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Selective Catalytic Hydrogenations of Nitriles, Ketones, and Aldehydes by Well-Defined Manganese Pincer Complexes

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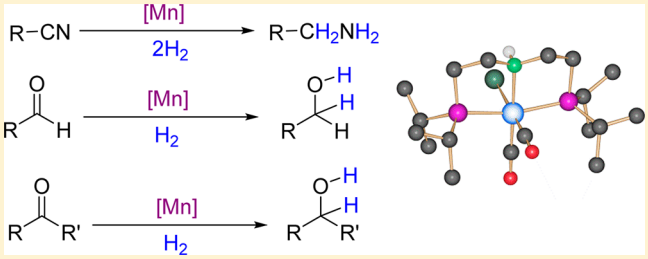
Supporting Information

ABSTRACT: Hydrogenations constitute fundamental processes in organic chemistry and allow for atom-efficient and clean functional group transformations. In fact, the selective reduction of nitriles, ketones, and aldehydes with molecular hydrogen permits access to a green synthesis of valuable amines and alcohols. Despite more than a century of developments in homogeneous and heterogeneous catalysis, efforts toward the creation of new useful and broadly applicable catalyst systems are ongoing. Recently, Earth-abundant metals have attracted significant interest in this area. In the present study, we describe for the first time specific molecular-defined manganese complexes that allow for the hydrogenation of various polar functional groups. Under optimal conditions, we achieve good functional group tolerance, and industrially important substrates, e.g., for the flavor and fragrance industry, are selectively reduced.



INTRODUCTION

Catalytic hydrogenations are of utmost importance in organic synthesis and play a key role in the production of numerous bulk products and intermediates in the chemical industry. From an ecological point of view, reductions using molecular hydrogen as reducing agent represent one of the most efficient and atom-economical transformations.[1] In general, heterogeneous catalysts are well established in the hydrogenation of non-demanding polar functional groups, which often takes place at high temperatures and/or pressures.[2] The complementary development of well-defined homogeneous complexes that allow for selective reduction under milder conditions constitutes a cutting-edge endeavor in modern catalyst design.[3] In this context, the introduction of bifunctional metal−ligand catalysis by Noyori for the catalytic hydrogenation of carbonyl compounds represents a breakthrough.[4] Since then, significant progress has been made in this field using mainly noble metal complexes,[5] namely ruthenium, iridium, and rhodium. However, in terms of sustainability, such precious metals ought to be replaced by inexpensive and widely abundant first-row base metals.[6]

Seminal progress in this area includes the hydrogenation of ketones enabled by iron catalysts by the groups of Casey,[7] Morris,[8] and Milstein[9] (Figure 1). In this respect, our group[10] as well as others[11] have demonstrated the applicability of Fe pincer complexes for a variety of hydrogenation and dehydrogenation reactions.[12] Meanwhile, pincer-based Co complexes have been successfully applied in the hydrogenation of carbonyl compounds, imines, alkenes, and nitriles.[13] Compared to the present success with defined iron and cobalt catalysts, other base metal complexes of nickel,[14] copper,[15] and zinc[16] have been scarcely reported for hydrogenation reactions and should offer potential for new applications.

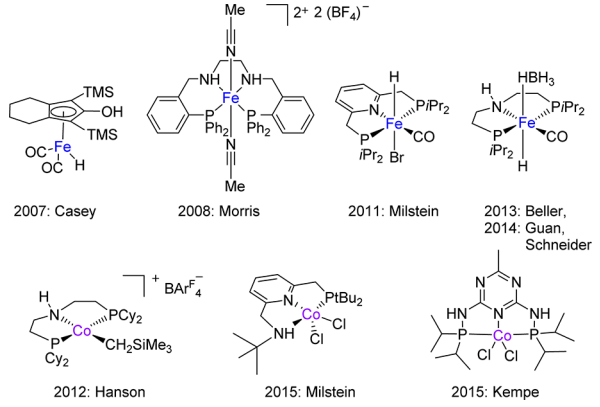


Figure 1. Selected examples of non-precious-metal catalytic systems for (de)hydrogenation reactions.

Despite all these efforts, one of the most common metals, manganese, is basically unknown for catalytic hydrogenations.[17] In fact, manganese is the third most abundant transition metal in the Earth's crust, after iron and titanium, and is absolutely necessary for development, metabolism, and the antioxidant system in humans. Today, millions of tons of manganese ore are used mainly for iron and steel manufacture. Without a

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doubt, this element represents a highly attractive candidate for the design of new catalysts.[18] While manganese complexes are frequently used in oxidations, they are generally not employed for catalytic reductions, and only special hydrosilylation, electrocatalytic reactions, and very recently dehydrogenations are known.[19] Here, we describe for the first time the application of manganese pincer complexes in catalytic hydrogenations of nitriles, ketones, and aldehydes.

RESULTS AND DISCUSSION

Catalyst Preparation. Based on our expertise using specific Fe and Ru pincer complexes for the dehydrogenation of methanol[10a,20] and the related hydrogenations of carbon dioxide and carboxylic acid derivatives, we became interested in the preparation of defined manganese PNP as a class of pincer ligands is used.

Until now, such manganese complexes have been sparsely discussed in the literature and have not been used in catalysis.[21] At the start of this project, four manganese pincer complexes bearing two different PNP ligands were prepared (Figure 2).

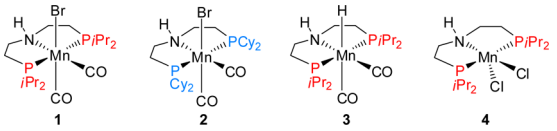
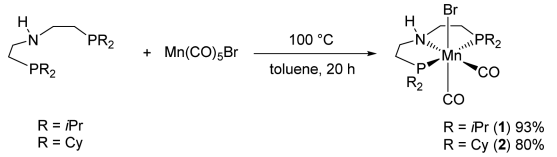


Figure 2. Manganese complexes used for this study.

An initial attempt, i.e., reaction of $MnCl_2$ with the isopropyl-tagged PNP ligand, afforded **4**. The molecular structure of this complex was confirmed by X-ray diffraction analysis (see Supporting Information (SI), section V). In order to prepare the potentially active carbonyl-ligated manganese hydride complex, **4** was reacted with CO, but unfortunately no reaction occurred. Hence, an alternative strategy was envisioned: Upon reaction of commercially available $[MnBr(CO)_5]$ with the corresponding PNP ligands in toluene at 100 °C, air-stable dicarbonyl manganese complexes **1** and **2** were conveniently prepared in a straightforward manner without the need for additional CO treatment (Scheme 1).

Scheme 1. Synthesis of Manganese Pincer Complexes



The resulting bright yellow complexes were fully characterized by NMR and infrared (IR) spectroscopy, high-resolution mass spectrometry, X-ray,[22] and elemental analysis (see SI). The IR (attenuated total reflection) spectra of **1** and **2** contain strong CO stretching vibrations at 1903, 1815 cm^{-1} and 1913, 1826 cm^{-1}, respectively, which clearly indicate the coordination of two CO ligands to the metal center. X-ray analysis reveals that one of the CO ligands is located *trans* to the nitrogen atom and the other CO is located trans to the bromide ligand (Figure 3).

Advantageously, complexes **1** and **2** are highly stable and do not decompose easily in the presence of air. In fact, exposing complex **1** as a solid for 25 days to air did not result in any decomposition (see Figures SI 7 and SI 8)! However, in the presence of strong base, deprotonation of the coordinated amine will promote the liberation of the halide anion. The resulting amido manganese complex should activate molecular hydrogen via heterolytic splitting to form an active Mn-hydride species. Thus, we thought these complexes represent ideal drop-in catalysts for practical hydrogenations.

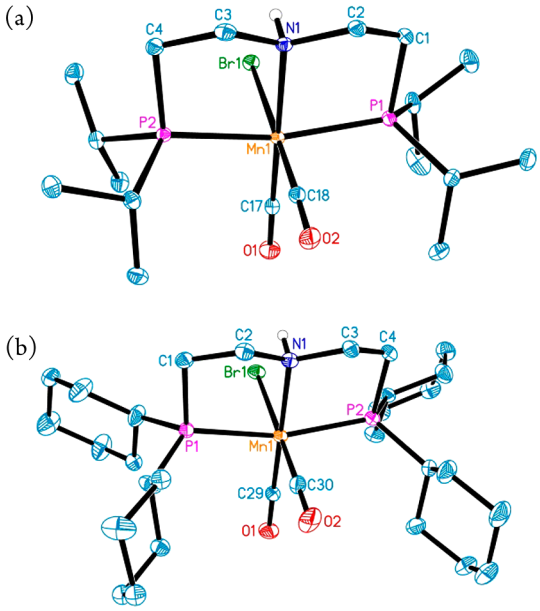
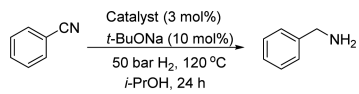


Figure 3. Molecular structure of complexes **1** (a) and **2** (b). Only one of the two molecules of the asymmetric unit is depicted. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms except of that attached to nitrogen are omitted for clarity.

Catalysis. Having some potential manganese catalysts in hand, we started to investigate their behavior in the hydrogenation of nitriles, ketones, and aldehydes. Based on the recent interest in the selective reduction of carboxylic acid derivatives,[23] our initial attempts focused on the hydrogenation of benzonitrile as benchmark substrate (Table 1). Catalytic experiments were performed with complexes **1**–**6** (3 mol% cat., 120 °C, 50 bar H_2, 24 h). In the presence of **1** some activity was observed, but no desired product (5% benzyl alcohol; see Table SI 7) was formed. In contrast, combining **1** with 10 mol% of

Table 1. Manganese-Catalyzed Hydrogenation of Benzonitrile[a]



entry	complex	conv (%)[b]	yield (%)[b]
1	**1**	>99	98
2	**2**	>99	87
3[c]	**3**	>99	81
4	**4**	0	0
5	$[MnBr(CO)_5]$ (**5**)	0	0
6	$CpMn(CO)_3$ (**6**)	0	0

[a]Reaction conditions: substrate (0.5 mmol), **1**–**6** (0.015 mmol), *t*-BuONa (0.05 mmol), *i*-PrOH (1 mL), 24 h, 120 °C, 50 bar H_2. [b]Conversion and yield were determined by GC analysis using hexadecane as an internal standard. [c]Under similar conditions in the presence of base, complex **3** gave 81% yield of benzylamine. Without base, only 42% yield was observed.

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base (*t*-BuONa), which should form a more active amido manganese complex, vide supra, resulted in 98% of benzylamine! To the best of our knowledge, this represents the first catalytic hydrogenation using a molecularly defined manganese complex.

Interestingly, complex **3** (see SI, section IV), which can be generated from **1** upon addition of base and H_2 and also prepared by treatment with sodium triethylborohydride, produced benzylamine in 81% yield. The lower product yield in the benchmark reaction using the hydride complex **3** is explained by its lower stability. Starting from complex **1**, slow formation of the active complex **3** should take place, and potential decomposition reactions of this active species are minimized.

In addition to **1**, the related complex **2** also allowed for hydrogenation in high yield (87%). However, Mn(II) species **4** and the commercially available complexes **5** and **6** in the presence and absence of the pincer ligand gave no products. Evaluation of critical reaction parameters in the presence of complex **1** revealed optimal results in toluene as solvent and *t*-BuONa as base (see Table SI 7). Notably, significant activity is observed even in the presence of 2 mol% catalyst and 30 bar of hydrogen (see Table SI 7).

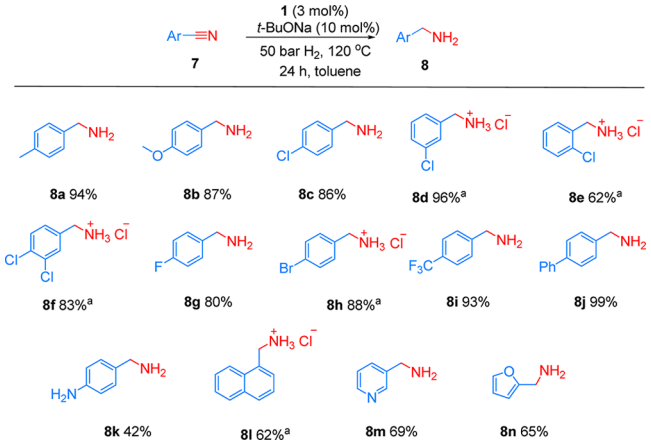
The applicability of catalyst system **1** is demonstrated in the selective hydrogenation of various nitriles, including substituted aromatic, benzylic, aliphatic nitriles and dinitriles (Schemes 2 and 3). In general, electron-donating and electron-withdrawing substituents, e.g., chloride, fluoride, bromide, and the more labile amino group, as well as heterocycles are well tolerated. Notably, the reduction of 4-(trifluoromethyl)benzonitrile was easily scaled up to 5 g, and **8i**·HCl was isolated in 95% yield.

Next, we explored the activity of the manganese catalyst toward a collection of more demanding aliphatic nitriles. As an example, benzyl nitrile was successfully hydrogenated to the corresponding amine **10a** in 96% isolated yield. Notably, the conjugated nitrile afforded a mixture of the corresponding unsaturated (53%) and saturated (25%) amines. Interestingly, the isolated double-bond-containing 5-hexene nitrile was selectively hydrogenated to amine **10j** without affecting the double bond. Finally, the 1,4-disubstituted benzonitrile **10k** was reduced to the diamine and isolated in 80% under the standard reaction conditions.

Apart from nitriles, selective hydrogenation of ketones (Scheme 4) and aldehydes (Scheme 5) to the corresponding primary and secondary alcohols took place in the presence of 1 mol% of complex **1** and 3 mol% *t*-BuONa. Under these conditions, the manganese-based catalyst tolerates other reducible groups such as lactams (**12e**), esters (**12f**), and isolated C=C bonds (**12i**, **12j**). Notably, the cyclopropyl-substituted ketone furnished a quantitative yield of **12b**, indicating that the reaction does not proceed via stable radical intermediates. Additionally, the heterocyclic substrate 1-benzylpiperidin-4-one and 4-chromanone were converted into alcohols **12g** and **12h**, respectively.

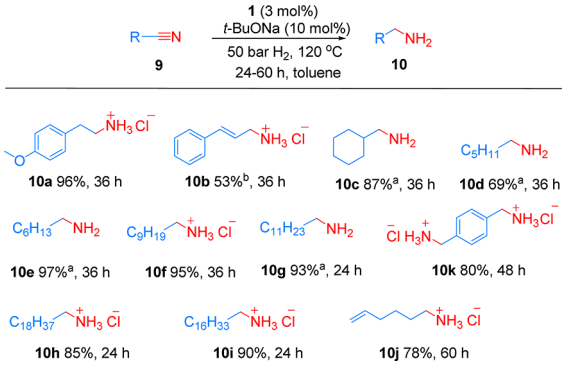
α,β-Unsaturated aldehydes reacted selectively under mild conditions (10 bar H_2, 60 °C; Scheme 5). Here, in all cases only the carbonyl group was reduced to give the corresponding unsaturated alcohol. Accordingly, 2-octynal gave oct-2-yn-1-ol in excellent isolated yield (96%). In addition, several natural products, e.g., citronellal (3,7-dimethyloct-6-enal), perillaldehyde, and 5-hydroxymethylfurfural (HMF) gave the corresponding primary alcohols in moderate to excellent yield.

Scheme 2. Catalytic Hydrogenation of Various (Hetero)aromatic Nitriles



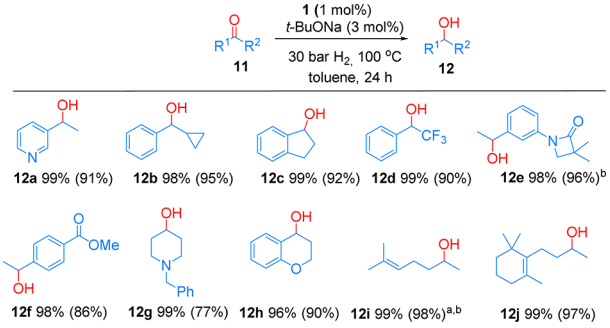
[a]Isolated yield. Reaction conditions: substrate (0.5 mmol), **1** (0.015 mmol), *t*-BuONa (0.05 mmol), toluene (1 mL), 24 h, 120 °C, 50 bar H_2. Conversion (>99%) and yield were determined by GC analysis using hexadecane as an internal standard.

Scheme 3. Catalytic Hydrogenation of Aliphatic Nitriles and Dinitriles



[a]GC yield. [b]25% corresponding saturated amine. Reaction conditions: substrate (0.5 mmol), **1** (0.015 mmol), *t*-BuONa (0.05 mmol), toluene (1 mL), 24–60 h, 100–120 °C, 50 bar H_2. Isolated as a HCl salt. Conversion (>99%) was determined by GC analysis using hexadecane as an internal standard.

Scheme 4. Mn-Catalyzed Hydrogenation of Ketones



[a]GC yield. [b]48 h. Reaction conditions: substrate (1 mmol), **1** (0.01 mmol), *t*-BuONa (0.03 mmol), toluene (1 mL), 24–48 h, 100 °C, 30 bar H_2. Conversion was determined by GC (isolated yield in parentheses).

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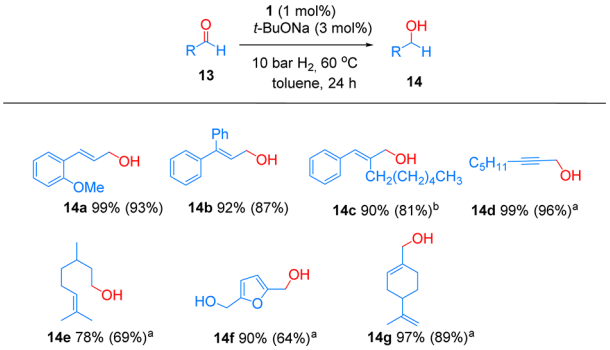
Scheme 5. Selective Hydrogenation of Aldehydes



[a]100 °C, 30 bar H_2. [b]3% saturated alcohol observed. Reaction conditions: substrate (1 mmol), **1** (0.01 mmol), *t*-BuONa (0.03 mmol), toluene (1 mL), 24 h, 60 °C, 10 bar H_2. Conversion was determined by GC (isolated yield in parentheses).

These substrates are also applied on larger scale as monomers for polymers (HMF) or intermediates in the flavor and fragrance industry. Unfortunately, the isolation of the bisbenzylic alcohol **14f** was difficult because some decomposition occurred during separation and isolation.

Mechanistic Investigations. To gain insight into the nature of the catalytic active manganese species, NMR investigations were carried out using complex **1** in the presence of *t*-BuONa in toluene-d_8 under 5 bar H_2 at room temperature. After 1 h, a red-orange solution formed which clearly exhibited a hydride triplet signal at −5.67 ppm in the ^{1}H NMR spectrum Figure 4c. Additionally, IR (toluene) measurements showed full

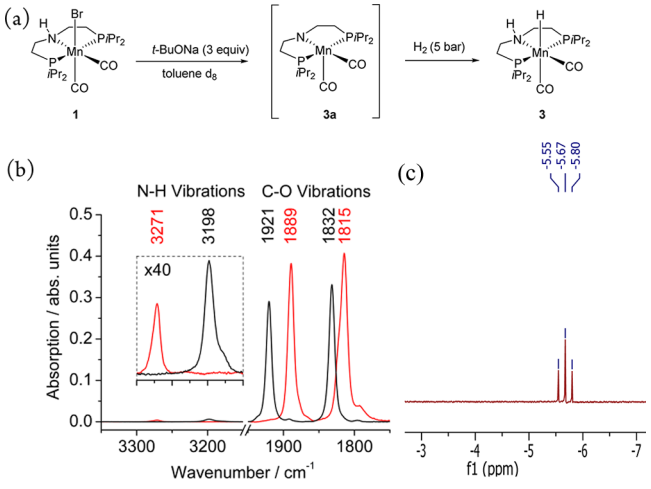
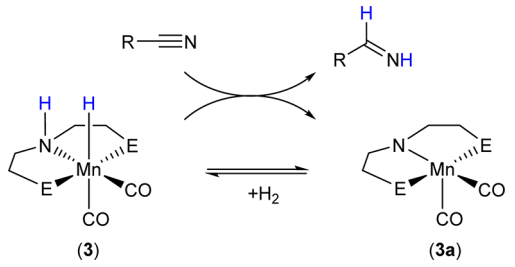


Figure 4. (a) Formation of the manganese hydride complex. (b) IR spectra and frequencies (cm^{-1}) of complex **1** (black) and in situ-generated complex **3** (red) recorded in toluene at 25 °C. Inset: 40× magnification of the N−H signals. (c) ^{1}H NMR (toluene-d_8) spectrum of complex **3** (hydride region).

conversion of **1** into **3** and an unchanged coordination of the pincer ligand and the two CO ligands (Figure 4b). As compared to the bromide ligand, the hydride ligand is much better σ donor, which explains the higher electron density at the manganese center. As a consequence, the N−H frequency rises (3198 →3271 cm^{-1}) and the C−O frequencies fall (symmetric, 1921 → 1889 cm^{-1}; asymmetric, 1832 →1815 cm^{-1}), due to the increased back donation from the manganese to the π-anti-bonding orbitals on the carbonyl ligand. These shifts are in good agreement with DFT frequency calculations (Figure SI 29). The presence and position of the hydride ligand are confirmed by using D_2 for the in situ generation of the deuterated analogue (**3b**) of **3**. Deuteration affects the resonance interaction between the stretching vibrations of the Mn−H and the opposite C−O bond. Thereby, the signal of the asymmetric C−O vibration is shifted to lower frequencies (1815 →1810 cm^{-1}). This effect is also confirmed by DFT calculations (Figure SI 30).

To illustrate the catalytic activity of complex **3**, further DFT calculations were performed on the hydrogenation of acetonitrile, and all computational details are given in the Supporting Information. In agreement with a previous study using an iron-based catalyst,[10c] we propose an outer-sphere mechanism involving a simultaneous transfer of the hydride from the Mn center (Mn−H) and the proton from the nitrogen (N−H) to the nitrile to give the corresponding imine (Scheme 6). The catalyst should then be regenerated by addition of

Scheme 6. Proposed Outer-Sphere Mechanism for Nitrile Hydrogenation [E = P(isopropyl)$_2$]



molecular hydrogen. The formed imine can undergo a second reaction cycle and is finally reduced to the corresponding amine.

To show the reversibility between the hydride **3** and amido complex **3a**, we computed the energetic parameters, including the barrier and reaction energy for the concerted H_2 elimination. For the Mn complex **3**, the computed Gibbs free energy barrier for H_2 elimination is 20.2 kcal/mol. In general, the reaction is slightly exergonic by 0.2 kcal/mol. Hence, a well-balanced equilibrium can be established under a H_2 atmosphere. For the regeneration of catalyst **3** via addition of H_2, the barrier is 20.4 kcal/mol. Interestingly, we found that the dissociation of the equatorial CO ligand is endergonic by 41.0 kcal/mol, indicating the stability of this CO coordination. This agrees well with the experimental results: spectroscopic studies of the reaction mixture, vide supra, proved the CO ligands to be still intact. Comparing the hydrogenation of acetonitrile (CH_3−CN) and benzonitrile (Ph−CN) using Mn complex **3** gave similar results, but the computed Gibbs free energy barrier is slightly higher (20.9 vs 17.8 kcal/mol, respectively). In contrast to nitrile hydrogenation via a concerted transfer of the N−H proton and Mn−H hydride (Figure 5), we found a stepwise mechanism for the hydrogenation of benzaldehyde: first, a transition state for Mn−H transfer to the carbon atom of the C═O group for the breaking of the Mn−H bond and the formation of the C−H bond, followed by an intermediate, and second, N−H proton transfer for the breaking of the N−H bond and the formation of the O−H bond. Relative to the starting materials (**3** + PhCHO), the free energy barrier of Mn−H hydride transfer is 15.64 kcal/mol, the intermediate is endergonic by 13.26 kcal/mol, and the N−H proton transfer

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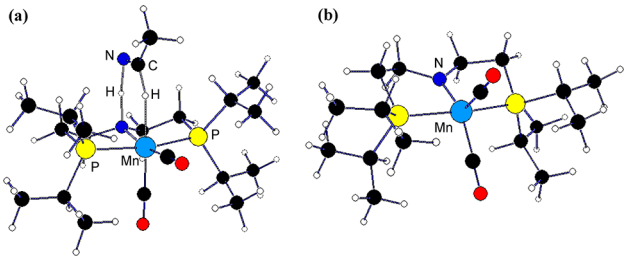

Figure 5. Catalytic intermediates: (a) transition state of the transfer of the protic hydrogen to the nitrile-nitrogen and hydride coordination to the corresponding carbon, and (b) amido complex **3a**.

has a free energy barrier of 11.94 kcal/mol. The overall reaction is exergonic by 3.5 kcal/mol. These results show that the potential energy surface for proton transfer is very flat. It is interesting to note that Jones et al.[11i] also reported a similar stepwise reaction mechanism for the hydrogenation of styrene by using the iron pincer complex, and this is also in contrast with the concerted mechanism for the hydrogenation of aldehyde by using the same catalyst.[24]

Finally, to evaluate the homogeneity of our catalytic system, poisoning experiments were performed in the presence of varying amounts of PMe_3, PPh_3, and Hg.[25] In all the cases, no significant effects on the hydrogenation of benzonitrile were observed (see SI, section X). The constant activity in the presence of PMe_3 or Hg can be explained by an outer-sphere hydrogenation mechanism of a molecular-defined catalyst species. The observed similar reduction rates in the presence of Hg indicate the homogeneous nature of the catalyst.

SUMMARY

In conclusion, we have shown for the first time that specific manganese pincer complexes constitute versatile reduction catalysts.[26] Contrary to traditional beliefs, molecular-defined manganese−amide centers permit the practical activation of molecular hydrogen. The developed precatalyst **1** is air-stable, easy to synthesize, and simple to activate by base and H_2. This catalytic system allows for the efficient and selective reduction of various polar functional groups, including aromatic and aliphatic nitriles as well as ketones and aldehydes.

EXPERIMENTAL SECTION

General Procedure for the Hydrogenation of Nitriles. Under an argon atmosphere, a vial was charged with **1** (0.015 mmol), *t*-BuONa (0.05 mmol), and 1 mL of dry toluene in that order. The orange-red solution was stirred briefly before the nitrile (0.5 mmol) was added. The capped vials were placed in the alloy plate, which was then transferred into the autoclave. Once sealed, the autoclave was purged three times with hydrogen and then pressurized to 50 bar, heated, and kept at 120 °C for 24 or 36 h under thorough stirring. After the reaction time, the autoclave was cooled to room temperature and depressurized, and the reaction mixture was analyzed by GC. The amine product was isolated as its HCl salt.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03709.

Additional experimental results, complex synthesis, optimization of reaction conditions, spectroscopic data, DFT calculations, and NMR spectra for isolated products (PDF)

X-ray crystallographic data for **1** (CIF)

X-ray crystallographic data for **2** (CIF)

X-ray crystallographic data for **4** (CIF)

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Notes

The authors declare no competing financial interest.

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(22) CCDC 1436386−1436388 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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(26) To rule out that impurities in the manganese could be catalyzing the reaction, we bought $Mn(CO)_5Br$ from different vendors (Alfa and Strem) and used these sources for the preparation of complex **1**. When the catalytic hydrogenation of benzonitrile was performed in the presence of complex **1** from different vendors, no significant difference in the yield of benzylamine was observed (Alfa = 91% and Strem = 95%). We thank a reviewer for pointing out this experiment to us.

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