Low-valent iron mono-diazadiene compounds: electronic structure and catalytic application

Lichtenberg, C.; Adelhardt, M.; Gianetti, T.L.; Meyer, K.; de Bruin, B.; Grützmacher, H.

DOI
10.1021/acscatal.5b01416

Publication date
2015

Document Version
Final published version

Published in
ACS Catalysis

License
Article 25fa Dutch Copyright Act

Citation for published version (APA):

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.
Low-Valent Iron Mono-Diazadiene Compounds: Electronic Structure and Catalytic Application

Crispin Lichtenberg,*† Mario Adelhardt,‡ Thomas L. Gianetti,† Karsten Meyer,‡ Bas de Bruin,§ and Hansjörg Grüßmacher*†

†Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland
‡Department of Chemistry & Pharmacy, Friedrich-Alexander University, Erlangen-Nürnberg (FAU), Egerlandstraße 1, D-91058 Erlangen, Germany
§van ’t Hoff Institute for Molecular Sciences, Department of Homogeneous Catalysis, Faculty of Science, Universiteit van Amsterdam, Postbus 94720, 1090 GS Amsterdam, The Netherlands

ABSTRACT: A series of monodiazadiene diolefin iron compounds, [Fe(trop2dad)(L)] (4; L = neutral ligand), has been prepared by one-electron oxidation of the Fe" species [NaFe(trop2dad)(thf)]2 (dad = diazadiene; trop = SH-dibenzo[a,d]cyclohepten-5-yl). The electronic structures of compounds 4 were investigated by NMR and Mössbauer spectroscopy, single-crystal X-ray diffraction, solid- and liquid-phase magnetic susceptibility measurements, and DFT calculations. Compounds of type 4 with labile ligands L were found to be active (pre)catalysts for the dehydrogenative coupling of (alkyl)amine–boranes. Remarkably high activities were observed, especially for the homogeneous dehydrogenative polymerization of methylamine–borane.

KEYWORDS: iron diazadiene compounds, electronic structure determination, methylamine–borane, dehydrogenative polymerization, homogeneous catalysis

INTRODUCTION

For decades, redox-active ligands have been investigated intensively from the coordination chemists’ point of view.1 More recently they have also been recognized as functional entities in homogeneously catalyzed reactions.2 Specifically, it was suggested that direct participation of such a ligand in redox events within a catalytic cycle is advantageous in the case of first-row transition-metal catalysts.3 The in-depth characterization of compounds containing redox-active ligands remains challenging, however, since electronic coupling between metal- or ligand-centered unpaired local spins can obscure the true electronic structure of the overall compound.

Diazadienes (dads) represent a prominent class of redox-active ligands. Examples of iron compounds with one or two diazadiene ligands, [Fe(dad)(L^n)] (L^n = π-acidic ligand) and [Fe(dad)2], were reported early on.5,6 However, it was only recently that the correct electronic structure of bis(diazadiene) compounds [Fe(dad)2] was revealed by a combination of spectroscopic, crystallographic, and theoretical techniques and methods.5,7 These compounds are best described as high-spin Fe" centers (local spin S = 2) antiferromagnetically coupled to two monoanionic dad radical ligands, (dad)" (local spin S = 1/2), which results in an overall S = 1 ground state. In contrast, the electronic structure of monodiazadiene species [Fe(dad)(L^n)] has remained largely unexplored.

Some catalytic applications of [Fe(dad)(L^n)], [Fe(dad)(X)] (X = halide), and [Fe(dad)2] have been reported. They include the hydrogenation of 1-hexene,8 (cyclo)dimerizations of dienes,5,9 cyclotrimerizations of alkynes,10 Diels–Alder type cyclizations of dienes with alkynes,11 and olefin polymerizations12 and require the addition of an external activator or initiator. Iron diazadiene compounds as catalysts for dehydrogenation reactions have not yet been reported to our knowledge. We described the anionic Ru hydride complex [RuH(trop2dad)] with a tetradeutate olefin diazadiene ligand (trop = SH-dibenzo[a,d]cyclohepten-5-yl) as a highly active catalyst for the dehydrogenation of methanol/water mixtures or pure formic acid to CO2 and H2.12 We became interested in the development of a related iron-based homogeneous catalyst for dehydrogenative oligo- and polymerization reactions that does not require an additional activator. In recent work, we showed that a multidentate trop-based olefin diamido ligand, (trop2dae)5+ (see 5 in Scheme 1), which is the hydrogenated version of the unsaturated trop:dad ligand, stabilizes low-valent iron centers.13 One of the main challenges under the inherently reducing reaction conditions is...
Scheme 1. Synthesis of \([\text{Fe}(\text{trop}_2\text{dad})(\text{L})] (4a–d)\) (Including Unsuccessful Approaches) and Chemically Reversible Interconversion of 2 and 4a

\[
\begin{align*}
1a (X = \text{Cl}), & \quad 1b (X = \text{Br}) \\
\text{exc. Na or NaH} & \quad \text{2 Na, 2 NaHg or 2 CoCp}_2
\end{align*}
\]

\[
\begin{align*}
\text{Na(thf)}_3 & \quad \text{FcPF}_6, \text{L} \\
\text{NaBH}_4 \text{ or NaO} & \text{Bu}
\end{align*}
\]

\[
\begin{align*}
\text{compare:} & \quad \text{Na(thf)}_3 \\
\text{[NaFe(trop}_2\text{dad})(\text{thf})_3] & \quad \text{L} = \text{thf (a), MeCN (b), PPh}_3 (c), P(\text{OME})_3 (d)
\end{align*}
\]

to prevent catalyst deactivation or modification by formation of small Fe particles.13–15

Here we report the synthesis, electronic structure investigation, and reactivity of the iron diolefin diazadiene compounds \([\text{Fe}(\text{trop}_2\text{dad})(\text{L})] (\text{L} = \text{neutral ligand})\). These compounds are among the most active base-metal catalysts for the dehydrogenative polymerization of methylamine–borane.

## RESULTS AND DISCUSSION

### Synthesis of Low-Valent Fe Compounds

The low-valent iron diazadiene ate complex \([\text{NaFe}(\text{trop}_2\text{dad})(\text{thf})_3]\) (2) can be accessed from \([\text{FeBr}_2(\text{trop}_2\text{dad})](\text{thf})]\) (1b) with an excess of elemental sodium or NaH as reducing agent (Scheme 1).16

The anionic part of this contact ion pair contains a low-spin \((\text{ls})^2\)-Fe center to which a diamido ethylene ligand is coordinated: that is, the two-electron -reduced form \((\text{trop}_2\text{dad})_2\). Electrochemical data suggest that the product of a one-electron oxidation of 2, that is, the neutral complex \([\text{Fe}(\text{trop}_2\text{dad})]\), should be a stable compound. However, attempts to prepare such a complex in a stoichiometric reaction from 1a or 1b failed. Lithium or sodium alkyls such as \([\text{MCH}_2\text{SiMe}_3]\) (M = Li, Na) have been successfully used as homogeneous reducing agents for FeII halides with diazadiene or the saturated diaminoethylene ligand \((\text{H}_2\text{trop}_2\text{dad})\), which gives 5 as a product.16,17

However, the reaction of \([\text{FeCl}_2(\text{trop}_2\text{dad})]\) (1a) with \([\text{LiCH}_2\text{SiMe}_3]\) resulted in a nucleophilic attack on the two imine functionalities and concomitant single-electron reduction of the iron center to give the ls Fe species 3, which was isolated and characterized (for further details see the Supporting Information). Stoichiometric reactions of 1b with 2 equiv of Na, NaHg, or \([\text{CoCp}_2]\) as the reducing agent gave low yields of compound 2, free ligand, or \([\text{Fe}^{\text{II}}(\text{trop}_2\text{dad})]\),16 respectively, as the only isolable products. Thus, we pursued oxidation of 2, rather than reduction of 1a,b, as a synthesis strategy. Indeed, the reaction of 2 with 1 equiv of ferrocenium hexafluorophosphate gave intensely dark red \([\text{Fe}(\text{trop}_2\text{dad})(\text{thf})]\) (4a) in 81% yield, which was isolated with 0.5 equiv of \([\text{Na(thf)}_3]\text{PF}_6\) per formula unit in the crystal lattice. With similar protocols, dark brown compounds \([\text{Fe}(\text{trop}_2\text{dad})(\text{L})]\) (4b–d) could be isolated, where the thf ligand bound to the Fe center has been replaced by another \(\sigma\) donor \((\text{L} = \text{MeCN (4b)})\) or by a \(\sigma\) donor/π acceptor ligand \((\text{L} = \text{PPh}_3 (4c), P(\text{OME})_3 (4d)\) ). The chemical reversibility between ion pair 2 and neutral species of type 4 was demonstrated by the reaction of 4a with mild reducing agents such as NaBH₄ and NaOBut, from which compound 2 was isolated in 60–66% yield.

Compounds 4a–d were characterized by single-crystal X-ray diffraction studies (Figure 1, Table 1, and the Supporting Information). The Fe centers are five-coordinate, residing in square-pyramidal \((\tau_5 = 0 (4a)), 0.10 (4b)\), intermediate \((\tau_5 = 0.50 (4d))\), and distorted-trigonal-bipyramidal coordination geometries \((\tau_5 = 0.60 (4c))\).18

The monodentate ligand occupies the apical position in 4a,b, whereas it is found in an equatorial position in 4c. The changes in the coordination geometry from 4a,b to 4c,d are attributed to steric (4c,d) and electronic effects (4c: \(\pi – \pi\) interactions between the phenyl and benzogroups). The average Fe–N and Fe–(C=CH₃) bond lengths (1.89–1.92 and 1.97–2.00 Å) are within the range of those previously described for five-coordinate monodiazadiene iron compounds (1.89–1.93 and 1.97 Å) (C=CH₃: olefinic bonding sites).18,19 Note that the C=C(CH₃) and N units in axial positions in 4c,d interact more weakly with the Fe center than their counterparts in equatorial positions. This is ascribed to a thermodynamic trans effect and is reflected in longer Fe–(C=CH₃):Fe–N and shorter C=C(CH₃) distances (Supporting Information). The C=C(CH₃) and C=N(CH₃) bond lengths in the diazadiene ligand backbone are an important measure of the oxidation state of this type of ligand.5,20 In compounds 4a–d, these distances are intermediate between those in...
Table 1. Selected Bond Lengths (Å) and \( \tau_s \) Values for Compounds 4a–d

<table>
<thead>
<tr>
<th></th>
<th>4a (L = thf)</th>
<th>4b (L = NCMe)</th>
<th>4c (L = PPh₃)</th>
<th>4d (L = P(OMe)₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_s )</td>
<td>0</td>
<td>0.10</td>
<td>0.60</td>
<td>0.50</td>
</tr>
<tr>
<td>C=C(^{3s})</td>
<td>1.423(3)</td>
<td>1.420(4)</td>
<td>1.434(5)</td>
<td>1.430(2)</td>
</tr>
<tr>
<td>Fe=N</td>
<td>1.9203(17)</td>
<td>1.907(2)</td>
<td>1.910(3)</td>
<td>1.8928(13)</td>
</tr>
<tr>
<td>Fe–(C=C)</td>
<td>1.974(2)</td>
<td>1.991(3)</td>
<td>2.000(4)</td>
<td>1.9855(15)</td>
</tr>
<tr>
<td>Fe=E</td>
<td>2.141(2)</td>
<td>1.999(2)</td>
<td>2.3202(11)</td>
<td>2.1939(4)</td>
</tr>
<tr>
<td>C–Ndad</td>
<td>1.402(4)</td>
<td>1.389(4)</td>
<td>1.389(5)</td>
<td>1.392(2)</td>
</tr>
<tr>
<td>C=N</td>
<td>1.325(3)</td>
<td>1.331(3)</td>
<td>1.326(5)</td>
<td>1.3315(19)</td>
</tr>
</tbody>
</table>

\(^{4}\)Mean value. \(^{5}\)Individual values differ considerably (see text).

[FeX₂trop2dad] (1a,b) with a neutral trop2dad ligand (two short C=N\(^{3d}\) bonds and one long C=C\(^{3d}\) bond) and those in [NaFe(trop2dad)(thf)] (2) with a fully reduced dianionic (trop2dad)\(^{2-}\) ligand (two long C=C\(^{3d}\) bonds and one short C=C\(^{3d}\) bond). In 4a–d the C=C\(^{3d}\) and C=C\(^{3d}\) bond lengths are similar to those reported for [Fe\(^{0}\)(trop2dad)₂] and other Fe diazadiene compounds, which all contain monoanionic radical (dad)\(^{+}\) radicals. \(^{6,16}\) These structural data suggest monoanionic radical (trop2dad)\(^{+}\) ligands for compounds 4a–d and consequently an Fe\(^{0}\) oxidation state. Other five-coordinate iron dadd compounds with \( \pi \)-acidic ligands show comparable bonding parameters for the ligand backbone, although minor deviations occur in some cases.

It has been stated that the changes of the bonding parameters with respect to the free ligand are due to \( \pi \)-back donation, and molecular orbital calculations have been performed for a model compound. \(^{19,20}\) However, the recent detailed insights into the electronic structures of [Fe(dad)₂]-type compounds called for a deeper investigation of the electronic structures of 4a–d.

Electronic Structure of Low-Valent Fe Compounds.

Zero-field \(^{57}\)Fe Mössbauer spectroscopy of solid 4a–d at 77 K revealed a clean quadrupole doublet in each case, ruling out the presence of Fe-based impurities (Table 2 and the Supporting Information). 4a–d show isomer shifts of 0.43–0.22 mm/s, which are close to the isomer shifts observed for ls Fe\(^{0}\) centers coordinated by the bis(trop)diazadiene ligand as in [Fe(trop2dad)₂] (\( \delta = 0.37(1) \) mm/s) and ([NaFe(trop2dad)(thf)] (2; \( \delta = 0.21(1) \) mm/s). This result clearly excludes a hs Fe\(^{3+}\) electron configuration. \(^{16,21}\) The lower isomer shifts for 4c,d with their \( \pi \)-acidic phosphorus ligands in comparison to 4a,b indicate a higher \( \sigma \) electron density at Fe, which is a result of effective d(Fe) \( \rightarrow \) \( \sigma^{*}(P-R) \) electron back-donation. In the case of 4c,d, where a direct comparison of all Fe–ligand bond lengths is possible, shorter Fe–ligand bonds expectedly lead to a smaller isomer shift (Tables 1 and 2). \(^{21}\) The quadrupole splittings of 4a–d range from 1.11 to 1.69 mm/s.

SQUID magnetic susceptibility measurements were performed for 4a as a representative example (solid state, 1 T) and indicate that this compound is diamagnetic over a temperature range of 2–300 K. Frozen solutions of 4a in THF at 91 K are EPR silent. The experimental results therefore suggest that compounds 4a–d are best described as ls Fe\(^{0}\) centers with strong antiferromagnetic coupling to their monoanionic radical (trop2dad)\(^{+}\) ligands, although a closed-shell singlet electronic structure, ls Fe\(^{0}\)(L\(^{2-}\)) \( \leftrightarrow \) ls Fe\(^{0}\)(L\(^{2-}\)) (\( \pi \) back-donation model), with a net Fe\(^{0}\) oxidation state, cannot be fully excluded (vide infra). Thus, upon one-electron oxidation of [NaFe(trop2dad)-(thf)] (2), one electron is removed from the redox-active ligand rather than from the metal center to give compounds of type 4. This is in contrast with previous findings on the related iron bis(diiminobenzosemiquinonate), where a one-electron oxidation takes place at the metal center. \(^{22}\)

In order to gain further support for the electronic structure assignment, we performed DFT calculations on the full atom models of [Fe(trop2dad)(thf)] (4a) and [Fe(trop2dad)] (4e). \(^{23}\) Geometries were optimized with Turbomole at the DFT-D3, hybrid b3-lyp, def2-TZVP level, employing Grimme’s version 3 dispersion corrections, in three different electronic configurations: closed-shell singlet (\( S = 0 \); spin-restricted singlet), open-shell singlet (\( S = 0 \); spin-unrestricted singlet, broken symmetry approach), and triplet (\( S = 2 \); spin unrestricted) (Table 3).

Table 3. DFT Computed ZPE Corrected SCF Energies (kcal mol\(^{-1}\)) of Species 4a,e in Different Electronic Configurations

<table>
<thead>
<tr>
<th></th>
<th>closed-shell singlet (( S = 0 ))</th>
<th>triplet (( S = 1 ))</th>
<th>open-shell singlet(^{*}) (( S = 0 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>0</td>
<td>−92 (( \Delta S ) = 2.0341)</td>
<td>−162 (( \Delta S ) = 1.0799)</td>
</tr>
<tr>
<td>4e</td>
<td>0</td>
<td>−190 (( \Delta S ) = 2.0216)</td>
<td>−220 (( \Delta S ) = 1.1594)</td>
</tr>
</tbody>
</table>

\(^{*}\)Energy corrected for triplet spin contamination.

The closed-shell singlet configuration is perhaps best described with two resonance structures that contribute equally to the electronic ground state, ls Fe\(^{0}\)(L\(^{2-}\)) \( \leftrightarrow \) ls Fe\(^{0}\)(L\(^{2-}\)), one of which contains a neutral, low-spin d\(^{8}\) iron(0) center supported by a neutral trop2dad ligand (Fe\(^{0}\)(L\(^{2-}\))) and the other contains a dicaticonic, low-spin d\(^{6}\) iron(II) center supported by a dianionic trop2dad\(^{2-}\) ligand (Fe\(^{0}\)(L\(^{2-}\))). This description reflects a ligand to metal \( \sigma,\pi\) donation and metal to ligand \( \pi\) back-donation model. This model effectively corresponds to a net Fe\(^{0}\) system, but without invoking radical density on either the metal or the ligand. In contrast, the triplet and the open-shell singlet configurations are both best described as metallo-radical ligand radical Fe\(^{0}\)(L\(^{2-}\)) species, each containing a monocationic, low-spin d\(^{4}\) iron(II) center (\( S = 1/2 \)) supported by a monoanionic trop2dad\(^{+}\) radical-type ligand (\( S = 1/2 \)). They differ in the exchange-coupling interaction between the unpaired electrons centered on the metal and the ligand. In the open-shell singlet configuration these are antiferromagnetically coupled (leading to an overall \( S = 0 \) ground state), while in the triplet configuration they are ferromagnetically coupled (leading to an overall \( S = 1 \) ground state), as reflected by the spin density plots shown in Figure 2.
For both 4a and 4e, the triplet and open-shell singlet configurations are computed to be significantly stabilized over the respective closed-shell singlet configuration (Table 3), suggesting that these complexes might indeed be best described as Fe^I[L^+] species. For the thf adduct 4a, the open-shell singlet configuration is significantly stabilized over the triplet configuration, which is in agreement with the diamagnetic ground state of this species as determined experimentally. For complex 4e without thf, the computed triplet and open-shell singlet energies are much closer, which is in congruence with the experimentally observed paramagnetic shift and line broadening of the NMR signals of these complexes in solution (vide infra). As such, the data are consistent and are suggestive of electronic structures best described as (antiferromagnetically coupled) Fe^I[L^+] “ligand radical” complexes (for a more detailed discussion, see the Supporting Information). However, predicting relative energies of species in different spin state configurations with DFT methods can be troublesome, and the same can be expected when comparing the relative energies of closed-shell and open-shell singlet configurations. The assignment of neutral Fe(bpy)-type complexes containing redox-active bipyridine (and related) ligand scaffolds as an antiferromagnetically coupled Fe^I[L^+] species on the basis of DFT studies has recently been challenged on the basis of high-level CASSCF ab initio computations. High-level multi-reference ab initio methods (such as CASSCF) can accurately describe the electronic structure of open-shell singlet species but are (currently) too expensive for geometry optimizations (certainly for large systems such as complex 4a). Combined with the fact that the geometries and energies of 4a in the three different electronic structures under consideration are mutually dependent and vary widely (at least, according to DFT), comparing high-level ab initio single-point energies of different spin configurations, without performing geometry optimizations at the same level, could easily produce erroneous results due to a mismatch between the electronic structure and its optimal geometry. As such, it is doubtful if any of the currently available computational methods are able to unequivocally distinguish between open-shell singlet Fe^I[L^+] and closed-shell singlet Fe^I(L^0) ↔ Fe^III(L^2−) descriptions of species such as 4a. Both descriptions correspond to a (net) Fe^I system, and hence both descriptions in principle are in agreement with the experimental data. Furthermore, to the best of our knowledge, there are also no experimental methods available to unequivocally discriminate between closed-shell and open-shell singlet species in a straightforward manner, if the exchange coupling in the latter is strongly antiferromagnetic (thus leading to completely diamagnetic systems in both cases). Its low DFT energy in comparison to the closed-shell solution of 4a is perhaps in favor of an open-shell singlet Fe^I[L^+] ligand radical description. However, considering developments in the field and the well-known problems associated with assigning spin states on the basis of (hybrid) DFT calculations, we refrain from drawing any firm conclusions on this matter.

Compound 4a is not diamagnetic in solution. It shows a low effective magnetic moment in solution, which can be ascribed to an equilibrium according to [Fe(trop,dad)(thf)] (4a) ⇌ [Fe(trop,dad)] (4e) + THF. In agreement with this equilibrium, the observed effective magnetic moment is much smaller than that expected for pure Fe^III triplet (μ_{expected} = 2.83 μ_B for g = 2.0); it is solvent dependent (μ_{eff}(C_6D_6, 298 K, 0.02 M) = 1.9(1) μ_B, μ_{eff}(THF-d_8, 298 K, 0.02 M) = 1.3(1) μ_B), concentration dependent (μ_{eff}(C_6D_6, 298 K, 0.02 M) = 1.9(1) μ_B, μ_{eff}(C_6D_6, 298 K, 0.01 M) = 2.2(1) μ_B), and temperature dependent (μ_{eff}(Tol-d_8, 298 K, 0.02 M) = 1.8(1) μ_B, μ_{eff}(Tol-d_8, 243 K, 0.02 M) = 1.3(1) μ_B). An isotropic shift analysis of a 0.02 M toluene solution of 4a in the temperature range 233–298 K supports an equilibrium between singlet and triplet species (for details see the Supporting Information). Likewise, compounds 4b,c show low magnetic moments in solution, whereas 4d is diamagnetic and, as expected, is EPR silent (see the Experimental Section). Similar to the phenomenon described above, iron porphyrins show different spin states depending on the presence/absence and nature of additional neutral ligands. The possibility of controlling the spin state of a metal complex by the choice of a neutral ligand has been described for a trinuclear all-ferrous compound.

In THF-d_8 solution, NMR spectroscopic analysis of 4a reveals apparent C_2v symmetry, even at temperatures as low as ~40 °C. Thus, 4a undergoes a rapid transformation, by which its thf ligand is transferred from one side of the Fe–diazadiene plane to the other. For compound 4b, an analogous process takes place at 25 °C in MeCN-d_3 solution (apparent C_2v symmetry). However, it is slow on the NMR time scale at ~30 °C, as apparent C_2v symmetry is observed at this temperature. The neutral ligands in compounds 4a,b are labile in THF/MeCN solution, as shown by 1H NMR spectroscopy. Therefore, the dynamic processes described above are likely to be intermolecular: that is, associated with a dissociation and association step of L. Similarly, the PPh_3 ligand in 4c is labile, as suggested by similar 1H NMR spectra for 4b,c in MeCN-d_3 solution and by a very broad resonance in the 31P NMR spectrum of 4c in the same solvent. In contrast, compound 4d shows apparent C_2v symmetry in MeCN-d_3 already at 25 °C and no rapid displacement of the P(Ome)_3 ligand is observed. Overall, the ease of displacement of the neutral ligands in compounds 4a–d by THF or MeCN follows the reverse trend of the ligands’ π-acidities: THF > MeCN > PPh_3 > P(Ome)_3.

**Catalyzed Dehydrogenations.** Initiated by the pioneering work of Manners and Baker, (alkyl)ammonia–boranes, RH,N-BH_3 (R = alkyl, H), have been discussed as hydrogen storage devices and can be utilized as hydrogen transfer reagents. Moreover, they have been in the focus of research efforts as precursors for the synthesis of oligo- or polymeric BN materials. Polymeric compounds obtained from catalyzed dehydrocouplings of (alkyl)ammonia–boranes are isostructural with polyolefins and graphene but show different material properties due to the more polar nature of the BN bond. Potential applications for such materials include high-performance polymers and the use as a graphene support for (opto)electronic devices. Whereas methods for the synthesis of hydrocarbon polymers have been highly elaborated, those for the synthesis of the BN analogues still have the potential for further developments. For methylammonia–borane, MeH,N-BH_3 (MAB), dehydrocoupling can result in the formation of hydrocarbons.
Reactions with catalysts 4a,b show a short induction period, indicating that these compounds are not the catalytically active species. Formation of the active species could be a process such as substitution of the neutral ligand THF/McCN for a substrate molecule, or it could involve reduction of the molecular iron compounds to give catalytically active small Fe particles. For precious-metal catalysts, it has been demonstrated that both homogeneous and heterogeneous regimes are operative in MAB dehydrogenations. To our knowledge, this question has not been addressed for MAB dehydrogenation using base-metal catalysts. Increasing the polarity of the solvent (from toluene to THF) drastically lowers the rate of reaction, hinting at a heterogeneous regime (entry 5). Selective poisoning experiments with 0.1 or 0.2 equiv of P(OMe)3 per Fe being added to a running reaction still give full conversion after slightly increased reaction times, whereas addition of 2.0 equiv of P(OMe)3 per Fe shuts down the catalytic activity (entries 6–8 and the Supporting Information). These results indicate that in situ generated 4d is not an active (pre)catalyst for MAB dehydrogenation and also disfavors a scenario with catalytically active Fe particles. In comparison to 4a,b, the related, singly reduced species 2 is only moderately active in MAB dehydrogenation and an analogous Fe(I) compound with a saturated ligand backbone, \([\text{NaFe(trop2dae)(thf)}_3](S)\), is not active (dae = \(-\text{CH}_2\text{CH}_2\text{)}\) (entries 9 and 10).

When the substrate was changed to either amine–borane, \(\text{H}_2\text{N-BH}_3\) (AB), or dimethylamine–borane, \(\text{Me}_2\text{HN-BH}_3\) (DMAB), 5 mol % of compound 4a induced full to high conversion with respect to release of 1 equiv of \(\text{H}_2\) (Table 5).

### Table 5. Catalyzed Dehydrogenative Polymerization of Amine–Borane (AB) and Cyclodimerization of Dimethyleamine–Borane (DMAB)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>Monomer</th>
<th>Solvent</th>
<th>Time (min)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>AB</td>
<td>THF\textsuperscript{b}</td>
<td>300</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>4a</td>
<td>DMAB</td>
<td>Tol</td>
<td>385</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>AB</td>
<td>THF\textsuperscript{b}</td>
<td>210</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>DMAB</td>
<td>Tol</td>
<td>240</td>
<td>95</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>AB</td>
<td>MTBE</td>
<td>26</td>
<td>&lt;1</td>
</tr>
<tr>
<td>6\textsuperscript{c}</td>
<td>5</td>
<td>DMAB</td>
<td>Tol</td>
<td>240</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Conditions: 5 mol % catalyst loading, 23 °C, open system. \textsuperscript{b}1 mol % catalyst. \textsuperscript{c}Added after 2.5 min reaction time.

### Table 4. Catalyzed Dehydrogenative Polymerization of Methylamine–Borane (MAB)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive (amt equiv)</th>
<th>Time (min)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>8.5</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>4b</td>
<td>8.5</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>4a\textsuperscript{b}</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>THF as solvent</td>
<td>8.5/99/186</td>
<td>3 &gt;99</td>
</tr>
<tr>
<td>5</td>
<td>P(OMe)\textsubscript{3} (0.1) \textsuperscript{c}</td>
<td>101</td>
<td>&gt;99</td>
</tr>
<tr>
<td>6</td>
<td>P(OMe)\textsubscript{3} (0.2) \textsuperscript{d}</td>
<td>11</td>
<td>&gt;99</td>
</tr>
<tr>
<td>7</td>
<td>P(OMe)\textsubscript{3} (2.0) \textsuperscript{d}</td>
<td>12</td>
<td>&gt;97</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>15</td>
<td>63</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>227</td>
<td>70</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>15</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Conditions unless specified otherwise: 5 mol % catalyst, toluene, 23 °C, open system. \textsuperscript{b}1 mol % catalyst. \textsuperscript{c}Added after 2.5 min reaction time.

After 8.5 min, as indicated by the release of 1 equiv of \(\text{H}_2\), with virtually no small cyclic BN products being detected. Once isolated as a colorless solid, the poly-MAB product shows poor solubility in common organic solvents and was identified by IR spectroscopy. Mass spectrometry revealed signals of up to \(m/z\) 943, indicating at least 22 repeating units. This makes 4a,b the most active base-metal catalysts for the dehydrogenative polymerization of MAB. A turnover frequency of \(5.1 \times 10^2\) s\(^{-1}\) was determined for these reactions on the basis of the linear region of the time/convension plot (ca. 2–6 min reaction time). In order to determine if the dehydrogenative polymerization of MAB proceeds via a chain growth or a step growth mechanism, reactions were stopped before full conversion was reached. Analysis of the oligo-/polymeric material showed molecular weights clearly exceeding those predicted for a step growth mechanism using Carothers’ equation and thus suggests a chain growth mechanism to be operative, as reported for an iridium-catalyzed MAB dehydrogenation. Lowering the catalyst loading to 1 mol % resulted in 95% conversion after 20 min (entry 3). When 3 \(\times\) 20 equiv of MAB was used as a substrate in consecutive additions, full conversion was observed in each cycle, with much greater reaction times being necessary for the second and third cycles (entry 4). This suggests partial catalyst degradation, although no color change was observed during the reaction.
CONCLUSIONS

The FeІ compound [NaFe(trop2dad) (thf)3] (2) with a redox-active diazadiene (dad) diolefim ligand is susceptible to a chemically reversible one-electron oxidation to give the series of compounds [Fe(trop2dad)(L)] (4), L = thf, MeCN, PPh3, P(OMe)3 (4d); trop = 5H-dibenzo[a,d]cyclohepten-5-yl. Compounds 4 were studied by techniques including single-crystal X-ray analysis, magnetic susceptibility measurements, Mössbauer spectroscopy, and DFT calculations. On the basis of these investigations, we tentatively assign an open-shell singlet electronic structure to compounds 4 with a ls FeІ center antiferromagnetically coupled to a low-valent iron center under reducing conditions in catalysts, although Fe catalysts with even longer lifetimes under catalytic conditions would be desirable. With amine–borane and dimethylamine–borane as substrates, high catalyst activities were observed, although the outstanding performance with MAB is not reached. This exemplifies once more the sensitivity of the catalyst systems to minor steric and electronic changes of the substrate in dehydrogenative reactions. In future work, the use of these and related low-valent iron complexes in other dehydrogenative coupling processes will be investigated.

EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum-line Schlenk techniques or in an MBraun inert-atmosphere drybox containing an atmosphere of purified argon. C4D8, THF-d8, and MTBE were distilled before use from sodium benzophenone ketyl. CD2Cl2 was distilled before use from CaH2. THF, n-hexane, toluene, and MeCN were purified using an Innovative Technologies PureSolv system and stored over 4 or 3 Å molecular sieves, respectively. Sodium, mercury, NaOEt, [Co(C5H5)2], NaBH4, Me3HNBH4, H3N-BH3, and anhydrous FeBr3 were obtained from Sigma-Aldrich and used as received. NaH was obtained from Sigma-Aldrich as a dispersion in hexane, toluene, and MeCN were purified using an Innovative Technologies PureSolv system and stored over 4 or 3 Å molecular sieves, respectively. Sodium, mercury, NaOEt, [Co(C5H5)2], NaBH4, Me3HNBH4, H3N-BH3, and anhydrous FeBr3 were obtained from Sigma-Aldrich and used as received. NaH was obtained from Sigma-Aldrich as a dispersion in hexane, toluene, and MeCN were purified using an Innovative Technologies PureSolv system and stored over 4 or 3 Å molecular sieves, respectively. Sodium, mercury, NaOEt, [Co(C5H5)2], NaBH4, Me3HNBH4, H3N-BH3, and anhydrous FeBr3 were obtained from Sigma-Aldrich and used as received. NaH was obtained from Sigma-Aldrich as a dispersion in hexane, toluene, and MeCN were purified using an Innovative Technologies PureSolv system and stored over 4 or 3 Å molecular sieves, respectively. Sodium, mercury, NaOEt, [Co(C5H5)2], NaBH4, Me3HNBH4, H3N-BH3, and anhydrous FeBr3 were obtained from Sigma-Aldrich and used as received. NaH was obtained from Sigma-Aldrich as a dispersion in hexane, toluene, and MeCN were purified using an Innovative Technologies PureSolv system and stored over 4 or 3 Å molecular sieves, respectively. Sodium, mercury, NaOEt, [Co(C5H5)2], NaBH4, Me3HNBH4, H3N-BH3, and anhydrous FeBr3 were obtained from Sigma-Aldrich and used as received. NaH was obtained from Sigma-Aldrich as a dispersion in hexane, toluene, and MeCN were purified using an Innovative Technologies PureSolv system and stored over 4 or 3 Å molecular sieves, respectively. Sodium, mercury, NaOEt, [Co(C5H5)2], NaBH4, Me3HNBH4, H3N-BH3, and anhydrous FeBr3 were obtained from Sigma-Aldrich and used as received. NaH was obtained from Sigma-Aldrich as a dispersion in hexane, toluene, and MeCN were purified using an Innovative Technologies PureSolv system and stored over 4 or 3 Å molecular sieves, respectively.
H NMR (300 MHz, CDCl₃): δ 109.79 (br s, 2H), 5.03 (br s, 4 H), 3.46 (br s, 8 H), 2.02 (br s, 4H), −3.91 (br s 4H), −35.42 (br s, 2 H) ppm. Mp: 208 °C dec. ATR IR: δ 3047 (w), 3021 (w), 1645 (w), 1600 (w), 1561 (w), 1494 (m), 1462 (m), 1437 (m), 1396 (m), 1339 (w), 1311 (m), 1263 (w), 1247 (w), 1186 (w), 1163 (m), 1115 (m), 1049 (m), 1030 (s), 1007 (m), 974 (m), 950 (m), 876 (w), 828 (m), 809 (m), 799 (s), 771 (m), 746 (s), 738 (s), 728 (s) cm⁻¹. μ eff = 4.9 μ μ (Evans method). Anal. Calcld for C₃₆H₃₂FeN₂O (653.60 g/mol): C, 70.66; H, 7.55; N, 3.75. Found: C, 70.41; H, 4.65; N, 4.42. 

-[Fe(trop)₃(dad)](MeCN)·2(MeCN) (4b). FeC₅F₅ (26 mg, 79 μmol) was added to a solution of 2.05 (hexanes) (60 mg, 77 μmol) in MeCN/MTBE (2 mL, 1:3). The reaction mixture was filtered after 6 h and layered with hexanes (8 mL). After 14 h dark brown single crystals had formed and were filtered off. Small amounts of colorless solids (if present) can be removed manually or by washing with MeCN/hexanes. The product was dried under a stream of argon. Yield: 41 mg, 67 μmol, 87%. 

-H NMR (300 MHz, CDCl₃): δ 0.49 (br s, 9H, MeCN), 4.07 (br s, 4H, 10,11-H(OCH₃)), 5.22 (s, 2H, 5-H(OH)), 6.93–7.02 (m, 8H, H(aryl)), 7.11 (d, 4H, J = 6.7 Hz, H(OH)), 7.33 (2H, NCH), 7.39 (br s, 4H, H(aryl)) ppm. 1H NMR (500 MHz, 30 °C, MeCN-d₃): δ 1.96 (s, 9H, MeCN), 3.43 (br d, 2H, J = 9.6 Hz, 10–11-H(OCH₃)), 4.42 (br d, 2H, J = 9.6 Hz, 10–11-H(OCH₃)), 5.45 (s, 2H, 5-H(OH)), 6.91 (br t, 2H, J = 7.2 Hz, H(aryl)), 7.03 (s, 4H, H(aryl)), 7.09 (br t, 2H, J = 7.2 Hz, H(aryl)), 7.16 (s, 2H, H(aryl)), 7.24 (br d, 2H, J = 7.5 Hz, H(aryl)), 7.28 (br d, 2H, J = 6.5 Hz, H(aryl)), 7.42 (2H, H(aryl)), 7.59 (s, 2H, NCH) ppm. 13C NMR (126 MHz, 30 °C, CDCl₃): δ = 70.84 (s, 11,10-C(OH)), 76.82 (s, 5-C(OH)), 81.17 (s, 11,10-C(OH)), 122.28 (s, 5-C(OH)), 125.72 (s, 5-C(OH)), 125.77 (s, 5-C(OH)), 126.17 (s, 5-C(OH)), 126.43 (s, 5-C(OH)), 127.02 (s, 5-C(OH)), 127.74 (s, 5-C(OH)), 144.93 (s, 5-C(OH)) ppm. Quaternary carbon atoms were not detected in 1D or 2D NMR experiments, which was ascribed to poor solubility of 4b at low temperatures. Anal. Calcld for C₆H₁₄F₅N₃: Fe, 86.62. 1H NMR (THF-d₈, 298 K, 0.02 M) 2.01 (1H) μ μ (Evans method) ppm. 31P ATR IR: δ 3063 (w), 3037 (w), 2919 (w), 2887 (w), 2289 (w), 2251 (m), 1593 (m), 1484 (m), 1465 (s), 1406 (m), 1371 (w), 1339 (w), 1299 (m), 1271 (w), 1243 (m), 1207 (m), 1159 (m), 1127 (w), 1100 (m), 1076 (m), 1033 (m), 978 (w), 955 (w), 890 (m), 843 (m), 825 (m), 800 (m), 770 (m), 755 (s), 744 (s), 730 (s) cm⁻¹. Mp: 136–138 °C dec. UV/vis: λ max 264, 434 nm. 

[Fe(trop)₃(dad)](CH₃CN) (4c). FeC₅F₅ (26 mg, 79 μmol) and PPh₃ (41 mg, 156 μmol) were added to a solution of 2.05 (hexanes) (60 mg, 77 μmol) in THF (1.5 mL). After 3 h the reaction mixture was filtered and layered with hexanes.
(3.5 mL). After an additional 14 h dark brown single crystals had formed and were filtered off and dried in vacuo. Yield: 58 mg, 69 %mol, 90%.

1H NMR (500 MHz, MeCN-d3): δ 3.98 (br s, 4H, 10,11-H(Olefin), 5.42 (s, 2H, 5-HBenzyl), 6.98 (t, 4H, JHH = 7.5 Hz, 3.7-H/Arom), 7.07 (t, 4H, JHH = 7.5 Hz, 3.7/2.8-H/Arom), 7.22 (d, 4H, JHH = 7.5 Hz, 1.9/4.6-H/Arom), 7.29 (br d, 6H, JHH = 7.4 Hz, o-Ph), 7.36–7.41 (m, 13H, 4.6/1.9-H(Arom), m-Ph, p-Ph), 7.63 (br s, 2H, NCH) ppm. 13C NMR (100 MHz, THF-d8): δ 125.77 (s, 2/7-CArom), 126.16 (s, 3-CArom), 126.45 (s, 1-CArom), 127.02 (s, 7/2-CArom), 127.73 (s, 6/9-CArom), 127.86 (s, 9-CArom), 129.44 (s, 9/6-CArom), 130.20 (s, 1-CArom), 132.58 (s, 2-CArom), 133.43 (s, 3-CArom), 134.91 (s, 4-CArom), 140.50 (s, 5-CArom), 140.83 (s, 6-CArom), 141.98 (s, 7-CArom), 143.91 (d, JHH = 7.4 Hz, 8-H/Arom) ppm. 31P NMR (162 MHz, THF-d8): δ 14.41 (d, JHH = 1.9 Hz, 9a-C(Arom), quart) ppm. 11B NMR (126 MHz, THF-d8): δ 70.81 (s, 10-C(AOe)), 76.84 (s, 5-C(2Oe)), 81.19 (s, 11-C(AOe)), 122.25 (s, 8-C(Oe)), 125.72 (s, 4-C(2Arom)), 126.77 (s, 2.7-C(Arom)), 126.16 (s, 3-C(Arom)), 126.45 (s, 1-C(Arom)), 127.02 (s, 7/2-C(Arom)), 127.73 (s, 6/9-C(Arom)), 128.67 (s, 9/6-C(Arom)), 129.44 (m, 2-Ph), 129.99 (m, 3-Ph, p-Ph), 135.17 (br s, o-Ph), 135.85 (s, 4a-C(Arom)), 138.60 (s, ipso-Ph), 143.09 (s, 9a-C(Arom)), 143.99 (s, 11a-C(Arom)), 144.15 (s, 5a-C(Arom)), 144.94 (s, NCH) ppm. 13C-NMR (126 MHz, 70 °C, MeCN-d3): δ 77.39 (s, 10.11-C(Olefin)), 78.61 (s, 5-C(AOe)), 124.56 (s, 2.8-C(Arom)), 126.72 (s, 1.9-C(Arom)), 127.68 (s, 4.6-C(Arom)), 129.77 (s, 3.7-C(Arom)), 129.90 (s, o-m-Ph), 130.20 (s, p-m-Ph), 135.05 (s, m-Ph, p-Ph), 139.01 (s, ipso-Ph), 140.50 (s, 9a,11a-C(Arom)), 145.05 (s, 4a,5a-C(Arom)), 145.56 (s, NCH) ppm. 13P NMR (203 MHz, MeCN-d3): δ −7.36 (br s, pPH3) ppm. Resonances for hexanes were also detected. Anal. Calc. for Cs9H5FeN5P: C, 66.86; H, 5.58; N, 9.56. Found: C, 66.93; H, 5.58; N, 9.62. Evaporation of the filtrate and drying in vacuo. Once isolated, the poly-MAB (0.05 mmol) was added to a solution of [Fe(trop2dad)(P(OMe)3)] (4a, 61 mg, 83 %mol) in THF (2 mL). After 4 h, the reaction mixture was filtered and layered with hexanes (6 mL). After 1 day, single crystals of 2.05% (hexanes) were isolated by filtration and dried under a stream of argon. Cooling the filtrate to −30 °C gave a second crop of 2. Combined yield: method A, 43 mg, 55 %mol, 66%; method B, 39 mg, 50 %mol, 60%.

Analytical data were identical with those previously reported.16

Catalysis. Typical experiments were carried out on the 0.24 (DMAB) and 0.31 (MAB) mmol scale (with respect to monomer). The required amount of 2, 4a,b, or 5 was dissolved in the required solvent (3.0 mL). A solution of the monomer in the required solvent (2.0 mL for DMAB, 4.0 mL for MAB) was added through a rubber septum. For AB, typical experiments were carried out on the 0.32 mmol scale (with respect to monomer). The required amount of 2, 4a,b, or 5 was dissolved in the required solvent (3.0 mL) and added to a solution (in the case of THF) or suspension (other solvents) of the monomer in the required solvent (4.0 mL) through a rubber septum. In all cases, the gas evolved was collected in a buret setup and its volume determined. In poisoning experiments a stock solution of the poisoned monomer was added at the indicated reaction time. The total volume was corrected for the volume added in this process.

DMAB. After completion of the reaction, an aliquot of the reaction mixture was analyzed by 1H NMR spectroscopy after addition of 1/3 (v/v) of C6D6. The main component (>98%) was (Me3NBH2)2 (catalyst 2).11B NMR (96 MHz, Tol/C6D6 (2/1)): δ 4.8 (t, JHH = 113.0 Hz) ppm. For experiments with catalyst 4a,11B NMR analysis was carried out by performing the reaction in an NMR tube (closed system); in this case, the linear compound Me3HN-BH2-Me3N-BH4 and cyclic (Me3NBH2)2 were detected.11B NMR (96 MHz, C6D6): δ −13.6 (q, JHH = 92.4 Hz, Me3HN-BH2-Me3N-BH4), 1.5 (t, JHH = 109.1 Hz, Me3HN-BH2-Me3N-BH3), 4.8 (t, JHH = 112.8 Hz, (Me3NBH2)2) ppm.

Poly-MAB. After gas evolution had ceased, hexanes (6 mL) was added to the reaction mixture. The solid was isolated by filtration and dried in vacuo. Once isolated, the poly-MAB samples were poorly soluble in common organic solvents such as DMF, THF, toluene, and chloroform.
Data from the reaction with 5 mol % 4a as follows. MALDI-TOF-MS (DCTB matrix): m/z 355.51 [(CH₆BN)₁₂H₂]+; 387.55 [(CH₆BN)₁₃H]+; 398.57 [(CH₆BN)₁₄H₂]+; 429.61 [(CH₆BN)₁₅H]+; 441.62 [(CH₆BN)₁₆H]+; 484.68 [(CH₆BN)₁₇H]+; 515.73 [(CH₆BN)₁₈H]+; 527.74 [(CH₆BN)₁₉H]+; 569.81 [(CH₆BN)₂₀H]+; 601.85 [(CH₆BN)₂₁H]+; 613.86 [(CH₆BN)₂₂H]+; 655.92 [(CH₆BN)₂₃H]+; 698.98 [(CH₆BN)₂₄H]+; 724.03 [(CH₆BN)₂₅H]+; 773.08 [(CH₆BN)₂₆H]+; 785.09 [(CH₆BN)₂₇H]+; 827.15 [(CH₆BN)₂₈H]+; 870.21 [(CH₆BN)₂₉H]+; 913.27 [(CH₆BN)₃₀H]+; 943.31 [(CH₆BN)₃₁H]+; 955.32 [(CH₆BN)₃₂H]+.⁵²

After a reaction in toluene using 5 mol % of 4a as a catalyst was finished, an aliquot was removed and analyzed by ¹¹B NMR spectroscopy after addition of 1/3 (v/v) of C₆D₆ revealing poly-MAB (¹¹B NMR (96 MHz, C₆D₆): δ = −4.78 (unsolved t, BH₂ ppm) as the main component next to traces (<1%) of N-trimethylborazine (¹¹B NMR (96 MHz, C₆D₆): δ = 33.8 (d, 1⁄₃BH = 131.5 Hz, BH ppm).

For differentiating between chain growth and step growth mechanisms, reactions were stopped at 30% and 60% conversion, respectively. After addition of hexanes and removal of all volatiles under reduced pressure, an oily residue was obtained, which was analyzed by mass spectrometry.

Data for 30% conversion are as follows. MALDI-TOF-MS (DHB matrix): m/z 318 [(CH₆BN)₁₂NH₄]+; 362 [(CH₆BN)₁₃NH₄]+; 405 [(CH₆BN)₁₄NH₄]+; 447 [(CH₆BN)₁₅NH₄]+.

Data for 60% conversion are as follows. MALDI-TOF-MS (DHB matrix, m/z): 318 [(CH₆BN)₁₂NH₄]+; 362 [(CH₆BN)₁₃NH₄]+; 405 [(CH₆BN)₁₄NH₄]+; 447 [(CH₆BN)₁₅NH₄]+; 534 [(CH₆BN)₁₆NH₄]+; 576 [(CH₆BN)₁₇NH₄]+; 631 [(CH₆BN)₁₈NH₄-(H)₄]+.

Poly-AB. After gas evaporation had ceased, hexanes (6 mL) was added to the reaction mixture. The solid was isolated by filtration and dried in vacuo. Once isolated, the poly-AB samples were poorly soluble in common organic solvents such as DMF, THF, toluene, and chloroform.

ATR IR: ν = 3297 (w), 3247 (w), 2963 (w), 2362 (m), 1560 (s), 1397 (s) cm⁻¹.

After a reaction in THF using 5 mol % 4a as a catalyst was finished, an aliquot was removed and analyzed by ¹¹B NMR spectroscopy after addition of 1/3 (v/v) of THF-d₈. Only a broad signal at ca. −2.55 ppm was detected (traces of solubilized poly-AB and/or resonance from boron species in the glass of the NMR tube). This excludes the presence of μ-amino diborane and THF-soluble oligomers such as borazine, cyclic linear trimers, and cyclic trimers in quantities detectable in this experiment.⁵⁶⁻⁵⁰,⁵³⁻⁵⁵

Computational Methods. Geometry optimizations were carried out with the Turbomole program package⁵⁴ coupled to the PQS Baker optimizer via the BOpt package, at the DFT-D3/b3-lyp level, employing Grimme’s D3 dispersion corrections (disp3).⁵⁸ We used the def2-TZVP basis set for all geometry optimizations. All minima (no imaginary frequencies) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated.

The geometries for the open-shell singlet (singlet biradical) minima were evaluated employing the broken-symmetry protocol. The “real” energy εₒ of the (multideterminant) open-shell singlet species was estimated from the εₒ energies of the optimized single-determinant broken symmetry solutions and the εᵢ energies from a separate unrestricted triplet (mᵢ = 1) calculations at the same geometry with the same functional and basis set, using the approximate spin correction formula proposed by Noodleman and Yamagushi.⁶⁰

\[ \varepsilon_i \approx \frac{S_1 \varepsilon_0}{S_1 + S_0} \]

The optimized geometries of all species are supplied as separate files in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b04146.

Single-crystal X-ray analyses, Mössbauer spectroscopy, DFT calculations, isotropic shift analysis, and catalysis (PDF)
Crystallographic data for 1a (CIF)
Crystallographic data for 3 (CIF)
Crystallographic data for 4a (CIF)
Crystallographic data for 4b (CIF)
Crystallographic data for 4c (CIF)
Crystallographic data for 4d (CIF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail for C.L.: lichtenberg@inorg.chem.ethz.ch.
*E-mail for H.G.: hgruetzmacher@ethz.ch.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank M. Sc. J. Bloch for experimental contributions and Dr. L. Viciu for SQUID analyses. A Feodor Lynen Fellowship to C. L. generously hosted by Prof. Dr. François Diederich is gratefully acknowledged. Financial support by the Swiss National Science Foundation (SNF) and the ETH is gratefully acknowledged.

REFERENCES

(7) Substitution of one or both dad ligands for the related doubly deprotonated ε-phenylenediamine ligands leads to different electronic structures of the resulting complexes.⁶⁶
equilibrium constants of singlet/triplet equilibria for 4a–c merely on the basis of data obtained using the Evans method.


(32) Recently, a coordination-induced spin state change has also been reported for a MnII nitride complex: Kropp, H.; Scheuer, A.; Heinemann, F. W.; Bendix, J.; Meyer, K. Inorg. Chem. 2015, 54, 3562–3572.


(43) When 20 equiv of MAB was reacted with 4a on NMR scale in C6D6 the 1H NMR spectrum recorded after full conversion showed paramagnetically shifted resonances, which were not identical with those of 4a. This is in agreement with 4a acting as a precatalyst. After addition of another 20 equiv of MAB, the relative intensity of the paramagnetically shifted 1H NMR resonances had changed, suggesting that (partial) catalyst degradation takes place. Similarly, new paramagnetically shifted resonances were observed, the relative intensity of which changed in the course of the reaction, when DMAB was used as a substrate.

(44) Another possibility to explain reduced catalyst activity would be precipitation of the active species with the growing polymer. This possibility was ruled out because traces of solids. Furthermore, the filtrate showed the same catalytic activity upon addition of another 20 equiv of MAB, as observed in the same experiment without filtration.
(45) For studies of Fe-based catalysts operating homogeneously or heterogeneously in AB and DMAB dehydrogenation, see refs 13a, 14, and 48.


(47) Selective poisoning experiments with 0.1 equiv of P(OMe)3 per Fe only marginally decreased the rate of the reaction, suggesting homogeneous reaction conditions.


(49) Accurate results from combustion analysis proved to be difficult to obtain for compounds 4a–d. Alternative bulk methods of characterization are provided as evidence of the efficacy of the syntheses.

(50) Minor deviations from expected values are ascribed to trace amounts of residual solvent molecules.

(51) Minor contributions to the observed μeff due to (super) paramagnetic impurities cannot strictly be excluded.

(52) Formation of a poly-MAB species with a “BH2+” end group could invoke B–N bond cleavage as part of the polymerization mechanism or occur during the ionization process of the mass spectrometric analysis.


(54) Ahlrichs, R. Turbomole Version 6.5, Theoretical Chemistry Group, University of Karlsruhe.


