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

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§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 FeII species [NaFe(trop2dad)(thf)] (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 = 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, cryoscopic, and theoretical techniques and methods.6,7 These compounds are best described as high-spin FeII centers (local spin S Fe = 2) antiferromagnetically coupled to two mononanionic dad radical ligands, (dad)** (local spin S dad = 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)2] (X = halide), and [Fe(dad)2] have been reported. They include the hydrogenation of 1-hexene,8 (cyclo)dimerizations of dienes,5,9 cycloptimerizations of alkenes,10 Diels–Alder type cyclizations of dienes with alkenes, and olefin polymerizations11 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 tetradentate diolefin 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 diolefin diamido ligand, (trop2dae)2,5 (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...
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 dialkynedi diazadiene compounds [Fe(trop2dad)(L)] (L = 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 dialkynedi diazadiene ate complex [NaFe(trop2dad)(thf)]3 (2) can be accessed from [FeBr(trop2dad)] (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-excess of elemental sodium or NaH as reducing agent (Scheme 2) can be accessed from [FeBr(trop2dad)] (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-excess of elemental sodium or NaH as reducing agent (Scheme 2). Electrochemical data suggest that the product of a one-electron oxidation of 2, that is, the neutral complex [Fe(trop2dad)], 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 [MCH2SiMe3] (M = Li, Na) have been successfully used as homoogenous reducing agents for FeII halides with diazadiene or the saturated diaminoethylene ligand (H2trop2dae), which gives S as a product.6a,13a,17 However, the reaction of [FeCl(trop2dad)] (1a) with [LiCH2SiMe3] 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, Na/Hg, or [CoCp2] as the reducing agent gave low yields of compound 2, free ligand, or [FeII(trop2dad)], 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 [Fe(trop2dad)(thf)] (4a) in 81% yield, which was isolated with 0.5 equiv of [Na(thf)3]PF6 per formula unit in the crystal lattice. With similar protocols, dark brown compounds [Fe(trop2dad)(L)] (4b–d) could be isolated, where the thf ligand bound to the Fe center has been replaced by another σ donor (L = MeCN (4b)) or by a σ donor/π acceptor ligand (L = PPh3 (4c), P(OMe)3 (4d)). The chemical reversibility between iron pair 2 and neutral species of type 4 was demonstrated by the reaction of 4a with mild reducing agents such as NaBH4 and NaOtBu, 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 (τ5 = 0 (4a)), 0.10 (4b)), intermediate (τ5 = 0.50 (4d)), and distorted-trigonal-bipyramidal coordination geometries (τ5 = 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: π–π interactions between the phenyl and benzo groups). The average Fe–N and Fe–(C=Ctrop) 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=Ctrop = olefinic binding sites).5,19 Note that the C=Ctrop 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=Ctrop)/Fe–N and shorter C=Ctrop distances (Supporting Information). The C=Ctrop and N=Ntrop bond lengths in the diazadiene ligand backbone are an important measure of the oxidation state of this type of ligand.6a,20 In compounds 4a–d, these distances are intermediate between those in...
Table 1. Selected Bond Lengths (Å) and τ₅ Values for Compounds 4a–d

<table>
<thead>
<tr>
<th>Compound</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>τ₅</td>
<td>0</td>
<td>0.10</td>
<td>0.60</td>
<td>0.50</td>
</tr>
<tr>
<td>C=C(thf)</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>2.320(11)</td>
<td>2.1939(4)</td>
</tr>
<tr>
<td>C=C(bonded)</td>
<td>1.402(4)</td>
<td>1.389(4)</td>
<td>1.389(5)</td>
<td>1.382(2)</td>
</tr>
<tr>
<td>C=N</td>
<td>1.325(3)</td>
<td>1.331(3)</td>
<td>1.326(3)</td>
<td>1.3315(19)</td>
</tr>
</tbody>
</table>

“Mean value. "Individual values differ considerably (see text).”

Table 2. Zero-Field ⁵⁷Fe Mössbauer Parameters for 4a–d

<table>
<thead>
<tr>
<th>Compound</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>δ (mm/s)</td>
<td>0.43(1)</td>
<td>0.42(1)</td>
<td>0.33(1)</td>
<td>0.22(1)</td>
</tr>
<tr>
<td>ΔE₂₀₀ (mm/s)</td>
<td>1.69(1)</td>
<td>1.11(1)</td>
<td>1.31(1)</td>
<td>1.16(1)</td>
</tr>
</tbody>
</table>

Information. 4a–d show isomer shifts of 0.43–0.22 mm/s, which are close to the isomer shifts observed for ls Fe⁺ centers coordinated by the bis(trop)diazadiene ligand in [Fe(trop,dad)₂] (δ = 0.37(1) mm/s) and ([NaFe(trop,dad)(thf)] (2); δ = 0.21(1) mm/s). This result clearly excludes a hs Fe²⁺ electron configuration. The lower isomer shifts for 4c,d with their π-acidic phosphorus ligands in comparison to 4a,b indicate a higher s electron density at Fe, which is a result of effective d(Fe) → π*(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). 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⁺ centers with strong antiferromagnetic coupling to their monoanionic radical (trop,dad)⁻⁻ ligands, although a closed-shell singlet electronic structure, ls Fe⁰(L⁰) ↔ ls Fe⁰(L²⁻) (π back-donation model), with a net Fe²⁺ oxidation state, cannot be fully excluded (vide infra). Thus, upon one-electron oxidation of [NaFe(trop,dad)-(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.

In order to gain further support for the electronic structure assignment, we performed DFT calculations on the full atom models of [Fe(trop,dad)(thf)] (4a) and [Fe(trop,dad)] (4e). 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>Species</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>−92.2 (⟨S⟩ = 0.0341)</td>
<td>−16.2 (⟨S⟩ = 1.0799)</td>
<td></td>
</tr>
<tr>
<td>4e</td>
<td>−190.0 (⟨S⟩ = 2.0216)</td>
<td>−22.0 (⟨S⟩ = 1.1594)</td>
<td></td>
</tr>
</tbody>
</table>

*Energy corrected for triplet spin contamination.
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\(^{1}\{L^+\}^-\) 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\(^{1}\{L^+\}^-\) “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\(^{1}\{L^+\}^-\) 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\(^{1}\{L^+\}^-\) and closed-shell singlet Fe\(^{0}\{L^0\}^-\) descriptions of species such as 4a. Both descriptions correspond to a (net) Fe\(^{2+}\) 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\(^{1}\{L^+\}^-\) 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)] + THF. In agreement with this equilibrium, the observed effective magnetic moment is much smaller than that expected for pure Fe\(^{3}\) (μ\(_{\text{eff}}\) expected = 2.83 μB for g = 2.0); it is solvent dependent (μ\(_{\text{eff}}\)(C\(_6\)D\(_6\), 298 K, 0.02 M) = 1.9(1) μB, THF-d\(_8\)(298 K, 0.02 M) = 1.3(1) μB, concentration dependent (μ\(_{\text{eff}}\)(C\(_6\)D\(_6\), 298 K, 0.02 M) = 1.9(1) μB, THF-d\(_8\)(298 K, 0.01 M) = 2.2(1) μB), and temperature dependent (μ\(_{\text{eff}}\)(C\(_6\)D\(_6\), 298 K, 0.02 M) = 1.8(1) μB, THF-d\(_8\)(0.01 M) = 1.3(1) μB). 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\(_3\)v 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\(_2\)v symmetry). However, it is slow on the NMR time scale at −30 °C, as apparent C\(_2\)v 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 shows apparent C\(_2\)v symmetry (Table 3), 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.

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Catalyzed Dehydrogenations. Initiated by the pioneering work of Manners and Baker, (alkyl)ammonia–boranes, RH\(_2\)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 graphine 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 methylyammo-nia–borane, MeH\(_2\)N-BH\(_3\) (MAB), dehydrocoupling can result
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.58,59 To our knowledge, this question has not been addressed for MAB dehydrogenation using base-metal catalysts.5 Increasing the polarity of the solvent (from toluene to THF) drastically lowers the rate of reaction, hinting at a homogeneous regime (entry 5). Selective poisoning experiments46 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 Fe1 compound with a saturated ligand backbone, [NaFe(trop2dae)(thf)3] (5), is not active (dae = −CH3−CH−) (entries 9 and 10).

When the substrate was changed to either amine−borane, H3N−BH3 (AB), or dimethylamine−borane, Me2HN−BH3 (DMAB), 5 mol % of compound 4a induced full to high conversion with respect to release of 1 equiv of H2 (Table 5).

Table 4. Catalyzed Dehydrogenative Polymerization of Methylamine−Borane (MAB)44

<table>
<thead>
<tr>
<th>entry</th>
<th>cat.</th>
<th>additive (amt (equiv))</th>
<th>t (min)</th>
<th>conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>THF as solvent</td>
<td>101</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>4a</td>
<td>P(OMe)3 (0.1)′</td>
<td>11</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>4a</td>
<td>P(OMe)3 (0.2)′</td>
<td>12</td>
<td>&gt;97</td>
</tr>
<tr>
<td>4</td>
<td>4a</td>
<td>P(OMe)3 (2.0)′</td>
<td>15</td>
<td>63</td>
</tr>
<tr>
<td>5</td>
<td>4a</td>
<td>8,5/99/186</td>
<td>3 × &gt;99</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4a</td>
<td>THF as solvent</td>
<td>227</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
<td>4a</td>
<td>THF as solvent</td>
<td>15</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

*Conditions unless specified otherwise: 5 mol % catalyst, toluene, 23 °C, open system. †1 mol % catalyst. ‡Added after 2.5 min reaction time.

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.58,59 To our knowledge, this question has not been addressed for MAB dehydrogenation using base-metal catalysts.5 Increasing the polarity of the solvent (from toluene to THF) drastically lowers the rate of reaction, hinting at a homogeneous regime (entry 5). Selective poisoning experiments46 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 Fe1 compound with a saturated ligand backbone, [NaFe(trop2dae)(thf)3] (5), is not active (dae = −CH3−CH−) (entries 9 and 10).

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Table 5. Catalyzed Dehydrogenative Polymerization of Amine−Borane (AB) and Cyclodimerization of Dimethylamine−Borane (DMAB)44

<table>
<thead>
<tr>
<th>entry</th>
<th>cat.</th>
<th>monomer</th>
<th>solvent</th>
<th>t (min)</th>
<th>conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>AB</td>
<td>THF46</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>80</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>AB</td>
<td>THF46</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</td>
<td>5</td>
<td>DMAB</td>
<td>Tol</td>
<td>240</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

*Conditions: 5 mol % catalyst loading, 23 °C, open system. †Similar results with toluene as a solvent (298 min, 93%). ‡With toluene as a solvent, a higher rate of reaction is observed (106 min, 77%), but full conversion is not reached and poisoning experiments with 0.1 equiv of P(OMe)3 per Fe suggest heterogeneous conditions.

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.58,59 To our knowledge, this question has not been addressed for MAB dehydrogenation using base-metal catalysts.5 Increasing the polarity of the solvent (from toluene to THF) drastically lowers the rate of reaction, hinting at a homogeneous regime (entry 5). Selective poisoning experiments46 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 Fe1 compound with a saturated ligand backbone, [NaFe(trop2dae)(thf)3] (5), is not active (dae = −CH3−CH−) (entries 9 and 10).

When the substrate was changed to either amine−borane, H3N−BH3 (AB), or dimethylamine−borane, Me2HN−BH3 (DMAB), 5 mol % of compound 4a induced full to high conversion with respect to release of 1 equiv of H2 (Table 5).

Table 5. Catalyzed Dehydrogenative Polymerization of Amine−Borane (AB) and Cyclodimerization of Dimethylamine−Borane (DMAB)44

<table>
<thead>
<tr>
<th>entry</th>
<th>cat.</th>
<th>monomer</th>
<th>solvent</th>
<th>t (min)</th>
<th>conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>AB</td>
<td>THF46</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>80</td>
</tr>
<tr>
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<td>2</td>
<td>AB</td>
<td>THF46</td>
<td>210</td>
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<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</td>
<td>5</td>
<td>DMAB</td>
<td>Tol</td>
<td>240</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

*Conditions: 5 mol % catalyst loading, 23 °C, open system. †Similar results with toluene as a solvent (298 min, 93%). ‡With toluene as a solvent, a higher rate of reaction is observed (106 min, 77%), but full conversion is not reached and poisoning experiments with 0.1 equiv of P(OMe)3 per Fe suggest heterogeneous conditions.
CONCLUSIONS

The Fe \textsuperscript{I} compound \([\text{NaFe(trop}_{2} \text{dad})](\text{thf})_{3}\) \((2)\) with a redox-active diadazene (dad) diolefin ligand is susceptible to a chemically reversible one-electron oxidation to give the series of compounds \([\text{Fe(trop}_{2} \text{dad})](\text{L})\) \((4; \text{L} = \text{thf} (4a), \text{MeCN} (4b), \text{PPh}_3 (4c)), \text{P(OMe)}_3 (4d))\); \text{trop} = \text{SH-di benz}[a,d] -cyclohepten- S-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 Fe \textsuperscript{I} center antiferromagnetically coupled to a monoanionic ligand radical \((\text{trop}_{2} \text{dad})^{*−}\) \((S_{\text{total}} = 0)\), although a closed-shell singlet electronic structure, \(ls\text{Fe}^{0}\{(\text{L}^{0})\}\) \(\leftrightarrow\) \(ls\text{Fe}^{2\text{-}}\{(\text{L}^{2\text{-}})\}\), with a net Fe \textsuperscript{I} oxidation state remains possible. Solution magnetic susceptibility measurements and DFT calculations on \(4a\) suggest that the paramagnetic species \([\text{Fe(trop}_{2} \text{dad})]\) \((4e)\) with a dissociated thf ligand is formed in an equilibrium reaction. In compounds \(4\), the \(s\) electron density at Fe responds to the \(\pi\) acidity of the neutral ligand following the order \(\text{thf} \approx \text{MeCN} < \text{PPh}_3 < \text{P(OMe)}_3\) as evidenced by Mössbauer spectroscopy. Compounds \(4a, b\) were investigated as (pre)-catalysts for the dehydrogenative coupling of \((\text{alkyl})\text{amine}–\text{boranes}. They are the most active (pre)catalysts containing a relatively cheap and abundant metal for the dehydrogenative polymerization of methylamine–borane (MAB). Selective poisoning experiments suggest a homogeneously catalyzed reaction. This gives further evidence for the efficiency of trop type ligands to stabilize low-valent iron centers under reducing conditions in catalysis, 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 dehydrocoupling 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 a MBraun inert-atmosphere drybox containing an atmosphere of purified argon. C\textsubscript{D}\textsubscript{6}, THF-\textsubscript{d\textsubscript{4}}, and MTBE were distilled before use from sodium benzenophene ketyl. C\textsubscript{2}D\textsubscript{2}Cl\textsubscript{2} was distilled before use from CaH\textsubscript{2}, THF, \n-hexane, toluene, and MeCN were purified using an Innovative Technologies PureSol system and stored over 4 or 3 \(\AA\) molecular sieves, respectively. Sodium, mercury, NaO\textsubscript{t}Bu, [Co(C\textsubscript{6}H\textsubscript{4}Bu\textsubscript{3})\textsubscript{2}], NaB\textsubscript{H\textsubscript{4}}, Me\textsubscript{3}H\textsubscript{2}BH, H\textsubscript{2}N-BH\textsubscript{4}, and anhydrous FeBr\textsubscript{3} were obtained from Sigma-Aldrich and used as received. NaH was obtained from Sigma-Aldrich as a dispersion in mineral oil and was washed with \(n\)-hexane and dried in vacuo prior to use. Trop\(_{2}\)dad, [FeCl\(_{3}\)(thf)]\(_{1.5}\), [Li(CH\(_{3}\)SiMe\(_{3}\)]\(_{n}\), [NaFe(trop\(_{2}\)dae)(thf)]\(_{2}\), [Fe(C\(_{2}\)H\(_{4}\))\(_{2}\)][PF\(_{6}\)], and Me\(_{3}H\textsubscript{2}N\textsubscript{BH}\(_{4}\) were synthesized according to the literature. NMR spectra were recorded on Bruker instruments operating at 200, 250, 300, 400, or 500 MHz with respect to \(^{1}\text{H}\). \(^{1}\text{H}\) NMR chemical shifts are reported relative to SiMe\(_{4}\) using the residual \(^{1}\text{H}\) chemical shifts of the solvent as a secondary standard. \(^{13}\text{C}\) NMR chemical shifts are reported relative to BF\(_{4}\)\textsubscript{−}\text{OEt\(_{2}\)}. Infrared spectra were collected on a PerkinElmer Spectrum 2000 FT-IR-Raman spectrometer. UV/vis spectra were recorded on a UV/vis/NIR Lambda-19 spectrometer in a cell with a 0.5 cm path length. Elemental analyses were performed at the Mikroanalytik of ETH Zürich. For mass spectrometric MALDI-TOF experiments, a Bruker UltraFlex II MALDI-TOF-MS instrument and a trans-2-[3-(4-tert-butylyphenyl)-2-methyl-2-propenyliden|e]-malononitrile (DCTB) or 2,5-dihydroxybenzoic acid (DHB) matrix were used, and the laser power was adjusted to give appropriate peak intensities. Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop, and then transferred to the goniometer of an Oxford XCalibur, Bruker ApexI, ApexII, or Venture diffractometer equipped with a molybdenum X-ray tube (\(\lambda = 0.71073 \text{ Å}\)). The structures were solved using direct methods (SHELXS) completed by Fourier synthesis and refined by full-matrix least-squares procedures. CCDC 1409557–1409562 contain crystallographic information for compounds 1a, 3, and 4a–d. 

Fe Mössbauer spectra were recorded on a WissEl Mössbauer spectrometer (MRG-500) at 77 K in constant-acceleration mode. \(^{57}\text{Co}/\text{Rh}\) was used as the radiation source. WinNormos for Igor Pro software has been used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.20 mm/s. The temperature of the samples was controlled by an MBBC-HEO106 Mössbauer He/N\(_{2}\) cryostat within an accuracy of ±0.3 K. Isomer shifts were determined relative to \(α\)-iron at 298 K.

The EPR spectrum of \(4a\) was recorded on a JEOL JES-FA200 continuous wave spectrometer equipped with an X-band Gunn oscillator bridge, a cylindrical mode cavity, and a nitrogen cryostat. \(4a\) was freshly dissolved in THF in an approximately 0.5 mM concentration in an airtight J. Young quartz EPR tube under an atmosphere of purified argon. The solution in the tube was frozen in liquid nitrogen upon exiting the glovebox and kept frozen until measured. The spectrum was measured with the following parameters: temperature 91 K, frequency 8.947895 GHz, modulation amplitude 2 mT, microwave power 0.998 mW, modulation frequency 100 kHz, time constant 0.3 s.

The EPR spectrum of \(4d\) was recorded on a Bruker EMX spectrometer equipped with an X-band ER 041 XG microwave bridge. \(4d\) was freshly dissolved in THF in an approximately 0.5 mM concentration in an airtight J. Young quartz EPR tube under an atmosphere of purified argon. The spectrum was measured with the following parameters: temperature 298 K, frequency 4.999369 GHz, modulation amplitude 0.1 mT, microwave power 0.97 mW, time constant 0.04 s. Solid-state magnetic susceptibility measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-SS) in the temperature range 2–300 K in fields of 0.01 and 1 T. Both field-cooled (FC) and zero-field-cooled (ZFC) data were obtained.

\([\text{FeCl}_{2}(\text{trop}_{2}\text{dad})]\) \((1a)\) Toluene (8 mL) was added to a mixture of trop\(_{2}\)dad (500 mg, 1.15 mmol) and FeCl\(_{3}\)(thf)\(_{1.5}\) (269 mg, 1.15 mmol). The reaction mixture turned green and was stirred at ambient temperature for 16 h. All volatiles were removed under reduced pressure to give a green solid, which was dried in vacuo for 3 h. Yield: 646 mg, 1.15 mmol, quantitative.
Yield: 36 mg, 48 °C. 6236

11.27 (br s, 2H, 5-HBenzyl), 7.08 (br d, 4H, 3,7/2,8-HArom), 7.76 (br s, 4H,3

HOlefin), 6.73 (br t, 4H,3

HOlefin), 6.14 (br s, 2H, 5-HArom), 6.43 (br s, 2H, 5-HBenzyl), 6.73 (br t, 4H, 3

3065 (w), 3013 (w), 2973 (w), 2870 (w), 1595 (m), 1574 (w), 1484 (m), 1478 (m), 1463 (m), 1397 (w), 1357 (w), 1337 (w), 1302 (w), 1273 (w), 1248 (w), 1221 (w), 1204 (w), 1188 (w), 1159 (w), 1132 (w), 1099 (w), 1049 (s), 942 (w), 884 (s), 844 (s), 829 (s), 786 (s) 762 (w), 740 (s), 730 (s) cm⁻¹. Mp: 104 °C dec. UV/vis: λmax 206, 264, 446 nm.

Fe(trop2dad)(MeCN) (2:MeCN) (4b). FePF₆ (26 mg, 79 μmol) was added to a solution of 2:0.5(hexanes) (60 mg, 77 μmol) in MeCN/MTBE (2 mL:1). After 1 h the reaction mixture was filtered and washed with hexanes (8 mL). After 1 h dark brown single crystals had formed and were filtered off. Small amounts of colorless solids (if present) could be removed manually or by washing with MeCN/hexanes. The product was dried under a stream of argon. Yield: 41 mg, 67 μmol, 87%.

1H NMR (300 MHz, C₆D₆): δ 0.49 (br s, 9H, MeCN), 4.07 (br s, 4H, 10,11-HArom), 5.22 (s, 2H, 5-HArom), 6.93–7.02 (m, 8H, HArom), 7.11 (d, 4H, 3

JHH = 7.7 Hz, 5-HBenzyl), 7.20 (d, 4H, 3

JHH = 6.7 Hz, 7-HArom), 7.53 (s, 2H, NCH), 7.39 (br s, 4H, HArom) ppm. 1H NMR (500 MHz, THF) ppm: δ 1.96 (s, 9H, MeCN), 3.43 (br d, 2H, δ 9.00

δ = 27.0868(5) Å; β = 17.9322(3) Å; α = 17.9322(3) Å; β = 70.84 (s, 10/11-COlefin), 4.42 (br d, 2H, δ 9.6 Hz, 10/11-COlefin), 5.45 (s, 2H, 2

δHH = 6.72 Hz, H2Arom), 7.03 (s, 4H, H2Arom), 7.09 (br t, 2H, δ 7.2 Hz, H2Arom), 7.16 (s, 2H, H2Arom), 7.24 (br d, 2H, δ 7.5 Hz, H2Arom), 7.28 (br d, 2H, δ 6.5 Hz, H2Arom), 7.42 (s, 2H, H2Arom), 7.59 (s, 2H, NCH) ppm. 13C NMR (126 MHz – 30 °C, CDCl₃): δ = 70.84 (s, 10,11-COlefin), 76.82 (s, 5-CBenzyl), 81.17 (s, 11/10-COlefin), 122.28 (s, C₂), 125.72 (s, C₆), 125.77 (s, C₂), 126.17 (s, C₂), 126.43 (s, C₂), 127.02 (s, C₂), 127.74 (s, C₂), 128.27 (s, C₂), 144.93 (s, NCH) ppm. Quaternary carbon atoms were not detected in 1D or 2D NMR experiments, which was ascribed to poor solubility of 4a at low temperatures. Anal. Calcd for C₃₂H₂₆N₂O₂LiSi₂Fe: C, 68.34; H, 4.65; N, 4.42.50

Reaction of 1a with [CoCp₂]. [CoCp₂] (60 mg, 0.32 mmol) was added to a solution of 1a (100 mg, 0.15 mmol) in toluene (4 mL). The reaction mixture immediately turned dark brown and was warmed to room temperature. After 10 min, all volatiles were removed under reduced pressure. Toluene (1 mL) was added to the residue, and the solid part was separated by filtration. The filtrate was layered with hexanes (6 mL) and cooled to −30 °C. After 6 days, the microcrystalline solid part was isolated by filtration. It was redisolved in fluorobenzene (1.5 mL) and filtered. The filtrate was layered with hexanes (8 mL) to give microcrystalline 3 after 1 day, which was isolated by filtration and dried under a stream of argon. Yield: 36 mg, 48 μmol, 27%.

Yield: 104 mg, 125 μmol, 81%.

1H NMR (500 MHz, THF-d₈): δ 1.78 (br s, 2H, 14H-THF), 3.63 (br s, 14H-α-THF), 4.87 (br s, 4H, 10,11-HArom), 5.50 (br s, 2H, 5-HBenzyl), 6.95 (br s, 8H, HArom), 6.96 (br s, 4H, HArom), 6.97 (br s, 4H, HArom), 8.35 (br s, 2H, NCH) ppm. 13C NMR (126 MHz – 40 °C, THF-d₈): δ 26.20 (s, β-THF), 68.04 (s, α-THF), 78.03 (s, 5-CBenzyl), 81.61 (br s, 10,11-COlefin), 123.58 (s, C₂), 126.01 (s, C₂), 126.87 (s, C₂), 127.10 (s, C₂), 138.28 (s, C₂), 144.46 (s, C₂), 149.94 (s, NCH) ppm. 1H NMR (300 MHz, 25 °C, Tol-d₈): δ = −11.27 (br s, 2H, 5-HBenzyl) − 1.01 (br s, 4H, 2,8,3,7-HArom), 1.40 (m, 14H, β-THF), 2.65 (br s, 4H, 1,9/4,6-HArom), 3.55 (m, 14H, α-THF), 6.90 (br s, 4H, 3,7,2,8-HArom), 7.76 (br s, 4H, 4,6/1,9-HArom), 55.72 (br s, 4H, 10,11-HArom) ppm. A resonance for the HCN proton could not unambiguously be assigned to 25 °C (overlap with solvent signals possible). Chemical shifts are concentration dependent. 1H NMR (300 MHz, −40 °C, Tol-d₈): δ 1.18 (m, 14H, β-THF), 3.30 (m, 14H, α-THF), −4.64 (s, 2H, 5-HArom), 6.14 (br s, 4H, 10,11-HArom), 6.73 (br t, 4H, δHH = 7.4 Hz, 2,8,3,7-HArom), 6.96 (br t, 4H, δHH = 7.5 Hz, 3,7,2,8-HArom), 7.97 (br s, 2H, HCN, 7.08 (br d, 4H, δHH = 7.4 Hz, 1,9/4,6-HArom), 7.15 (br d, 4H, δHH = 7.5 Hz, 4,6/1,9-HArom) ppm. Anal. Calcd for C₄₄H₅₆N₂O₄LiSi₂Fe: C, 68.23; H, 4.29; N, 4.97. Found: C, 68.34; H, 4.65; N, 4.42.

| [LiOTf]Fe(bis(MeSICH₂)-trop2dad) (3) | A solution of [LiOTf]Fe(bis(MeSICH₂)-trop2dad) (3) was added to a suspension of 1a (100 mg, 0.18 mmol) in Et₂O (1 mL) at −30 °C. The reaction mixture immediately turned dark brown and was warmed to room temperature. After 10 min, all volatiles were removed under reduced pressure. Toluene (1 mL) was added to the residue, and the solid part was separated by filtration. The filtrate was layered with hexanes (6 mL) and cooled to −30 °C. After 6 days, the microcrystalline solid part was isolated by filtration. It was redisolved in fluorobenzene (1.5 mL) and filtered. The filtrate was layered with hexanes (8 mL) to give microcrystalline 3 after 1 day, which was isolated by filtration and dried under a stream of argon. Yield: 36 mg, 48 μmol, 27%. | | |
(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(Arom)), 5.42 (s, 2H, 5-H(Benzyl)), 6.98 (t, 4H, 3-JH(Arom) = 7.5 Hz, 2,8-JH(Arom)), 7.07 (t, 4H, 3-JH(Arom) = 7.5 Hz, 3,7-JH(Arom)), 7.22 (d, 4H, 4-JH(Arom) = 7.5 Hz, 1,9-H(Arom)), 7.29 (br d, 6H, 5-JH(Arom)), 7.36–7.41 (m, 13H, 1,9-H(Arom)), 3,6-H(Arom)), 7.38–7.40 (m, 13H, 4,6-H(Arom)), 7.62 (br s, 2H, NCH) ppm. 13C NMR (500 MHz, 70 °C, MeCN-d3): δ 4.02 (s, 4H, 10-H(Arom)), 4.44 (d, 2H, 3-JH(Arom) = 9.5 Hz, 11-H(Arom)), 5.44 (s, 2H, 5-H(Benzyl)), 6.91 (t, 2H, 3-JH(Arom) = 7.4 Hz, 8-H(Arom)), 7.02–7.04 (m, 4H, 2,7-H(Arom)), 7.09 (t, 2H, 2-JH(Arom) = 7.5 Hz, 3-H(Arom)), 7.14–7.16 (br m, 2H, 4-H(Arom)), 7.22–7.24 (br m, 6H, 6,7-H(Arom)), 7.24–7.27 (m, 4H, 6,9-H(Arom)), 7.30–7.33 (m, 3H, 3-H(Arom)), 7.39–7.42 (m, 8H, 1,9-H(Arom)), 7.56 (s, 2H, NCH) ppm. 11B NMR (126 MHz, –30 °C, MeCN-d3): δ 70.81 (s, 10-C(Arom)), 76.84 (s, 5-C(Arom)), 81.19 (s, 11-C(Arom)), 122.25 (s, 8-C(Arom)), 125.72 (s, 4-C(Arom)), 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 (s, m, Ph), 129.99 (s, 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(Arom)), 78.61 (s, 5-C(Arom)), 124.56 (s, 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, p-Ph), 130.20 (s, m, Ph), 135.05 (s, m, 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. 31P NMR (203 MHz, MeCN-d3): δ 7.76 (br s, pPPh2) ppm. Resonances for hexanes were also detected. Anal. Calcld for 1Ca4H38Fe3N2P·Fe: C 66.44%, H 4.6%, N 8.2%, P 4.2%. Found: C 66.47%, H 4.5%, N 8.2%, P 4.2% (Evans method).

After gas evolution had ceased, hexanes (6 mL) was added to the reaction mixture. The solid was 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, 86%; 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 poison 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 11B NMR spectroscopy after addition of 1/3 (v/v) of C6D6. The main component (>98%) was (MeNBH)2 (catalyst 2).11B NMR (96 MHz, Tol/C6D6 (2/1)): δ 4.8 (t, 1JH = 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-Me-NBH1 and cyclic (MeNBH2)2 were detected.11B NMR (96 MHz, C6D6): δ 13.6 (q, 1JH = 92.4 Hz, Me3HN-BH2-Me-NBH1), 1.5 (t, 1JH = 109.1 Hz, Me3HN-BH2-Me-NBH1), 4.8 (t, 1JH = 112.8 Hz, (MeNBH2)3). 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.

ATR IR: δ 3268 (w), 2961 (w), 2381 (m), 1618 (w), 1448 (m), 1413 (w), 1344 (s) cm⁻1.
Data from the reaction with 5 mol % 4a as follows. MALDI-TOF-MS (DCTB matrix): m/z 355.51 [(CH6BN)2BH2]+; 387.55 [(CH6BN)3H]+; 398.57 [(CH6BN)4BH2]+; 429.61 [(CH6BN)10H]+; 441.62 [(CH6BN)10BH2]+; 484.68 [(CH6BN)11BH2]+; 515.73 [(CH6BN)11H]+; 527.74 [(CH6BN)12BH2]+; 569.81 [(CH6BN)11BH3]+; 601.85 [(CH6BN)11H]+; 613.86 [(CH6BN)14BH2]+; 655.92 [(CH6BN)15BH2]+; 698.98 [(CH6BN)16BH2]+; 742.03 [(CH6BN)17BH2]+; 773.08 [(CH6BN)18H]+; 827.15 [(CH6BN)19BH2]+; 913.27 [(CH6BN)20BH2]+; 943.31 [(CH6BN)22H]+; 955.32 [(CH6BN)22BH2]+.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 = +3.38 (d, 1JH−BH = 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)2-NH4]+; 362 [(CH6BN)3-NH4]+; 405 [(CH6BN)4-NH4]+; 447 [(CH6BN)4-NH3]+.


Poly-AB. 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-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 % of 4a as 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. −2.25 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.58,41a,43

Computational Methods. Geometry optimizations were carried out with the Turbomole program package54 coupled to the PQS/Baker optimizer55 via the B0Opt package,56 at the DFT-D3/b3-lyp level, employing Grimme’s D3 dispersion corrections (disp3).58 We used the def2-TZVP basis set59 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 ε₁ of the (multideterminant) open-shell singlet species was estimated from the ε₀ energies of the optimized single-determinant broken symmetry solutions and the ε₁ energies from a separate unrestricted triplet (m = 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

ε₁ ≈ S₁²E₀ − S₀²E₁
S₁² − S₀²

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.5b01416.

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)

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REFERENCES
(7) Substitution of one or both dad ligands for the related doubly deprotonated e-phenylenediamine ligands leads to different electronic structures of the resulting complexes.66
in situ formed Fe particles can also be catalytically active (cf. ref 14).

(14) Depending on the Fe precursor and the reaction conditions, the possibility of trace impurities in the solid state (SQUID) but show an effective magnetic moment >0 in the suggested equilibrium scenario.

The possibility was ruled out because precipitation of the active species with the growing polymer. This was also observed in the case of the reaction mixture after filtration. This is in agreement with the reported dehydrogenation of 20 equiv of MAB did not yield significant amounts 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.

(34) Another possibility to explain reduced catalyst activity would be another mechanism, such as the formation of a Fe dimer from the Fe monomer. This mechanism has been proposed for the dehydrogenation of DMAB to afford 2,5-dimethylfuran (42).

A turnover frequency of 3.66 s⁻¹ was determined for the dehydrogenation of AB, heterogeneously catalyzed by in situ generated Fe nanoparticles.
(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.


(d) Calculations were performed using the Turbomole functional "b3-lyp", which is not completely identical with the Gaussian "BSLYP" functional.

