightforward ligand exchange reaction of  $[K(thf)_x][Co(\eta^4-cod)_2]$  with <sup>Ar</sup>BIAN (Ar = Dipp or Mes). The redox-active BIAN moiety in 1 and 2 may facilitate metal-centered redox processes by its ability to accommodate two electrons, while cod can serve as a placeholder for vacant coordination sites. We commenced our studies with dimethylamine-borane (NHMe2BH3, DMAB, Scheme 1 and Figure 2) as model substrate and monitored its consumption by <sup>11</sup>B-NMR spectroscopy. With 5 mol% catalyst loading of 1 at 25°C, DMAB was completely consumed within 34 h. The formation of two main products, tetramethyl-1,3-diaza-2,4-diboretane (74%) and N,N'-dimethylaminoborane (22%), and one minor BH<sub>3</sub>-containing compound (quartet at -9.5 ppm,  ${}^{1}J_{BH} = 134$  Hz) was observed. The less bulky pre-catalyst 2 was far less selective as illustrated by the observation of significant quantities of N.N'-dimethylaminoborane (19%) and unknown BH<sub>3</sub>-containing species (17%). We therefore employed pre-catalyst 1 for further dehydrogenation studies.

A kinetic analysis by <sup>11</sup>B-NMR spectroscopy showed that the reaction likely proceeded through a stepwise mechanism involving the linear intermediate **B** (Me<sub>2</sub>N-BH<sub>2</sub>-NMe<sub>2</sub>-BH<sub>3</sub>) and the unsaturated intermediate **C** (Me<sub>2</sub>N=BH<sub>2</sub>) (Scheme 1). As proposed by *Schneider* and co-workers for dehydrogenations catalyzed by a Ru-amido pincer complex and by *Weller* and co-workers with a cationic Rh-phosphine complex,<sup>[21]</sup> the loss of two molecules dihydrogen operates over two steps when the

reaction proceeds through **B**. In case of **C**, both dihydrogen molecules are eliminated in the first step and a cycloaddition gives the terminal product **D**. We cannot rule out that **B** was also converted into **D** by the loss of one molecule H<sub>2</sub>. The side product HB(NMe)<sub>2</sub> was reported for many catalytic DMAB hydrogenations in the literature.<sup>[5],[8],[9]</sup> Related mechanisms for DMAB dehydrogenation have also been described for dehydrogenation catalysts based on zirconium and iridium.<sup>[22]</sup> Monitoring the time-dependent H<sub>2</sub> formation (see the SI) revealed an induction period of approx. 1 min (SI, Figure S13). A comparison of the initial rates indicates that the catalytic dehydrogenation activity of **2** is five times higher than that of **1** (SI, Figure S13).

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Figure 2. Time-dependent  $^{11}B\text{-NMR}$  spectra (160.4 MHz, 300K, C6D6-capillary) of the DMAB-dehydrogenation with catalyst 1 (0.2 mmol DMAB in 2.5 mL THF).



**Scheme 1.** Dehydrogenation of dimethylamine-borane (NMe<sub>2</sub>HBH<sub>3</sub> = DMAB) (top); proposed mechanism based on observed intermediates (bottom).

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**Scheme 2.** Dehydrogenation of diisopropylamine-borane (a) and *N*-methylamine-borane (b).

Furthermore, we studied catalytic dehydrogenations with the sterically more demanding diisopropylamine-borane and the primary N-methylamine-borane (Scheme 2). These reactions have rarely been reported under base metal catalysis.[8],[23] Diisopropylamine-borane exclusively afforded the iminoborane <sup>i</sup>Pr<sub>2</sub>N=BH<sub>2</sub> after 72 h in THF, which exhibited the characteristic triplet at 34.8 ppm in the <sup>11</sup>B NMR spectrum (Figure 3, top). The formation of oligometric  $[MeHN-BH_2]_n$  (n = 6-11) from N-methylamine-borane was corroborated by ESI-MS and <sup>11</sup>B-NMR spectroscopy. The ESI-MS spectra showed peaks at m/z 186.3 to 443.6 at intervals of 43.1 (corresponding to the monomeric unit H<sub>2</sub>B-NMeH, see Figures S19-S21). <sup>11</sup>B-NMR spectra recorded in THF displayed a broad triplet at -4.8 ppm with the typical line broadening of  ${}^{1}J_{BH} = 106$  Hz. Significantly broader peaks are expected for a polymer (Figure 3, bottom).<sup>[24]</sup>



Figure 3. <sup>11</sup>B{<sup>1</sup>H}-NMR (128.4 MHz, 300K,  $C_6D_6$ ) of dehydrogenation products of diisopropylamine-borane- (top) and *N*-methylamine-borane (bottom) in THF.





The dehydrogenation of ammonia borane (AB) is of particular interest due its high hydrogen content of 19.6 wt%.[1] The cyclopentadienyl carbonyl cobalt and tripodal phosphine cobalt complexes reported by the groups of Waterman and Shubina,[8b,c] respectively, are the only previously reported molecular cobalt catalysts for the AB-dehydrogenation (Figure 1).<sup>[9]</sup> Hence, we sought to compare the properties of pre-catalyst 1 with these benchmark systems that both operate at elevated temperature (65°C). When 1 (5 mol%) was added to a solution of AB in THF, the evolution of H<sub>2</sub> commenced immediately. This indicates a rapid onset of catalytic dehydrogenation already at ambient temperature. The characterization of reaction intermediates (Scheme 3) was performed by <sup>11</sup>B-NMR spectroscopy. The starting material AB was completely consumed after 24 h. Borazine (30 ppm) and polyborazine (26 ppm) were identified as the two main soluble products. However, it is noteworthy that a white precipitate formed during the reaction in THF. This solid was studied by magic angle spinning (MAS) <sup>11</sup>B NMR spectroscopy with proton decoupling and cross-polarization (<sup>11</sup>B-CPMAS-NMR) as well as without cross-polarization from protons and with proton coupling. The <sup>11</sup>B MAS NMR spectrum of this material showed two signals at 2 ppm and -19 ppm (Figure 4). Proton decoupling (<sup>11</sup>B{<sup>1</sup>H} MAS NMR) reduced the linewidth of the -19 ppm resonance while it did not affect the signal at -2 ppm. The intensity of the former signal was strongly enhanced in the <sup>11</sup>B{<sup>1</sup>H} CPMAS spectrum. Thus, this signal should be assigned to a boron atom bonded to hydrogen(s). In contrast, the signal at -2 ppm may be assigned to a boron atom bearing no H atoms. We believe that this solid is polyaminoborane for which similar solid-state NMR data, particularly similar chemical shifts, were reported by Schneider and co-workers.[8]



Figure 4. <sup>11</sup>B-NMR spectra at 300 K of polyaminoborane; MAS at 6 kHz; relax = relaxation.

**Mechanistic studies of dehydrogenation.** AB dehydrogenation was directly monitored by  $H_2$  evolution at 1-12.5 mol% catalyst loading (Figure 5). An induction period was apparent at low catalyst concentrations, indicating that **1** might act as a precatalyst that is converted to the active catalyst species under reaction conditions. The formation of 0.5 equivalents  $H_2$  per AB

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was observed within the first 2 min with 5 mol% (10 mM) catalyst. Subsequently, the reaction became much slower, indicating catalyst deactivation and possibly a change in the reaction mechanism. A plot of the initial rates vs. catalyst concentrations (SI, Figure S16) showed a  $2^{nd}$  order rate in catalyst. A linear relationship between reaction rate and substrate concentration from 50 – 200 mM was established from dehydrogenations with different AB concentrations and constant catalyst concentration (SI, Figure S18). Higher substrate concentrations afforded no significant enhancement of the initial rate constant. Based on these data, the following rate law can be formulated:





Figure 5. Dehydrogenation of AB catalyzed with different catalyst loading of 1. Reaction conditions: 0.2 mmol (mM) AB in THF (1 mL) at  $25^{\circ}$ C.

Further mechanistic evidence was gathered from GC-MS investigations of the reaction mixtures, which documented the formation of cyclooctene and cyclooctane arising from (partial) hydrogenation of the 1,5-cyclooctadiene ligand in 1. No H<sub>2</sub> formation was observed in control experiments with NMe<sub>3</sub>BH<sub>3</sub> and NH<sub>3</sub>BEt<sub>3</sub>. A crossover experiment with a substrate mixture of NMe<sub>3</sub>BH<sub>3</sub> and NH<sub>3</sub>BEt<sub>3</sub> did not result in any H<sub>2</sub> formation. Consistently, no dehydrogenation products were observed by <sup>11</sup>B-NMR. These results proved that the presence of H-N and H-B entities within one molecule are required to enable dehydrogenation of amine-boranes. In an effort to gain more insight into the operating reaction mechanism, we performed dehydrogenations of the deuterated species ND<sub>3</sub>BH<sub>3</sub>, NH<sub>3</sub>BD<sub>3</sub>, and ND<sub>3</sub>BD<sub>3</sub>. Experiments with 5 mol% catalyst 1 and ND<sub>3</sub>BH<sub>3</sub> revealed a kinetic isotope effect (KIE) k(NH<sub>3</sub>BH<sub>3</sub>)  $k(ND_3BH_3) = 1.6$  (2° KIE), while with NH<sub>3</sub>BD<sub>3</sub> a negligible KIE  $k(NH_3BH_3) / k(NH_3BD_3)$  of 0.9 was observed. This is strongly indicative of a participation of a protic H-N in the rate determining step. Fully deuterated ammonia borane (ND<sub>3</sub>BD<sub>3</sub>) showed a strong KIE k(NH<sub>3</sub>BH<sub>3</sub>) / k(ND<sub>3</sub>BD<sub>3</sub>) of 2.0 (Figure 6).

Complementing the kinetic studies, we conducted poisoning experiments in order to study the nature of the catalytically active

species.<sup>[25]</sup> The analysis of changes of catalyst activity by the presence of selective catalyst poisons is an instructive tool for the distinction between homotopic and heterotopic catalysis pathways.<sup>[19],[26]</sup> Mercury (675 equiv. per [Co]) and P(OMe)<sub>3</sub> (0.2 equiv. per catalyst) barely had an influence on the overall reaction rate (5 mol% catalyst, see Figure 7). Both additives are known to selectively poison heterogeneous catalysts.<sup>[19],[25],[26]</sup> A complementary experiment was performed with the strong  $\pi$ -ligand dibenzo[a,e]cyclooctatetraene (dct), which selectively deactivates soluble metal complexes in low oxidation states and therefore is a powerful poison of homogeneous catalysts. [19], [25]-[27] Addition of AB to a solution of the catalyst (5 mol% 1) and dct (2 equiv. per [Co]) significantly slowed down the reaction. The inhibition was not complete as dct underwent partial hydrogenation to *E/Z*-dibenzocyclooctene and dibenzocyclooctane (GC-MS). These poisoning studies support the notion of a homotopic reaction mechanism.



Figure 6. Observation of kinetic isotope effects in the dehydrogenation of ammonia borane. Reaction conditions: 5 mol% 1, 0.2 mmol AB, THF (1 mL), 25°C.



**Figure 7.** Poisoning experiments in the dehydrogenation of AB. Reaction conditions: 5 mol% **1**, 0.2 mmol AB, THF (1 mL), 25°C.

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The insight gained by these studies can be summarized in a tentative mechanistic scheme (Scheme 3). Catalysis is initiated by the (partial) hydrogenation the cyclooctadiene ligand. This results in an induction period observed in the reaction-time profiles at low catalyst concentrations. The poisoning studies indicate that a homogeneous (molecular) catalyst is operative, while the 2<sup>nd</sup> order rate law with respect to cobalt suggests that the rate-determining step involves two cobalt atoms. While the exact structure of the active species still remains obscure presently, it should be noted that numerous transition metal hydrides catalyze amine-borane dehydrogenation,<sup>[1]</sup> and there is literature precedent for dinuclear cobalt hydride complexes.<sup>[33]</sup> A dinuclear cobalt hydride species thus might be a plausible oncycle intermediate. The basic nature of the hydride ligands might explain why N-H transfer appears to be rate determining in this case.



**Scheme 3.** Summary of the mechanistic information gained for amine-borane dehydrogenation and transfer transfer hydrogenation ( $X = CR_2$ , NHR").

Scope of transfer hydrogenations. Next, we expanded the catalytic applications of 1 and 2 to transfer hydrogenations of C=C and C=N bonds using AB as formal hydrogen donor. Only a few molecular cobalt catalysts are known to be competent in transfer hydrogenations of olefins and imines (Figure 1).<sup>[9]</sup> We performed initial studies with the combination of NH<sub>3</sub>BH<sub>3</sub> and α-methylstyrene (SI, Table S1). Pre-catalysts 1 and 2 gave similar results. Optimizations with 1 showed best activities and full conversion at 5 mol% catalyst loading and equimolar concentrations of alkene and AB (0.2 mol L<sup>-1</sup> in THF, see SI: Table S1). Allylbenzene, linear  $\alpha$ -olefins, and 4-octene were successfully hydrogenated under these conditions (Figure 8). Complete hydrogenation of 1,1-diphenylethylene proceeded within 40 h at ambient temperature. The reaction conditions were compatible with ethers, esters, amines, CF<sub>3</sub>, F, and free alcohols (Figure 8). Minor dehydrohalogenation (3%) was observed for 4-chloro-α-methylstyrene. Alkyl cinnamates underwent competitive carbonyl hydrogenation to give 3-phenyl-1-propanol. Challenging trisubstituted olefins such as 1-phenylcyclopentene, 1-phenylcyclohexene, and 1,1',2-triphenylethylene as well as arene moieties remained untouched even at elevated temperatures and with an excess of AB. Hydrogenation of such unsaturated functions could be realized by applying external H<sub>2</sub> pressure (vide infra). The scope of transfer hydrogenations was

extended to imines and quinoline derivatives (Figure 9). Hydrogenations of quinolines are of particular interest due to the formation of 1,2,3,4-tetrahydroquinolines, which constitute key motifs of several bioactive compounds.<sup>[30],[31]</sup>



**Figure 8.** Transfer hydrogenation of alkenes with **1** (5 mol%). Standard conditions: alkene and AB (each 0.2 mmol), THF (1 mL); yields were determined by quantitative GC vs. internal *n*-pentadecane. [a] 40 h.

Very few heterogeneous catalysts for the transfer hydrogenation of quinolines and related *N*-heterocycles were described by *Beller* and co-workers,<sup>[28]</sup> while molecular catalysts are also scarce.<sup>[30]</sup> Using catalyst **1**, various quinolines was hydrogenated to 1,2,3,4-tetra-hydroquinolines at room temperature within 16 h. The equimolar stoichiometry of quinolines and AB underlines the high efficacy of catalyst **1** as 2 equiv. H<sub>2</sub> per AB are being transferred. Quinoxaline containing two C=N bonds was fully hydrogenated.

**Mechanistic studies of transfer hydrogenation.** We investigated the reaction-time profile of the hydrogenation of  $\alpha$ -methyl-styrene (blue curve in Figure 10). The reaction onset is very fast (50% conversion after 3 min) and very similar to the dehydrogenation of AB (Figure 5). The reaction between  $\alpha$ -methyl-styrene and AB under an atmosphere of 1 bar D<sub>2</sub> showed no deuterium incorporation after 5 min (GC-MS, see SI: Figure S31). This indicates a direct (i.e. intramolecular) hydrogen

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Figure 9. Transfer hydrogenation of imines. Standard conditions: substrate (0.2 mmol), THF (1 mL); yields were determined by quantitative GC vs. internal *n*-pentadecane. Conditions for isolated (isol.) substrates: substrate (0.4 mmol), THF (2 mL).

transfer from AB to the alkene (see Scheme 3 above) which is orders of magnitude faster than the reduction of the alkene by D<sub>2</sub>. Furthermore, this observation argues against a stepwise mechanism involving H<sub>2</sub> formation from AB followed by cobaltcatalyzed hydrogenation of the alkene. Deuterated cumenes (appr. 15-20%, mostly cumene-d<sub>1</sub>, little cumene-d<sub>2-7</sub>) were only observed after long reaction times (16 h, GC-MS, see SI: Figures S30 and S32).<sup>[32]</sup> Catalyst poisoning studies with dct suggested that the reaction follows a homotopic mechanism. The reaction was immediately inhibited after dct addition at 50% conversion (1.0 equiv. per [Co], Figure 10). The partial hydrogenation of the catalyst poison dct to a mixture of dibenzocyclooctene and dibenzocyclooctane resulted in the recovery of low catalyst activity after a few minutes (GC-MS).





Hydrogenation of alkenes. The inefficacy of the transfer hydrogenation protocol for sterically hindered and some functionalized substrates prompted us to develop а hydrogenation protocol that would combine the rapid catalyst activation mechanism by catalytic amounts of AB with a hydrogenation mechanism in the presence of (super)stoichiometric amounts of H<sub>2</sub> gas (Table 1).<sup>[34],[35],[36]</sup> Precatalyst 2 proved slightly more active than 1 in the hydrogenation of the model substrate 1,1',2-triphenylethylene. With 3 mol% of 2, the hydrogenation proceeded cleanly at 20 bar H<sub>2</sub> and 60°C in the presence of several amine-boranes as catalyst activators. Amines and BH3 THF were unreactive; NMe2HBH3 fared much poorer than AB.

 Table 1. Screening of different additives in the hydrogenation of 1,1',2-triphenylethylene with catalyst 2.

	Ph	<b>2</b> (3 mol%)	Ph L <mark>H</mark>
	Ph Ph	20 bar <mark>H<sub>2</sub>,</mark> 60°C, 24 h THF (1 mL)	Ph Ph
6		+ additive (30 mol%)	

Additive	Yield (conversion) in [%]	
w/o	0 (0)	
NMe <sub>2</sub> HBH <sub>3</sub>	92	
NH <sub>3</sub> BH <sub>3</sub>	> 99	
NH <sub>3</sub> BH <sub>3</sub> <sup>[b]</sup>	> 99	
NEt <sub>3</sub>	0 (13)	
Pyridine	1 (14)	
Piperidine	0 (12)	
BH₃· (THF)	2 (52) <sup>[c]</sup>	

[a] Standard conditions: **2** (3 mol%), substrate (0.2 mmol) in THF (1 mL). Yields of hydrogenated products were determined by quantitative GC vs. internal *n*-pentadecane. [b] catalyst **1** instead of **2**. [c] possibly due to hydroboration of triphenylethylene.

The general conditions were applied to a series of trisubstituted olefins (Figure 11). It is noteworthy that, unlike the transfer hydrogenation protocol, no dehalogenation was observed for 4-halo- $\alpha$ -methylstyrenes (X = Cl, Br) under these hydrogenation conditions. Naphthalene and pinene were hydrogenated at elevated temperature.

#### Conclusions

We have shown that for the first time that highly reduced cobalt anions such as  $[K(thf)_{1.5}{DippBIAN}Co(\eta^4-cod)]$  (1) can be used as active catalysts for the dehydrogenation of ammonia borane (AB) and related amine-boranes under mild conditions. The activity of 1 surpasses that of other molecular cobalt catalysts by

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**Figure 11.** Substrate scope of alkene hydrogenations involving AB-mediated catalyst activation. Bonds in blue indicate sites of  $\pi$ -bond hydrogenation. Standard conditions: 0.2 mmol alkene, THF (1 mL). Yields determined by quantitative GC-FID vs. internal *n*-pentadecane; conversions given in parentheses if <90%.

Waterman<sup>[10]</sup> and Shubina<sup>[11]</sup> (Figure 1), which require elevated temperatures for an effective dehydrogenation reaction. Pre-catalyst 1 displayed a similar activity as Peter's PBP pincer complex<sup>[9]</sup> for the dehydrogenation of DMAB. A mixture of polyaminoborane, borazine, polyborazine was obtained using catalyst **1**, indicating that >1 equiv.  $H_2$  was released from AB. Reaction monitoring and poisoning experiments strongly indicate the operation of a homotopic catalyst. Transfer hydrogenation of olefins, imines, and quinolines have attracted increased attention only recently.<sup>[28],[29]</sup> Catalyst 1 is also able to catalyze such transformations effectively, which involved the transfer of up to 2 equiv. H<sub>2</sub> from AB. Mechanistic studies documented that the ratedetermining step likely involves proton transfer from the amineborane, while the rate law suggested that more than one Co atom may be involved. Poisoning experiments again supported a homogeneous mechanism.  $[K(thf){^{Mes}BIAN}Co(\eta^{4}-cod)]$  (2) exhibited similarly good catalytic activity in the transfer hydrogenation reaction between AB and alkenes/imines. A related protocol was used for the hydrogenation of challenging trisubstituted olefins which involved catalyst activation by AB and subsequent hydrogenation under 10 bar H<sub>2</sub>. This initial study demonstrates the significant potential of highly reduced  $\alpha$ -diimine cobaltate for (de)hydrogenation reactions for the first time. The results have direct ramifications for the development of related reductive transformations and H<sub>2</sub> storage processes under base metal catalysis, which are the subject on on-going investigation in our laboratories.

#### **Experimental Section**

See the supporting information for experimental details.

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- a) A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.* 2010, *110*, 4079–4124. b) A. Rossin, M. Peruzzini, *Chem. Rev.* 2016, *116*, 8848– 8872.
- [2] a) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* 2007, 0, 2613–2626. b) N. C. Smythe, J. C. Gordon, *Eur. J. Inorg. Chem.* 2010, 2010, 509–521
- [3] a) A. Staubitz, A. Presa Soto, I. Manners, Angew. Chem. Int. Ed. 2008, 47, 6212–6215; Angew. Chem. 2008, 120, 6308–6311. b) A. Ledoux, P. Larini, C. Boisson, V. Monteil, J. Raynaud, E. Lacôte, Angew. Chem. Int. Ed. 2015, 54, 15744–15749; Angew. Chem. 2015, 127, 15970–15975.
   c) E. M. Leitao, T. Jurca, I. Manners, Nature Chem. 2013, 5, 817–829.
- [4] a) S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S.-P. Luo, Q. Liu, J. Am. Chem. Soc. 2016, 138, 8588–8594. b) E. Korytiaková, N. O. Thiel, F. Pape, J. F. Teichert, Chem. Commun. 2017, 53, 732–735.
- [5] Selected examples for Ru, Pd, Rh, and Ir: a) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *Chem. Commun.* 2001, 962–963. b) A. Staubitz, A. Presa Soto, I. Manners, *Angew. Chem. Int. Ed.* 2008, 47, 6212–6215; *Angew. Chem.* 2008, 120, 6308–6311. c) N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black, K. Fagnou, *J. Am. Chem. Soc.* 2008, 130, 14034–14035. d) A. Friedrich, M. Drees, S. Schneider, *Chem. Eur. J.* 2009, 15, 10339–10342. e) T. M. Douglas, A. B. Chaplin, A. S. Weller, X. Yang, M. B. Hall, *J. Am. Chem. Soc.* 2009, 131, 15440-15456. f) A. Rossin, G. Bottari, A. M. Lozano-Vila, M. Paneque, M. Peruzzini, A. Rossi, F. Zanobini, *Dalton Trans.* 2013, 42, 3533–3541. f) E. H. Kwan, H. Ogawa, M. Yamashita, *ChemCatChem* 2017, 9, 2457–2462.
- [6] a) A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. Schmedt auf der Günne, I. Manners, *J. Am. Chem. Soc.* 2010, *132*, 13332–13345. b) T. Jurca, T. Dellermann, N. E. Stubbs, D. A. Resendiz-Lara, G. R. Whittell, I. Manners, *Chem. Sci.* 2018, *9*, 3360.
- [7] a) T. Kakizawa, Y. Kawano, K. Naganeyama, M. Shimoi, *Chem. Lett.* **2011**, *40*, 171–173. b) S. Muhammad, S. Moncho, E. N. Brothers, A. A. Bengali, *Chem. Commun.* **2014**, *50*, 5874–5877. c) M. Gediga, C. M. Feil, S. H. Schlindwein, J. Bender, M. Nieger, D. Gudat, *Chem. Eur. J.* **2017**, *23*, 11560–11569. d) H. R. Sharpe, A. M. Geer, T. J. Blundell, F. R. Hastings, M. W. Fay, G. A. Rance, W. Lewis, A. J. Blake, D. L. Kays, *Catal. Sci. Technol.* **2018**, *8*, 229–235.

[8] a) J. R. Vance, A. P. M. Robertson, K. Lee, I. Manners, *Chem. Eur. J.* 2011, *17*, 4099–4103. b) R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P.-H. Lin, S. Maguire, M. Murugesu, B. L. Scott, N. C. Smythe, *J. Am. Chem. Soc.* 2012, *134*, 5598–5609. c) P. Bhattacharya, J. A. Krause, H. Guan, *J. Am. Chem. Soc.* 2014, *136*, 11153–11161. d) J. R. Vance, A. Schäfer, A. P. M. Robertson, K. Lee, J. Turner, G. R. Whittell, I. Manners, *J. Am. Chem. Soc.* 2014, *136*, 3048–3064. e) A. Glüer, M. Förster, V. R. Celinski, J. Schmedt auf der Günne, M. C. Holthausen, S. Schneider, *ACS Catal.* 2015, *5*, 7214–7217. f) C. Lichtenberg, M.

# **FULL PAPER**

Adelhardt, T. L. Gianetti, K. Meyer, B. de Bruin, H. Grützmacher, ACS Catal. 2015, 5, 6230–6240. g) C. Lichtenberg, L. Viciu, M. Adelhardt, J. Sutter, K. Meyer, B. de Bruin, H. Grützmacher, Angew. Chem. Int. Ed. 2015, 54, 5766–5771; Angew. Chem. 2015, 127, 5858–5863. h) A. M. Lunsford, J. H. Blank, S. Moncho, S. C. Haas, S. Muhammad, E. N. Brothers, M. Y. Darensbourg, A. A. Bengali, Inorg. Chem. 2016, 55, 964–973. i) N. T. Coles, M. F. Mahon, R. L. Webster, Organometallics 2017, 36, 2262–2268. j) U. Chakraborty, S. Demeshko, F. Meyer, C. Rebreyend, B. de Bruin, M. Atanasov, F. Neese, B. Mühldorf, R. Wolf, Angew. Chem. Int. Ed. 2017, 56, 7995–7999; Angew. Chem. 2017, 129, 8107–8112. k) F. Anke, D. Han, M. Klahn, A. Spannenberg, T. Beweries Dalton Trans. 2017, 46, 6843–6847, I) J. Turner, N. F. Chilton, A. Kumar, A. L. Colebatch, G. R. Whittell, H. A. Sparkes, A. S. Weller, I. Manners, Chem. Eur. J. 2018; DOI: 10.1002/chem.201705316.

- a) T.-P. Lin, J. C. Peters, J. Am. Chem. Soc. 2013, 135, 15310–15313.
   b) G. Ganguly, T. Malakar, A. Paul, ACS Catal. 2015, 5, 2754–2769.
- [10] J. K. Pagano, J. P. W. Stelmach, R. Waterman, *Dalton Trans.* 2015, 44, 12074–12077.
- [11] S. Todisco, L. Luconi, G. Giambastiani, A. Rossin, M. Peruzzini, I. E. Golub, O. A. Filippov, N. V. Belkova, E. S. Shubina, *Inorg. Chem.* 2017, 56, 4296–4307.
- [12] a) R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* 2007, 129, 1844–1845. b) M. Vogt, B. de Bruin, H. Berke, M. Trincado, H. Grützmacher, *Chem. Sci.* 2011, *2*, 723–727. c) A. P. M. Robertson, R. Suter, L. Chabanne, G. R. Whittell, I. Manners, *Inorg. Chem.* 2011, *50*, 12680–12691. d) S.-K. Kim, S.-A. Hong, H.-J. Son, W.-S. Han, A. Michalak, S.-J. Hwang, S. O. Kang, *Dalton Trans.* 2015, *44*, 7373–7381.
- [13] reviews on properties of BIAN derivatives and their coordination chemistry with s- and p-block elements: a) N. J. Hill, I. Vargas-Baca, A. H. Cowley, *Dalt. Trans.* 2009, *9226*, 240; b) I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, *Angew. Chem. Int. Ed.* 2003, *42*, 3294; *Angew. Chem.* 2003, *115*, 3416–3420.
- [14] Selected examples of (BIAN)Pd(olefin)-catalyzed hydrogenations: a) R. van Asselt, C. J. Elsevier, J. Mol. Catal. A 1991, 65, L13–L19. b) R. van Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, R. Benedix, Recl. Trav. Chim. Pays-Bas 1994, 113, 88–98. c) M. W. Van Laren, C. J. Elsevier, Angew. Chem. Int. Ed. 1999, 38, 3715–3717; Angew. Chem. 1999, 11, 3926–3929.
- [15] a) F. S. Wekesa, R. Arias-Ugarte, L. Kong, Z. Sumner, G. P. McGovern, M. Findlater, *Organometallics* 2015, *34*, 5051–5056; b) M. J. Supej, A. Volkov, L. Darko, R. A. West, J. M. Darmon, C. E. Schulz, K. A. Wheeler, H. M. Hoyt, *Polyhedron* 2016, *114*, 403–414; c) M. Villa, D. Miesel, A. Hildebrandt, F. Ragaini, D. Schaarschmidt, A. Jacobi von Wangelin, *ChemCatChem* 2017, *9*, 3203–3209.
- [16] Review on metalate anions highlighting the pioneering work of Jonas and Ellis: J. E. Ellis, *Inorg. Chem.* 2006, 45, 3167–3186.
- [17] a) W. W. Brennessel, J. Young Victor G., J. E. Ellis, Angew. Chem. Int. Ed. 2002, 41, 1211–1215; Angew. Chem. 2002, 114, 1259–1263. b) W.
   W. Brennessel, R. E. Jilek, J. E. Ellis, Angew. Chem. Int. Ed. 2007, 46, 6132–6136; Angew. Chem. 2007, 119, 6244–6248.
- [18] a) K. Jonas, R. Mynott, C. Krüger, J. C. Sekutowski, Y.-H. Tsay, Angew. Chem. Int. Ed. Engl. 1976, 15, 767–768; Angew. Chem. 1976, 88, 808– 809.
- [19] a) D. Gärtner, A. Welther, B. R. Rad, R. Wolf, A. Jacobi von Wangelin, Angew. Chem. Int. Ed. 2014, 53, 3722–3726; Angew. Chem. 2014, 126, 3796–3800. b) P. Büschelberger, D. Gärtner, E. Reyes-Rodriguez, F. Kreyenschmidt, K. Koszinowski, A. Jacobi von Wangelin, R. Wolf, Chem. Eur. J. 2017, 23, 3139–3151.
- [20] S. Pelties, T. Maier, D. Herrmann, B. de Bruin, C. Rebreyend, S. Gärtner, I. G. Shenderovich, R. Wolf, *Chem. Eur. J.* 2017, 23, 6094–6102.
- [21] a) A. Friedrich, M. Drees, S. Schneider, *Chem. Eur. J.* 2009, *15*, 10339–10342. b) L. J. Sewell, G. C. Lloyd-Jones, A. S. Weller, *J. Am. Chem. Soc* 2012, *134*, 3598-3610.
- [22] a) O. W. Metters, S. R. Flynn, C. K. Dowds, H. A. Sparkes, I. Manners, D. F. Wass, ACS Catal. 2016, 6, 6601-6611. b) E. M. Titova, E. S.

Osipova, A. A. Pavlov, O. A. Fillippov, S. V. Safranov, E. S. Shubina, N. V. Belkova, *ACS Catal.* **2017**, 7, 2325-2333. c) L. Luconi, E. S. Osipova, G. Giambastiani, M. Peruzzini, A. Rossin, N. V. Belkova, O. A: Fillippov, E. M. Titova, A. A. Pavlov, E. S. Shubina, *Organometallics* **2018**, *37*, 3142-3153.

- [23] Dehydrogenation of diisopropylamino borane: a) C. A. De Albuquerque Pinheiro, C. Roiland, P. Jehan, G. Alcaraz, *Angew. Chem. Int. Ed.* 2018, 57, 1519; *Angew. Chem.* 2018, 130, 1535. b) ref. [11c].
- [24] Selected examples for dehydrogenation of methylamine-borane to poly-N-methylaminoborane or [MeHN-BH<sub>2</sub>]<sub>3</sub>: a) A. Staubitz, A. Presa Soto, I. Manners, Angew. Chem. Int. Ed. 2008, 47, 6212–6215; Angew. Chem. 2008, 120, 6308–6311. b) Y. Kawano, M. Uruichi, M. Shimoi, S. Taki, T. Kawaguchi, T. Kakizawa, H. Ogino, J. Am. Chem. Soc. 2009, 131, 14946–14957. c) T. Kakizawa, Y. Kawano, K. Naganeyama, M. Shimoi, Chem. Lett. 2011, 40, 171–173. e) G. M. Adams, A. L. Colebatch, J. T. Skornia, A. I. McKay, H. C. Johnson, G. C. Lloyd Jones, S. A. Macgregor, N. A. Beattie, A. S. Weller, J. Am. Chem. Soc. 2018, 140, 1481. f) see also ref. [6a], [7k].
- Selected reviews on homotopic vs. heterotopic catalysis: a) R. H. Crabtree, *Chem. Rev.* 2012, *112*, 1536–1554. b) V. Artero, M. Fontecave, *Chem. Soc. Rev.* 2013, *42*, 2338–2356. c) J. F. Sonnenberg, R. H. Morris, *Catal. Sci. Technol.* 2014, *4*, 3426–3438.
- [26] a) P. Büschelberger, E. Reyes-Rodriguez, C. Schöttle, J. Treptow, C. Feldmann, A. Jacobi von Wangelin, R. Wolf, *Catal. Sci. Technol.* 2018, 8, 2648–2653. b) S. Sandl, F. Schwarzhuber, S. Pöllath, J. Zweck, A. Jacobi von Wangelin, *Chem. Eur. J.* 2018, *24*, 3403–3407.
- [27] a) D. R. Anton, R. H. Crabtree, Organometallics 1983, 2, 855–859. b) S.
   Chaffins, M. Brettreich, F. Wudl, Synthesis 2002, 2002, 1191–1194. c)
   G. Franck, M. Brill, G. Helmchen, Org. Synth. 2012, 89, 55–65.
- [28] F. Chen, B. Sahoo, C. Kreyenschulte, H. Lund, M. Zeng, L. He, K. Junge, M. Beller, *Chem. Sci.* 2017, *8*, 6239–6246.
- [29] a) G. Zhang, S. K. Hanson, *Chem. Commun.* 2013, *49*, 10151–10153. b)
  G. Zhang, Z. Yin, J. Tan, *RSC Adv.* 2016, *6*, 22419–22423. c) S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S.-P. Luo, Q. Liu, *J. Am. Chem. Soc.* 2016, *138*, 8588–8594. d) J. R. Cabrero-Antonino, R. Adam, K. Junge, R. Jackstell, M. Beller, *Catal. Sci. Technol.* 2017, *7*, 1981–1985. e) V. G. Landge, J. Pitchaimani, S. P. Midya, M. Subaramanian, V. Madhu, E. Balaraman, *Catal. Sci. Technol.* 2018, *8*, 428–433.
- [30] Examples for cobalt-catalyzed imine and quinoline hydrogenation: a) K.
   Kobayashi, T. Okamoto, T. Oida, S. Tanimoto, *Chem. Lett.* **1986**, *15*, 2031–2034. b) R. Xu, S. Chakraborty, H. Yuan, W. D. Jones, *ACS Catal.* **2015**, *5*, 6350–6354.
- [31] Reviews on 1,2,3,4-tetrahydroquinoline chemistry: a) A. R. Katritzky, S. Rachwal, B. Rachwal, *Tetrahedron* **1996**, *52*, 15031–15070. b) V. Sridharan, P. A. Suryavanshi, J. C. Menéndez, *Chem. Rev.* **2011**, *111*, 7157–7259.
- [32] <sup>2</sup>H NMR spectroscopy of the obtained H/D-cumene mixture showed on average that 20% of the methine positions and 18% of the methyl positions bear D atoms. The higher deuteration level of the methyl positions may indicate the operation of a mono-deuterium atom transfer to the alkene or possibly an H/D-exhange via benzyl radical intermediates.
- [33] Selected examples of dinuclear cobalt hydrides: a) M. D. Fryzuk, J. B. Ng, S. J. Rettig, J. C. Huffman, K. Jonas, *Inorg. Chem.* **1991**, *30*, 2437–2441. b) J. L. Kersten, A. L. Rheingold, K. H. Theopold, C. P. Casey. R. A. Widenhoefer, C. E. C. A. Hop, *Angew. Chem.* **1992**, *104*, 1364-1366. c) K. Ding, W. W. Brennessel, P. L. Holland, *J. Am. Chem. Soc.* **2009**, *131*, 10804–10805.
- [34] a) Catalytic Hydrogenation Ed.: L. Cerveny), Elsevier, Amsterdam, 1986.
  b) The Handbook of Homogeneous Hydrogenation (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, 2007. c) P. J. Chirik, Acc. Chem. Res. 2015, 48, 1687.
- [35] Selected examples of Co-catalyzed alkene hydrogenations: a) Q. Knijenenburg, A. D. Horton, H. van der Heijden, B. de Bruin, P. H. M. Budzelaar, W. A. Gal J. Mol. Catal. A. Chem. 2005, 232, 151–159. b) G.

## **FULL PAPER**

Zhang, B. L. Scott, S. Hanson, *Angew. Chem. Int. Ed.* **2012**, *51*, 12102-12106; *Angew. Chem.* **2012**, *124*, 12268-12272. c) M. R. Friedfeld, M. Shevlin, J. M. Hoyt, S. W. Krska, M. T. Tudge, P. J. Chirik, *Science* **2013**, *342*, 1076. d) R. P. Yu, J. M. Darmon, C. Milsmann, G. W. Margulieux, S. C. E. Stieber, S. DeBeer, P. J. Chirik, *J. Am. Chem. Soc* **2013**, *135*, 13168–13184. e) M. R. Friedfeld, G. W. Margulieux, B. A. Schäfer, P. J.

Chirik, J. Am. Chem. Soc. 2014, 136, 13178–13181. f) M. R. Friedfeld, H. Zhong, R. T. Ruck, M. Shevlin, P. J. Chirik, Science 2018, 360, 888.
[36] A related approach for the activation of cobalt catalysts with AB as an additive has recently been reported for regioselective olefin isomerization with N,N,P pincer complexes: X. Liu, W. Zhang, Y. Wang, Z.-X. Zhang, L. Jiao, Q. Liu, J. Am. Chem. Soc. 2018, 140, 6873–6882

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A new class of cobalt catalysts with redox-active bisiminoacenaphthene diimine (BIAN) ligands efficiently catalyzes transfer hydrogenation and dehydrogenation reactions of amineboranes. Alkenes, imines and quinolines were effectively reduced with ammonia borane (AB) as a dihydrogen surrogate. Moreover, AB can be used as an initiator for the hydrogenation of highly challenging trisubstituted olefins.



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Amine-borane Dehydrogenation and Transfer Hydrogenation Catalyzed by α-Diimine Cobaltates