

## UvA-DARE (Digital Academic Repository)

### Low-Valent Iron(I) Amido Olefin Complexes as Promoters for Dehydrogenation Reactions

Lichtenberg, C.; Viciu, L.; Adelhardt, M.; Sutter, J.; Meyer, K.; de Bruin, B.; Grützmacher, H.

#### DOI

[10.1002/anie.201411365](https://doi.org/10.1002/anie.201411365)

[10.1002/ange.201411365](https://doi.org/10.1002/ange.201411365)

#### Publication date

2015

#### Document Version

Final published version

#### Published in

Angewandte Chemie, International Edition

#### License

Article 25fa Dutch Copyright Act

[Link to publication](#)

#### Citation for published version (APA):

Lichtenberg, C., Viciu, L., Adelhardt, M., Sutter, J., Meyer, K., de Bruin, B., & Grützmacher, H. (2015). Low-Valent Iron(I) Amido Olefin Complexes as Promoters for Dehydrogenation Reactions. *Angewandte Chemie, International Edition*, 54(19), 5766-5771. <https://doi.org/10.1002/anie.201411365>, <https://doi.org/10.1002/ange.201411365>

#### General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

#### Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

# Low-Valent Iron(I) Amido Olefin Complexes as Promoters for Dehydrogenation Reactions\*\*

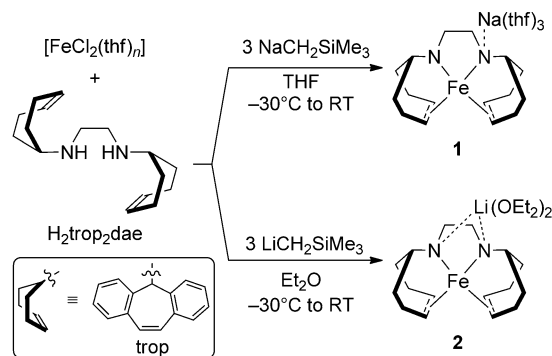
Crispin Lichtenberg,\* Liliana Viciu, Mario Adelhardt, Jörg Sutter, Karsten Meyer, Bas de Bruin,\* and Hansjörg Grützmacher\*

**Abstract:**  $Fe^I$  compounds including hydrogenases show remarkable properties and reactivities. Several iron(I) complexes have been established in stoichiometric reactions as model compounds for  $N_2$  or  $CO_2$  activation. The development of well-defined iron(I) complexes for catalytic transformations remains a challenge. The few examples include cross-coupling reactions, hydrogenations of terminal olefins, and azide functionalizations. Here the syntheses and properties of bimetallic complexes  $[MFe^I(trop_2dae)(solv)]$  ( $M = Na$ ,  $solv = 3 thf$ ;  $M = Li$ ,  $solv = 2 Et_2O$ ;  $trop = 5H$ -dibenzo[*a,d*]cyclo-hepten-5-yl,  $dae = (N-CH_2-CH_2-N)$ ) with a  $d^7$  Fe low-spin valence-electron configuration are reported. Both compounds promote the dehydrogenation of *N,N*-dimethylaminoborane, and the former is a precatalyst for the dehydrogenative alcoholysis of silanes. No indications for heterogeneous catalyses were found. High activities and complete conversions were observed particularly with  $[NaFe^I(trop_2dae)(thf)_3]$ .

$Fe^I$  compounds including hydrogenases<sup>[1a]</sup> show remarkable properties and reactivities.<sup>[2–6]</sup> The anion  $[Fe(C(SiMe_3)_3)_2]^-$  is a single-molecule magnet with a high spin-reversal barrier.<sup>[2a]</sup> In stoichiometric reactions, iron(I) diketiminates, iron(I) tris(phosphino)borates, and related species have been established as model compounds for  $N_2$  activation<sup>[4a–c,1,5a,f]</sup> and for the cleavage and coupling of  $CO_2$ .<sup>[4d,e]</sup> The development of well-defined iron(I) complexes for catalytic transformations, however, remains a challenge. The few examples include cross-coupling reactions,<sup>[2b,3]</sup> hydrogenations of terminal olefins,<sup>[4f]</sup> and azide functionalizations.<sup>[4h,5i]</sup> Here we report the

syntheses and properties of bimetallic complexes  $[MFe^I(trop_2dae)(solv)]$  with a  $d^7$  Fe low-spin valence-electron configuration ( $M = Na$ ,  $solv = 3 thf$  (**1**);  $M = Li$ ,  $solv = 2 Et_2O$  (**2**);  $trop = 5H$ -dibenzo[*a,d*]cyclo-hepten-5-yl,  $dae = (N-CH_2-CH_2-N)$ ). Compounds **1** and **2** promote the dehydrogenation of *N,N*-dimethylaminoborane, and **1** is a precatalyst for the dehydrogenative alcoholysis of silanes. No indications for heterogeneous catalyses were found. High activities and complete conversions were observed particularly with  $[NaFe^I(trop_2dae)(thf)_3]$  (**1**).

The olefinic binding sites in trop-type ligands stabilize unusual low oxidation states of transition-metal centers.<sup>[7]</sup> We recently reported a low-valent Ru compound with a bis(trop)diamino ligand,  $[Ru(H_2trop_2dae)]$ , which acts as a homogeneous molecular catalyst for the conversion of methanol and water into hydrogen and carbon dioxide.<sup>[8]</sup> This prompted us to investigate the  $H_2trop_2dae$  ligand (Scheme 1) as a supporting ligand for new low-valent iron complexes.



**Scheme 1.** Synthesis of complexes **1** and **2** from  $[FeCl_2(thf)_n]$ ;  $n = 1.5$ ; **2**:  $n = 0$ .

The reaction of the amine  $H_2trop_2dae$  with one equiv of  $[FeCl_2(thf)_{1.5}]$  and three equiv of  $[Na(CH_2SiMe_3)]$  as base and reducing agent in THF at  $-30^\circ C$  gave the bis(amido)-diolefin complex  $[NaFe(trop_2dae)(thf)_3]$  (**1**; Scheme 1). Compound **1** was isolated as a deep red, single-crystalline material, which is soluble in polar solvents such as THF but also in aromatic hydrocarbons. To study the influence of the counterion,<sup>[9]</sup>  $[LiFe(trop_2dae)(Et_2O)_2]$  (**2**) was synthesized in a similar manner by using a slight excess of  $[Li(CH_2SiMe_3)]$ .

Compound **2** was isolated as deep-red single crystals and shows a solubility similar to that of **1**. The reactions leading to the formation of compounds **1** and **2** are complex and involve at some stage ligand coordination, deprotonation, salt meta-

[\*] Dr. C. Lichtenberg, Dr. L. Viciu, Prof. Dr. H. Grützmacher  
Department of Chemistry and Applied Biosciences, ETH Zürich  
Vladimir-Prelog-Weg 1, 8093 Zürich (Switzerland)  
E-mail: lichtenberg@inorg.chem.ethz.ch  
hgruetzmacher@ethz.ch

Prof. Dr. B. de Bruin  
Universiteit van Amsterdam, Faculty of Science, van 't Hoff Institute  
for Molecular Sciences Department of Homogeneous Catalysis  
Postbus 94720, 1090 GS Amsterdam (The Netherlands)  
E-mail: B.deBruin@uva.nl

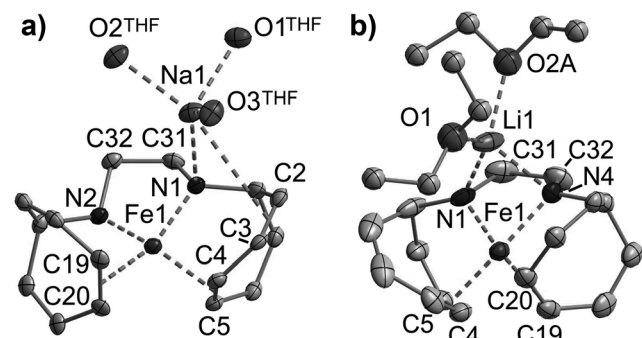
M. Adelhardt, Dr. J. Sutter, Prof. Dr. K. Meyer  
Department of Chemistry & Pharmacy  
Friedrich-Alexander University, Erlangen–Nürnberg (FAU)  
Egerlandstrasse 1, 91058 Erlangen (Germany)

[\*\*] We thank Dr. Frank Krumeich for scientific support with SEM  
analyses and Dr. Eckard Bill for helpful discussions. C.L. is grateful  
for a Feodor Lynen fellowship generously hosted by Prof. François  
Diederich.

Supporting information for this article is available on the WWW  
under <http://dx.doi.org/10.1002/anie.201411365>.

thesis, and redox reactions. In this respect it is noteworthy that the presence of tetramethylethylenediamine (TMEDA) as a chelating ligand led to a possible intermediate en route to the formation of species analogous to **1** and **2**, which could be isolated and fully characterized (see the Supporting Information, compound **3**).

The solid-state molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction studies (Figure 1). The iron atom in **1** is coordinated by the two

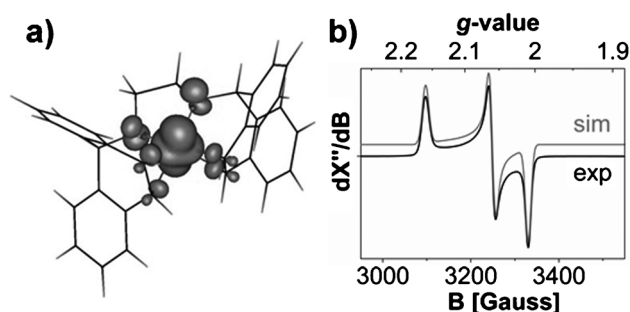


**Figure 1.** Molecular structure of [NaFe(trop<sub>2</sub>dae)(thf)<sub>3</sub>] (**1**) (a, left) and [LiFe(trop<sub>2</sub>dae)(OEt<sub>2</sub>)<sub>2</sub>] (**2**) (b, right) in the solid state;<sup>[35]</sup> displacement ellipsoids are shown at the 50% probability level; annulated C<sub>6</sub>H<sub>4</sub> groups, C atoms of THF ligands, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1**: Fe1–N1 1.900(4), Fe1–N2 1.860(3), Fe1–(C4–C5) 1.931(4), Fe1–(C19–C20) 1.924(4), C4–C5 1.435(6), C19–C20 1.438(5), Na1–N1 2.469(4); (N/(C=C)–Fe1–N/(C=C)) 84.77(14)–97.88(15); angle sum around Fe1 369. **2**: Fe1–N1 1.899(3), Fe1–N2 1.950(4), Fe1–(C4–C5) 1.928(6), Fe1–(C19–C20) 1.939(6), Li1–N1 2.160(11), Li1–N2 2.095(11), C4–C5 1.416(8), C19–C20 1.415(10), Fe1–Li1 2.756(8); (N/(C=C)–Fe1–N/(C=C)) 79.37(18)–97.08(10); angle sum around Fe1 362.

amide functionalities and the two olefinic groups of the (trop<sub>2</sub>dae)<sup>2-</sup> ligand. Taking the centroids of the C=C<sub>trop</sub> units as coordination points, this results in a distorted square-planar coordination sphere around Fe1 ( $\Sigma^\circ = 369^\circ$ ). Planar coordination spheres have occasionally been reported for tetracoordinate iron(II) compounds, but are rare for iron(I) compounds.<sup>[11]</sup> The five-membered ring (Fe1–N1–C31–C32–N2) adopts a twisted conformation with the carbon atoms located above and below the N1–Fe1–N2 plane. As a consequence of the additional interaction with the sodium cation Na1, the Fe1–N1 distance (1.900(4) Å) is slightly longer than Fe1–N2 (1.860(3) Å), and N1 resides in a slightly more pyramidal coordination sphere ( $\Sigma(\text{C}/\text{Fe}1\text{--N1}\text{--C}) = 343^\circ$ ;  $\Sigma(\text{C}/\text{Fe}1\text{--N2}\text{--C}) = 350^\circ$ ).<sup>[12]</sup> The Fe1–N1/2 distances are 0.02–0.05 Å shorter than those in pseudotetrahedral nitrosyl amide complexes [Fe(N<sup>t</sup>BuAr<sub>F</sub>)<sub>2</sub>(NO)(L)] (Ar<sub>F</sub> = 2,5-C<sub>6</sub>H<sub>3</sub>FMe, L = NC<sub>5</sub>D<sub>5</sub>, PEt<sub>3</sub>) and about 0.09 Å shorter than those in square-planar complexes of type [Fe(β-diketiminato)L<sub>2</sub>] (L = CO, CN<sup>t</sup>Bu).<sup>[5a,h,6a]</sup> The C=C<sub>trop</sub> bonds, C4=C5 and C19=C20, are rather long (1.415–1.438 Å) and indicate significant electron back-donation from the iron center into the π\* orbital of the olefinic binding site (for shorter coordinated C=C bonds see Refs. [2b,5e]). Compound **2** also shows a distorted planar coordination geometry around Fe1, but both nitrogen atoms

of the (trop<sub>2</sub>dae)<sup>2-</sup> ligand interact with the Li ion (Figure 1b).<sup>[13]</sup> In comparison to **1**, this results in slightly elongated Fe1–N1/2 bonds (0.04 Å in average), shortened C=C<sub>olefin</sub> bonds (0.02 Å in average), a smaller angle sum C/Fe–N2–C around N2 ( $\Delta = -15.1(3)^\circ$ ), and in a decreased N1–Fe1–N2 angle ( $\Delta = -5.40(2)^\circ$ ). The five-membered ring (Fe1–N1–C31–C32–N2) in **2** shows an envelope conformation with Fe1 displaced by 1.09 Å from the N1–C31–C32–N2 plane.

The subtle structural differences between **1** and **2** and their resulting electronic structures in the solid state were further investigated by <sup>57</sup>Fe Mössbauer spectroscopy at 77 K (see the Supporting Information). The isomer shift of compound **1** ( $\delta = 0.20(1) \text{ mm s}^{-1}$ ) is significantly smaller than that of **2** ( $\delta = 0.28(1) \text{ mm s}^{-1}$ ), which indicates a higher electron density in the Fe s orbitals of **1** and is in agreement with the smaller average Fe–L bond lengths in **1**.<sup>[14]</sup> The lower symmetry of the ligand environment in **1** leads to a larger quadrupole splitting ( $|\Delta E_{\text{O}}| = 2.87(1) \text{ mm s}^{-1}$ ) compared to **2** ( $|\Delta E_{\text{O}}| = 2.01(1) \text{ mm s}^{-1}$ ). These quadrupole splittings fall in the usual range for literature-known Fe<sup>I</sup> complexes ( $|\Delta E_{\text{O}}| = 0.89\text{--}3.48 \text{ mm s}^{-1}$ ).<sup>[4c,6e]</sup> However, other Fe<sup>I</sup> complexes generally show larger isomer shifts (from  $\delta = 0.28 \text{ mm s}^{-1}$  to  $1.09 \text{ mm s}^{-1}$ , which indicates lower electron density in Fe s orbitals).<sup>[1b,2a,15]</sup> Remarkably, Fe<sup>II</sup> and Fe<sup>III</sup> compounds with a fourfold planar coordination geometry as in **1** and **2** show similar isomer shifts [Fe<sup>II</sup>: 0.14–0.59; Fe<sup>III</sup>: 0.23–0.37  $\text{mm s}^{-1}$  but associated with much larger  $|\Delta E_{\text{O}}|$ : Fe<sup>II</sup>: 1.16–4.63; Fe<sup>III</sup>: 3.02–5.16  $\text{mm s}^{-1}$ ].<sup>[10,16,17]</sup> The low Fe<sup>II</sup>/Fe<sup>III</sup>-like isomer shifts for **1** and **2** are possibly a consequence of metal-to-ligand electron back-donation. DFT calculations on **1** and **2** gave optimized structures in good agreement with the single-crystal X-ray data (see the Supporting Information). Derivatives [MFe(trop<sub>2</sub>dae)(L)<sub>n</sub>] (M = Li, Na; L = neutral ligand bound to M; n = 0–3) and counterion-free [Fe(trop<sub>2</sub>dae)]<sup>-</sup> were also investigated. All species are mainly metal-centered radicals with significant spin polarization to the nitrogen donors and olefinic carbon atoms of the (trop<sub>2</sub>dae)<sup>2-</sup> ligand (Figure 2a). Hence, they are best described as low-spin d<sup>7</sup> Fe<sup>I</sup> species hosted by dianionic (trop<sub>2</sub>dae)<sup>2-</sup> ligands. Significant differences between the electronic structures of **1** and **2** arise from the larger g anisotropy, higher Fe spin density, and higher NBO charge at Fe for **2** (see Table S2 in the Supporting Information). These differences are mainly due to the coordination mode of the alkali metal (terminal as in



**Figure 2.** a) Spin density plot of [Fe(trop<sub>2</sub>dae)]<sup>-</sup> (for colored Figure see the Supporting Information); b) experimental and simulated X-band EPR spectrum of **2** in THF containing 0.1 M [N(<sup>n</sup>Bu)<sub>4</sub>][PF<sub>6</sub>].

1 versus bridging as in **2**), which can be controlled by choice of the neutral ligand L (see derivatives **2b–d** in the Supporting Information). The nature of the alkali metal itself has a smaller effect.

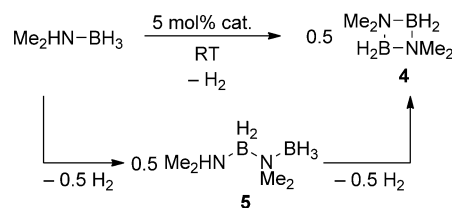
The electronic structures of **1** and **2** were further investigated by EPR spectroscopy at 20 K. Undiluted powdered solids of **1** and **2** gave X-band EPR spectra of reasonable quality which are clearly distinct from each other (see Figure S10 in the Supporting Information). The X-band EPR spectra of **1** and **2** in frozen THF containing 0.1 M  $[\text{N}(\text{nBu})_4][\text{PF}_6]$  are highly similar, thus indicating the formation of the free anion  $[\text{Fe}(\text{trop}_2\text{dae})]^-$  in both cases. Rhombic signals without any (resolved) hyperfine couplings were observed which are characteristic for low-spin  $d^7$   $\text{Fe}^{\text{I}}$  species (Figure 2b).

The experimental  $g$  values ( $g_x = 2.009$ ,  $g_y = 2.060$ ,  $g_z = 2.160$ ) are in reasonable agreement with those predicted by DFT calculations (see Table S2 in the Supporting Information). Unexpectedly, EPR spectroscopic analysis of **1** and **2** in toluene glasses at 20 K revealed broad and complex signals which are ascribed to aggregation phenomena (see Figure S13 in the Supporting Information). The spectra also show weak “half-field signals” which can be observed when  $S = 1/2$  systems weakly interact in the matrix (see Figure S14 in the Supporting Information).<sup>[18]</sup> The spectra of **1** and **2** in toluene are clearly different, thus indicating distinct aggregation behavior.

The low-spin  $d^7$  electron configuration of **1** was further confirmed by SQUID magnetization measurements. In an applied field of 1 T, an effective magnetic moment of  $\mu_{\text{eff}} = 1.96 \mu_{\text{B}}$  at 300 K was determined, which is almost invariant over a temperature range of 10–300 K (see the Supporting Information).<sup>[19]</sup> This value is close to the spin-only value of  $1.80 \mu_{\text{B}}$  for one unpaired electron (for  $g = 2.076$ ). In good agreement with this result, determination of the effective magnetic moment in benzene solution by the Evans method gave  $\mu_{\text{eff}} = 2.0(1) \mu_{\text{B}}$  for compounds **1** and **2**. A cyclic voltammogram of **1** in THF at 23 °C at a scan rate of  $0.2 \text{ V s}^{-1}$  shows a quasireversible redox wave with  $E_{1/2} = -2.24 \text{ V}$  versus  $\text{Fc}/\text{Fc}^+$  (see the Supporting Information), probably for an  $\text{Fe}^{\text{I}}$  to  $\text{Fe}^0$  conversion, while irreversible oxidation half-waves were recorded at  $-0.56 \text{ V}$  and at  $0.05 \text{ V}$  versus  $\text{Fc}/\text{Fc}^+$ . The large splitting of about 1.7 V between the oxidation and reduction waves indicates a high stability of the  $\text{Fe}^{\text{I}}$  complexes **1** and **2** with respect to disproportionation.

No reaction of **1** with  $\text{H}_2$  (1.5 bar,  $T = 25^\circ\text{C}$ ) was observed in nonpolar solvents.<sup>[20]</sup> However, substrates with “krypto”-hydrogen, that is hydrogen in the form of  $\text{H}^{\delta+}$ ,  $\text{H}^{\delta-}$ ,<sup>[21]</sup> such as  $N,N$ -dimethylaminoborane (DMAB;  $\text{Me}_2\text{HN}-\text{BH}_3$ ), are efficiently dehydrogenated.<sup>[22]</sup> Few iron-based catalysts have been reported for the dehydrogenation of DMAB.<sup>[23]</sup> Recent studies by Manners and co-workers show that in situ generated Fe nanoparticles are frequently catalytically active and only  $[\text{Fe}(\text{C}_3\text{H}_5)\text{I}(\text{CO})_2]$  acts as a homogeneous catalyst.<sup>[23a,b,24]</sup> In an open system, 5 mol % of **1** and **2** were used as catalysts for the dehydrogenation of DMAB in toluene at room temperature (Table 1 and see the Supporting Information). Under these conditions, the  $\text{LiFe}^{\text{I}}$  species **2** showed only moderate activity (4 h, 35 %, entry 1) and  $[\text{LiFe}(\text{trop}_2\text{dae})-$

**Table 1:** Dehydrogenation of DMAB with Fe catalysts **1**, **2**, and **2d**.<sup>[a]</sup>



Entry	Cat.	Additive/poison (equiv)	$t$ [h]	Conv. [%]
1	<b>2</b>	–	4.0	35
2	<b>2d</b>	–	4.0	< 5
3	<b>1</b>	–	4.0	> 99 <sup>[b]</sup>
4 <sup>[c]</sup>	<b>1</b>	–	1.3	> 99
5	<b>1</b>	15-crown-5 (1)	10	59
6	<b>1</b>	$[(\text{nBu})_4\text{N}]\text{Br}$ (1)	5.1	> 99
7 <sup>[c,d]</sup>	<b>1</b>	–	10	> 99
8 <sup>[e]</sup>	<b>1</b>	–	$3 \times 4$	$3 \times > 99$
9	<b>1</b>	THF as solvent	2.5	6
10	<b>1</b>	$\text{PPh}_3$ (0.2)	5.4	> 99
11	<b>1</b>	$\text{P}(\text{OMe})_3$ (0.1)	5.9	> 99

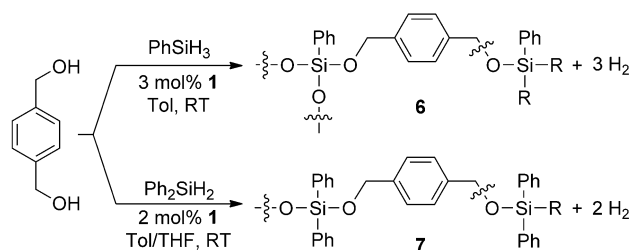
[a] Conditions: 0.048 M DMAB in toluene, 5 mol % catalyst. [b] **4** was identified by  $^{11}\text{B}$  NMR spectroscopy after completion of the reaction. [c] Overall concentrations increased by a factor of two. [d]  $\text{Me}_2\text{DN}-\text{BH}_3$  was used as a substrate. [e]  $3 \times 20$  equiv of DMAB used in consecutive additions.

( $\text{thf}$ )<sub>2</sub> (**2d**) was almost inactive (entry 2). In contrast, the  $\text{NaFe}^{\text{I}}$  compound **1** led to full conversion after 4 h (entry 3), giving the 1,3-diaza-2,4-diboretane **4** as sole product (see Table 1). The rate constant  $k_{\text{obs}}$  at early stages of the reaction increased by a factor of 2.1(2) upon increasing the overall concentrations by a factor of 2.0, and full conversion was reached after 1.3 h (entry 4, see also the Supporting Information). In contrast, additives such as 15-crown-5 or  $[(\text{nBu})_4\text{N}]\text{Br}$  decrease the reaction rate, which suggests that a solvent-separated ion pair with the  $[\text{Fe}(\text{trop}_2\text{dae})]^-$  anion is not the most active species (entries 5 and 6). The use of deuterated  $\text{Me}_2\text{NDBH}_3$  as a substrate and **1** as a catalyst revealed a kinetic isotope effect of 2.0(2), thus indicating that deprotonation of the amino group is one of the rate-limiting steps (entry 7, and see the Supporting Information). Reactions of **1** with stoichiometric amounts of  $\text{Me}_3\text{NBH}_3$  showed no H abstraction; however, an alteration of the B-H stretching frequencies in the solid-state IR spectrum of the solid obtained after workup indicate weak interactions of the  $\text{BH}_3$  group with **1**. According to  $^{11}\text{B}$  NMR studies, such interactions might be present in toluene solutions of **1**, but not of **2** (see the Supporting Information). Catalyst **1** remains active after dehydrogenation of 20 equiv of DMAB, which was shown by consecutive addition of fresh substrate. Overall, at least  $3 \times 20$  equiv of DMAB are dehydrogenated without any loss of activity (entry 8). In a closed system, the linear species **5** (see Table 1) was detected as the major intermediate by  $^{11}\text{B}$  NMR spectroscopy.<sup>[25–27]</sup> Only traces of monomeric intermediate  $\text{Me}_2\text{N}=\text{BH}_2$  were detected.

When the reaction is carried out in THF, the conversion rate drops significantly (entry 9). In selective-poisoning experiments (with 0.2 equiv of  $\text{PPh}_3$  or 0.1 equiv of  $\text{P}(\text{OMe})_3$

per Fe)<sup>[23a]</sup> with **1** as catalyst, the reactions proceed to completion albeit at decreased rates (entries 10 and 11). Time-conversion plots for DMAB dehydrogenation with **1** as a catalyst do not show an induction period. Small aliquots of the reaction solutions were analyzed by scanning electron microscopy (SEM) and gave no indications for the formation of Fe nanoparticles. Although the reaction mechanism remains obscure, these results indicate that **1** acts as a homogeneous catalyst in the dehydrogenation of DMAB. Catalyst **1** has a very high activity compared to [Fe(C<sub>5</sub>H<sub>5</sub>)I(CO)<sub>2</sub>], which requires 9 h and continuous irradiation with UV light for full conversion.<sup>[23a]</sup> The counterion effect, Na<sup>+</sup> > Li<sup>+</sup>, may indicate that catalytically more-active aggregated species are formed with compound **1**<sup>[28,29]</sup> and/or more effective substrate coordination by the [Na(thf)<sub>3</sub>]<sup>+</sup>-containing species.

Complex **1** also efficiently catalyzes the reaction of silanes with alcohols as an *intermolecular* variant of the release of “krypto”-hydrogen.<sup>[30]</sup> We are especially interested in the dehydrogenative alcoholysis of silanes with diols to yield oligo- or poly(alkyl silyl ethers) which has been scarcely exploited to date.<sup>[31–33]</sup> The use of iron-based catalysts for this type of reaction is unprecedented. The simple methanolysis of PhSiH<sub>3</sub><sup>[34]</sup> is efficiently catalyzed with 3 mol% of **1** (1 mol% per Si–H bond), and complete conversion is reached after 5 min in toluene (*T* = 25 °C). The reaction solution remains homogeneous and at least three consecutive catalytic runs can be performed without apparent loss in activity (see the Supporting Information). In reactions between 1,4-benzenedimethanol as the diol and phenylsilane or diphenylsilane, three or two equivalents of H<sub>2</sub> are released and full conversion is reached after 15 min or 54 min, respectively (Scheme 2). Products **6** and **7** were isolated as off-white solids



**Scheme 2.** Dehydrogenative coupling of alcohols with silanes catalyzed by **1**.

with at least nine (in the case of **6**) or nineteen (in the case of **7**) repeating units with respect to Si, as indicated by mass spectrometric analysis.

In summary, the trop-amine-type ligand (trop<sub>2</sub>dae)<sup>2-</sup> strongly stabilizes low-valent iron species, thereby allowing the synthesis of rare examples of heterobimetallic d<sup>7</sup> iron(I) amide complexes and their application as homogeneous catalysts. The structures, electronic properties, aggregation behavior in solution, and especially the reactivities depend sensitively on the counterion [Na(thf)<sub>3</sub>]<sup>+</sup> versus [Li(Et<sub>2</sub>O)<sub>2</sub>]<sup>+</sup>. Although the benchmark performance of [Ni<sup>I</sup>(O<sub>2</sub>CCF<sub>3</sub>)(NHtrop<sub>2</sub>)]<sup>[7a]</sup>—another metalloradical first row transition-

metal complex, but with a low-valent d<sup>9</sup> nickel(I) center—is not reached, [NaFe(trop<sub>2</sub>dae)(thf)<sub>3</sub>] (**1**) is a remarkable dehydrogenation catalyst especially for the syntheses of oligo/poly(silyl ethers) from polyols and silanes. We believe that this reaction has the potential of becoming an atom-economic method for the synthesis of oligo- and polymeric alkyl silyl ethers under mild conditions, generating no waste, only hydrogen as a valuable by-product.

**Keywords:** aminoboranes · condensation reactions · dehydrogenation · heterometallic complexes · low-valent iron.

**How to cite:** *Angew. Chem. Int. Ed.* **2015**, *54*, 5766–5771  
*Angew. Chem.* **2015**, *127*, 5858–5863

- [1] a) C. Tard, C. J. Pickett, *Chem. Rev.* **2009**, *109*, 2245–2274; b) R. M. Davydov, M. P. McLaughlin, E. Bill, B. M. Hoffman, P. L. Holland, *Inorg. Chem.* **2013**, *52*, 7323–7325.
- [2] a) J. M. Zadrozny, D. J. Xiao, M. Atanasov, G. J. Long, F. Grandjean, F. Neese, J. R. Long, *Nat. Chem.* **2013**, *5*, 577–581; b) A. Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard, C. W. Lehmann, *J. Am. Chem. Soc.* **2008**, *130*, 8773–8787; c) K. Jonas, P. Klusmann, R. Goddard, *Z. Naturforsch. B* **1995**, *50*, 394–404; d) C. G. Werncke, P. C. Bunting, C. Duhayon, J. R. Long, S. Bontemps, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* **2015**, *54*, 245–248; *Angew. Chem.* **2015**, *127*, 247–250.
- [3] a) C. J. Adams, R. B. Bedford, E. Carter, N. J. Gower, M. F. Haddow, J. N. Harvey, M. Huwe, M. A. Cartes, S. M. Mansell, C. Mendoza, D. M. Murphy, E. C. Neeve, J. Nunn, *J. Am. Chem. Soc.* **2012**, *134*, 10333–10336; b) R. B. Bedford, E. Carter, P. M. Cogswell, N. J. Wower, M. F. Haddow, J. N. Harvey, D. M. Murphy, E. C. Neeve, J. Nunn, *Angew. Chem. Int. Ed.* **2013**, *52*, 1285–1288; *Angew. Chem.* **2013**, *125*, 1323–1326; c) R. B. Bedford, P. B. Brenner, E. Carter, T. Gallagher, D. M. Murphy, D. R. Pye, *Organometallics* **2014**, *33*, 5940–5943; d) R. B. Bedford, P. B. Brenner, E. Carter, J. Clifton, P. M. Cogswell, N. J. Gower, M. F. Haddow, J. A. Kehl, D. M. Murphy, E. C. Neeve, M. L. Neidig, J. Nunn, B. E. R. Snyder, J. Taylor, *Organometallics* **2014**, *33*, 5767–5780.
- [4] a) T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2003**, *125*, 10782–10783; b) S. D. Brown, T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2003**, *125*, 322–323; c) M. P. Hendrich, W. Gunderson, R. K. Behan, M. T. Green, M. P. Mehn, T. A. Betley, C. C. Lu, J. C. Peters, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 17107–17112; d) C. C. Lu, C. T. Saouma, M. W. Day, J. C. Peters, *J. Am. Chem. Soc.* **2007**, *129*, 4–5; e) C. T. Saouma, C. C. Lu, M. W. Day, J. C. Peters, *Chem. Sci.* **2013**, *4*, 4042–4051; f) H. Fong, M.-E. Moret, Y. Lee, J. C. Peters, *Organometallics* **2013**, *32*, 3053–3062; g) J. L. Kisko, T. Hascall, G. Parkin, *J. Am. Chem. Soc.* **1998**, *120*, 10561–10562; h) N. P. Mankad, P. Müller, J. C. Peters, *J. Am. Chem. Soc.* **2010**, *132*, 4083–4085; i) M. T. Mock, C. V. Popescu, G. P. A. Yap, W. G. Dougherty, C. G. Riordan, *Inorg. Chem.* **2008**, *47*, 1889–1891; j) Y. Lee, J. C. Peters, *J. Am. Chem. Soc.* **2011**, *133*, 4438–4446; k) M.-E. Moret, J. C. Peters, *Angew. Chem. Int. Ed.* **2011**, *50*, 2063–2067; *Angew. Chem.* **2011**, *123*, 2111–2115; l) S. E. Creutz, J. C. Peters, *J. Am. Chem. Soc.* **2014**, *136*, 1105–1115; m) Y. Lee, R. A. Kinney, B. M. Hoffman, J. C. Peters, *J. Am. Chem. Soc.* **2011**, *133*, 16366–16369; n) J. S. Anderson, J. C. Peters, *Angew. Chem. Int. Ed.* **2014**, *53*, 5978–5981; *Angew. Chem.* **2014**, *126*, 6088–6091.
- [5] a) J. M. Smith, A. R. Sadique, T. R. Cundari, K. R. Rodgers, G. Lukat-Rodgers, R. J. Lachicotte, C. J. Flaschenriem, J. Vela, P. L. Holland, *J. Am. Chem. Soc.* **2006**, *128*, 756–769; b) K. P. Chiang, C. C. Scarborough, M. Horitani, N. S. Lees, K. Ding, T. R. Dugan, W. W. Brennessel, E. Bill, B. M. Hoffman, P. L. Holland,

- Angew. Chem. Int. Ed.* **2012**, *51*, 3658–3662; *Angew. Chem.* **2012**, *124*, 3718–3722; c) M. M. Rodriguez, B. D. Stubbart, C. C. Scarborough, W. W. Brennessel, E. Bill, P. L. Holland, *Angew. Chem. Int. Ed.* **2012**, *51*, 8247–8250; *Angew. Chem.* **2012**, *124*, 8372–8375; d) S. A. Stoian, Y. Yu, J. M. Smith, P. L. Holland, E. L. Bominaar, E. Münck, *Inorg. Chem.* **2005**, *44*, 4915–4922; e) G. Bai, P. Wie, A. K. Das, D. W. Stephan, *Dalton Trans.* **2006**, 1141–1146; f) K. P. Chiang, S. M. Bellows, W. W. Brennessel, P. L. Holland, *Chem. Sci.* **2014**, *5*, 267–274; g) Y. Yu, M. Smith, C. J. Flaschenriem, P. L. Holland, *Inorg. Chem.* **2006**, *45*, 5742–5751; h) Y. Yu, A. R. Sadique, J. M. Smith, T. R. Dugan, R. E. Cowley, W. W. Brennessel, C. J. Flaschenriem, E. Bill, T. R. Cundari, P. L. Holland, *J. Am. Chem. Soc.* **2008**, *130*, 6624–6638; i) R. E. Cowley, M. R. Golder, N. A. Eckert, M. H. Al-Afyouni, P. L. Holland, *Organometallics* **2013**, *32*, 5289–5298; j) J. M. Smith, R. J. Lachicotte, K. A. Pittard, T. R. Cundari, G. Lukat-Rodgers, K. R. Rodgers, P. L. Holland, *J. Am. Chem. Soc.* **2001**, *123*, 9222–9223.
- [6] a) S. L. Stokes, W. M. Davis, A. L. Odom, C. C. Cummins, *Organometallics* **1996**, *15*, 4521–4530; b) Y. Nakajima, Y. Nakao, S. Sakaki, Y. Tamada, T. Ono, F. Ozawa, *J. Am. Chem. Soc.* **2010**, *132*, 9934–9936; c) Y.-F. Lin, Y. Nakajima, F. Ozawa, *Dalton Trans.* **2014**, *43*, 9032–9037; d) C. Vogel, F. W. Heinemann, J. Sutter, C. Anthon, K. Meyer, *Angew. Chem. Int. Ed.* **2008**, *47*, 2681–2684; *Angew. Chem.* **2008**, *120*, 2721–2724; e) G. Ung, J. Rittle, M. Soleilhavoup, G. Bertrand, J. C. Peters, *Angew. Chem. Int. Ed.* **2014**, *53*, 8427–8431; *Angew. Chem.* **2014**, *126*, 8567–8571; f) C.-Y. Lin, J. C. Fettinger, F. Grandjean, G. Long, P. P. Power, *Inorg. Chem.* **2014**, *53*, 9400–9406.
- [7] a) M. Vogt, B. de Bruin, H. Berke, M. Trincado, H. Grützmacher, *Chem. Sci.* **2011**, *2*, 723–727; b) H. Schönberg, S. Boulmaâz, M. Wörle, L. Liesum, A. Schweiger, H. Grützmacher, *Angew. Chem. Int. Ed.* **1998**, *37*, 1423–1426; *Angew. Chem.* **1998**, *110*, 1492–1494.
- [8] R. E. Rodríguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones, H. Grützmacher, *Nat. Chem.* **2013**, *5*, 342–347.
- [9] For example: a) B. Conway, A. R. Kennedy, R. E. Mulvey, S. D. Robertson, J. G. Álvarez, *Angew. Chem. Int. Ed.* **2010**, *49*, 3182–3184; *Angew. Chem.* **2010**, *122*, 3250–3252; b) C. Lichtenberg, T. P. Spaniol, J. Okuda, *Inorg. Chem.* **2012**, *51*, 2254–2262; c) D. R. Armstrong, E. Brammer, T. Cadenbach, E. Hevia, A. R. Kennedy, *Organometallics* **2013**, *32*, 480–489.
- [10] Square-planar coordination geometries have been reported for some Fe<sup>II</sup> species, for example: a) E. J. Hawrelak, W. H. Bernskoetter, E. Lobkovsky, G. T. Yee, E. Bill, P. J. Chirik, *Inorg. Chem.* **2005**, *44*, 3103–3111; b) S. C. Bart, K. Chlopek, E. Bill, M. W. Bouwkamp, E. Lobkovsky, F. Neese, K. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 13901–13912; c) G. Muller, J. Sales, J. Vinaixa, J. Tejada, *Inorg. Chim. Acta* **1982**, *60*, 227–230.
- [11] Two Fe<sup>I</sup>-β-diketiminato complexes with square-planar coordination geometries have been reported, but were cocrystallized with a pentacoordinate Fe species or were unstable in solution, thus preventing a more detailed experimental investigation.<sup>[5a,h]</sup> Square-planar low-valent Fe compounds have been reported, for which a clear assignment of the redox state of the metal center was hampered by the redox activity of the ligand: J. Scott, I. Vidyaratne, I. Korobkov, S. Gambarotta, P. H. M. Budzelaar, *Inorg. Chem.* **2008**, *47*, 896–911.
- [12] Na1 is found in a distorted trigonal bipyramidal coordination geometry with two thf molecules and N1 in the equatorial positions and one thf molecule and the aromatic C2–C3 bond of the trop moiety in the apical positions.
- [13] It is important to note that the role of the neutral ligands L is crucial for the coordination chemistry of [LiFe(trop<sub>2</sub>dae)(L)<sub>2</sub>] type compounds. [LiFe(trop<sub>2</sub>dae)(Et<sub>2</sub>O)(thf)] (**2b**) shows bonding parameters similar to **2**, whereas [LiFe(trop<sub>2</sub>dae)(2-Me-THF)<sub>2</sub>] (**2c**) and [LiFe(trop<sub>2</sub>dae)(thf)<sub>2</sub>] (**2d**) show bonding parameters similar to **1** (see the Supporting Information).
- [14] The experimentally determined isomer shifts are well reproduced by DFT calculations. The experimentally determined quadrupole splittings deviate from calculated values (see the Supporting Information).
- [15] These compounds show high-spin electron configurations, which also contributes to their higher isomer shifts.
- [16] P. Gütllich, E. Bill, A. X. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry*, Springer, Heidelberg, **2011**.
- [17] N. Roy, S. Sproules, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2008**, *47*, 10911–10920.
- [18] For example: D. Bravo-Zhivotovskii, I. Ruderfer, S. Melamed, M. Boroshansky, B. Tumanskii, Y. Apeloig, *Angew. Chem. Int. Ed.* **2005**, *44*, 739–743; *Angew. Chem.* **2005**, *117*, 749–753.
- [19] At a lower applied field of 0.01 T, an increased effective magnetic moment of  $\mu_{\text{eff}} = 3.25 \mu_{\text{B}}$  at 300 K was determined, which could be due to uncompensated interfacial ferromagnetically aligned spins oriented by small magnetic fields (for details and discussion see the Supporting Information).
- [20] Under similar conditions, decomposition of **1** was observed in polar media such as THF (see the Supporting Information) and olefins such as 1-octene (10 equiv) were not hydrogenated.
- [21] H. Berke, *ChemPhysChem* **2010**, *11*, 1837–1849.
- [22] a) A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, *110*, 4023–4078; b) A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.* **2010**, *110*, 4079–4124; c) G. Alcaraz, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* **2010**, *49*, 7170–7179; *Angew. Chem.* **2010**, *122*, 7326–7335.
- [23] a) 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; b) J. F. Sonnenberg, R. H. Morris, *ACS Catal.* **2013**, *3*, 1092–1102; c) 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; d) J. R. Vance, A. P. M. Robertson, K. Lee, I. Manners, *Chem. Eur. J.* **2011**, *17*, 4099–4103; e) T. Miyazaki, Y. Tanabe, M. Yuki, Y. Miyake, Y. Nishibayashi, *Organometallics* **2011**, *30*, 2394–2404.
- [24] The same behavior was assumed for [Fe(C<sub>3</sub>H<sub>5</sub>)Cl(CO)<sub>2</sub>], [Fe-(C<sub>5</sub>H<sub>9</sub>)(OSO<sub>2</sub>CF<sub>3</sub>)(CO)<sub>2</sub>], and [Fe(C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(THF)]X (X = BF<sub>4</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>) but not analyzed in detail.<sup>[23a]</sup>
- [25] After 52 min: 18% DMAB, 21% **4**, 56% **5**, 2% Me<sub>2</sub>NBH<sub>2</sub>, 3% BH-containing species (possibly Me<sub>2</sub>NBH); conditions: C<sub>6</sub>D<sub>6</sub>, RT, 9 mol% **1**. Similar result with 5 mol% **1**.
- [26] The same was observed when **2** or **3** were used as catalysts.
- [27] Formation of H<sub>2</sub> was detected by <sup>1</sup>H NMR spectroscopy in these reactions.
- [28] Compounds **1** or **2c** could be re-isolated after having been in toluene solution; that is, full degradation can be excluded.
- [29] Na<sub>2</sub>(trop<sub>2</sub>dae)<sub>2</sub>, generated in situ from H<sub>2</sub>trop<sub>2</sub>dae and 2 equiv of [NaN(SiMe<sub>3</sub>)<sub>2</sub>], was inactive for DMAB dehydrogenation under identical conditions.
- [30] a) W. Sattler, G. Parkin, *J. Am. Chem. Soc.* **2012**, *134*, 17462–17465; b) A. Rit, T. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2013**, *52*, 4664–4667; *Angew. Chem.* **2013**, *125*, 4762–4765; c) D. Mukherjee, R. R. Thompson, A. Ellern, A. D. Sadow, *ACS Catal.* **2011**, *1*, 698–702.
- [31] Y. Kawakami, Y. Li, *Des. Monomers Polym.* **2000**, *3*, 399–419.
- [32] a) Y. Li, Y. Kawakami, *Macromolecules* **1999**, *32*, 8768–8773; b) Y. Li, Y. Kawakami, *Macromolecules* **1999**, *32*, 6871–6873; c) Y. Li, M. Seino, Y. Kawakami, *Macromolecules* **2000**, *33*, 5311–5314; d) J. Cella, S. Rubinsztajn, *Macromolecules* **2008**, *41*, 6965–6971.
- [33] The catalysts applied for this type of reaction are precious-metal catalysts (Pd, Rh), which mostly require long reaction times or slightly elevated reaction temperatures (Ref. [32a–c]), a notable

exception is [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] for the synthesis of poly(aryl silyl ethers) (Ref. [32d]).

- [34] Simple alcoholysis reactions  $R_{(4-n)}SiH_n + x ROH$  ( $x \geq n$ ) have been reported: a) S. Chang, E. Scharer, M. Brookhart, *J. Mol. Catal. A* **1998**, *130*, 107–119; b) S. Rommel, L. Hettmanczyk, J. E. M. N. Klein, B. Plietker, *Chem. Asian J.* **2014**, *9*, 2140–2147.
- [35] CCDC 999856 (**1**), 999857 (**2**), 999858 (**3**), 1033680 (**2b**), 1033681 (**2c**), 1033682 (**2d**), 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](http://www.ccdc.cam.ac.uk/data_request/cif).

Received: November 24, 2014

Published online: March 12, 2015