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Manganese Catalyzed Hydrogenation of Azo (N=N) Bonds to Amines

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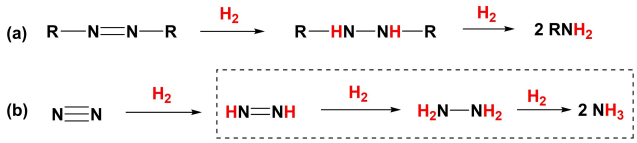
Abstract: We report the first example of homogeneously catalyzed hydrogenation of the N=N bond of azo compounds using a complex of an earth-abundant-metal. The hydrogenation reaction is catalyzed by a manganese pincer complex, proceeds under mild conditions, and yields amines, which makes this methodology a sustainable alternative route for the conversion of azo compounds. A plausible mechanism involving metal-ligand cooperation and hydrazine intermediacy is proposed based on mechanistic studies.

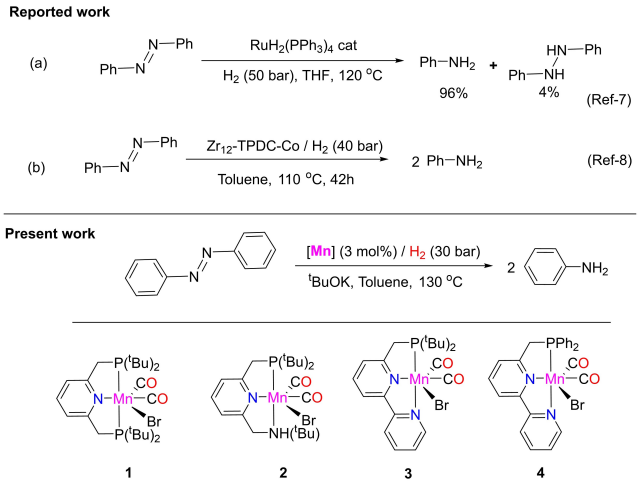
Keywords: Manganese; Catalytic hydrogenation; Azo (N=N) bond; Amines; Ligand metal cooperation

Transition metal catalyzed hydrogenation of unsaturated bonds is one of the most fundamental transformations in organic synthesis.[1] In the literature, a wide range of hydrogenation reactions have focused on the catalytic hydrogenation of polar multiple bonds such as C=O, C=N, nitriles etc.[2] On the other hand, reports of catalytic hydrogenation of nonpolar multiple bonds are mainly limited to C–C multiple bonds.[3] Hydrogenative cleavage of N=N multiple bonds are crucial steps in the degradation of azo dyes. The incomplete hydrogenation of azo compounds forms hydrazo intermediates. Hydrogenation of azo compounds up to the corresponding amines is challenging, and is relevant to the direct ammonia synthesis from molecular nitrogen, in which hydrogenation of hydrazine is a key step (Scheme 1).[4] The catalytic hydrogenation of azo compounds to the corresponding amine(s) is a useful transformation since amines are essential intermediates for pharmaceuticals, and agricultural chemicals.[5] Moreover the azo compound hydrogenation procedure is a sustainable alternative to the dye degradation process to avoid water pollution by textile industries.[6a] Although heterogeneous and bio-catalyzed transformation of azo compounds to amines are reported,[6] most of them involve very harsh reaction conditions resulting in a need to develop alternative sustainable methods for the hydrogenation of azo compounds to amines.

There are few reports of catalytic hydrogenation of azo compounds under hydrogen pressure either in the presence of supported catalysts or in homogeneous phase. In 2005, Frediani and coworkers reported a ruthenium catalyzed hydrogenation of azobenzene under hydrogen pressure (Scheme 2, a).[7] Lin group reported hydrogenation of azobenzene and hydrazobenzene to aniline using hydrogen pressure by a heterogeneous process using a supported cobalt catalyst (Scheme 2, b).[8] Very recently (during preparation



Scheme 1. Conversion of unsaturated N–N bonds to amines via hydrogenation of hydrazine intermediacy.



Scheme 2. Reported catalytic hydrogenation of azo compounds (above) and the manganese complexes (1-4) employed in this study (present work).

of this manuscript), another heterogeneous procedure for the catalytic hydrogenation of azobenzene using Mo_3S_4 clusters has been reported.[9] Cleavage of azo derivatives into the corresponding amine(s) via transfer hydrogenation or using hydrogen donors were reported but both these reports also need stoichiometric additives.[10] Most of the literature reports on conversion of azo compounds to amines are based on the reduction of azobenzene or hydrazobenzene as an intermediate of nitro compounds reduction reaction.[9,10a,11] Despite all those reports, a straightforward, green, waste-free, cost-effective homogeneous catalytic system is challenging.

In recent years there has been much interest in the development of catalysts based on earth-abundant-metals for a variety of (de)hydrogenation reactions.[12] We and others have reported on pincer catalysts based on earth-abundant-metals for the catalytic hydrogenation of several carbonyl compounds such as aldehydes, ketones, imides, esters, amides, carbamates and ureas.[13] Despite such strong interest in using earth-abundant-metal complexes for hydrogenation reactions, catalytic hydrogenation of azo compounds to amines using an earth-abundant-metal complex is still unknown. We report here the hydrogenation of azo compounds to amines catalyzed by a pincer complex of the earth-abundant manganese.

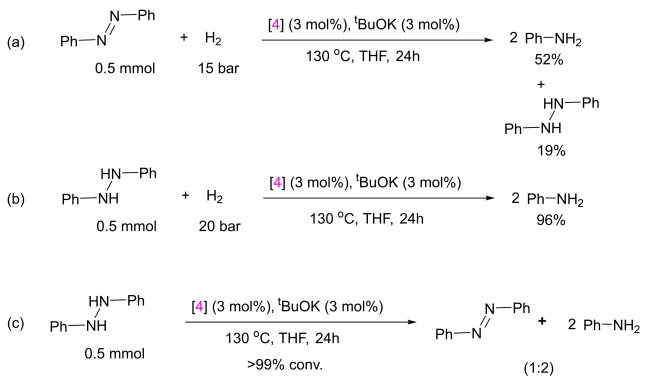
We started our investigation by studying the catalytic hydrogenation of azobenzene employing manganese pincer complexes (**1-4**, Scheme 2) developed in our group for various (de)hydrogenation reactions. Employing the Mn-PNP complex **1** (3 mol%), which is the first manganese complex reported for catalytic (de)hydrogenation reactions,[14] did not result in any conversion of azobenzene under 30 bar of H_2 at 110 °C for 24 h (Table 1, entry 1). Complex **2** was reported by us as the first complex of earth-abundant-metal for the dehydrogenative synthesis of cyclic imides as well as for the hydrogenation of esters and organic carbonates.[13f,15] Interestingly, complex **2** catalyzed the hydrogenation of azobenzene under the conditions described above in 35% conversion forming aniline in 27% yield as detected by GC-MS (Table 1, entry 2). At longer reaction time (36 h) and higher temperature (120 °C), the azobenzene conversion increased to 60% and aniline was detected in 52% yield. Using the Mn-PNN-bipyridyl complex **3** (3 mol%), previously reported to catalyze the dehydrogenative synthesis of hydrazones,[16] only 15% conversion of the azobenzene was obtained (entry 4). We have recently reported complex **4**, bearing PPh_2 groups is a very active catalyst for the hydrogenation of urea and carbamate derivatives.[17] Interestingly, performing the catalytic hydrogenation reaction using complex **4** (3 mol%) and ^{t}BuOK (3 mol%) resulted after 24 h in 65% conversion of azobenzene and aniline was detected in 56% yield (Table 1, entry 5). After 36 h, in THF, 74% conversion of the azobenzene was obtained to form aniline in 68% yield. Moreover, 93% conversion of the azobenzene was obtained using 3 mol% of complex **4** at 30 bar pressure upon increasing the reaction temperature (130 °C) and time (48 h), forming aniline in 87% isolated yield (entry 7). Changing the H_2 pressure to 15 bar resulted in a lower conversion (74%) and lower yield of aniline (52%) with 1,2-diphenylhydrazine as a minor product (entry 8, Scheme 3a).

Following the successful hydrogenation of azobenzene, we attempted to utilize the manganese complex **4** for the catalytic hydrogenation of azobenzene deriva-

Table 1. Manganese catalyzed hydrogenation of azobenzene to aniline.[a]

entry	[Mn]	solvent	Temp (°C).	T (h)	conv. (%)	Aniline (%)
1	**1**	Toluene	110	24	–	–
2	**2**	Toluene	110	24	35	27
3	**2**	Toluene	120	36	60	52
4	**3**	Toluene	120	24	15	–
5	**4**	Toluene	120	24	65	56[b]
6	**4**	THF	120	36	74	68
7	**4**	THF	130	48	93	87[c]
8[d]	**4**	THF	130	48	74	52[b]

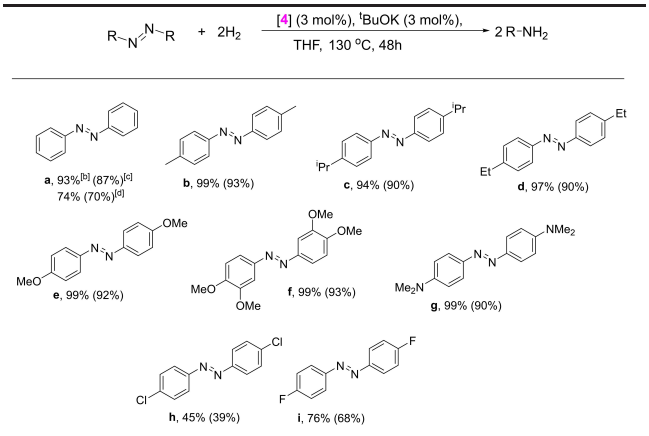
Reaction conditions: [a] Azobenzene (1 mmol), Mn-cat (0.03 mmol), ^{t}BuOK (0.03 mmol), 2 mL solvent, 30 bar H_2.
[b] The rest of product was 1,2-Diphenylhydrazine.
[c] Isolated yield.
[d] 15 bar pressure was used. All yields and conversions are calculated using GC-MS and ^{1}H NMR with mesitylene as internal standard.



Scheme 3. Manganese catalyzed hydrogenation of 1,2-diphenylhydrazine.

tives, the nonpolar symmetrical N=N bonds. Remarkably, using complex **4** (3 mol%) in the presence of ^{t}BuOK (3 mol%) under H_2 (30 bar) at 130 °C for 48 h in THF, a variety of azo derivatives were hydrogenated to corresponding aniline derivatives (Table 2). Azobenzene derivatives with electron donating groups (entries a-g) afforded better yields of corresponding amines than those bearing electron withdrawing groups (entries h-i). Azobenzene derivatives, like p-bromo, p-iodo, p-CF_3 and p-nitro azobenzene did not give any amines after hydrogenation. Interestingly 3.3'-azopyridine gave hydrazo compound as major product after hydrogenation but no aminopyridine. Unsymmetrical azo derivatives, bearing two different aromatic groups, also undergo hydrogenation under these catalytic conditions to produce corresponding amines (Table 3, entries j-o). Unfortunately using this catalytic system, we were unable to hydrogenate aliphatic azo compounds such as 1,2-di-tert-butyldiazene and 1,2 dicyclohexyldiazene, which remain unreacted. This maybe due to the higher electron density on the azo group in case of aliphatic azo compounds, which results in an unfavorable Mn–H hydride transfer step to the azo group.

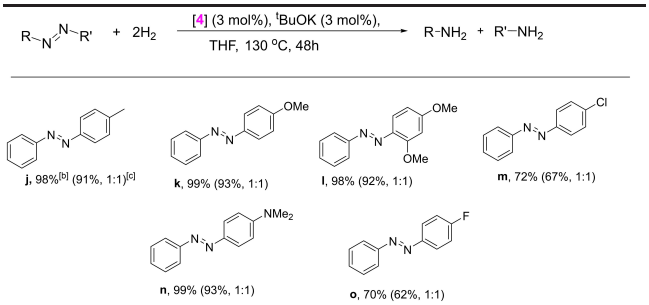
Table 2. Manganese catalyzed hydrogenation of symmetrical azobenzene derivatives.[a]



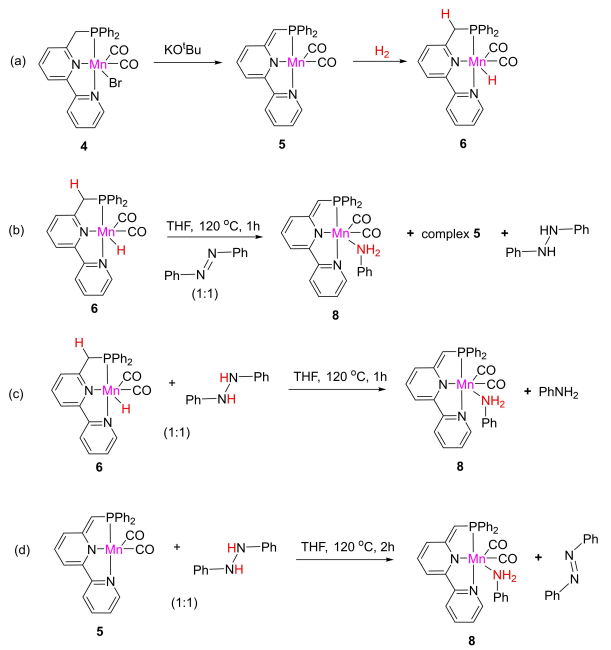
[a] Reaction conditions: Complex **4** (0.03 mmol), ^{t}BuOK (0.03 mmol), azobenzene derivatives (1 mmol), H_2 (30 bar), THF (2 mL), 130 °C (bath temperature), reaction time: 48 h.
[b] Conversions were determined by GC-MS and/or ^{1}H NMR spectroscopy using mesitylene as an internal standard.
[c] All isolated yields were in brackets.
[d] Complex **5** was used as catalyst without any base.

We have recently reported that complex **4** in presence of ^{t}BuOK undergoes deprotonation to form the dearomatized complex **5**[17] that reacts with hydrogen to form the manganese hydride complex **6** (Scheme 4a). Performing the catalytic hydrogenation under the conditions described in Table 2 using complex **5** as catalyst without adding base resulted in 74% conversion of azobenzene and 70% of aniline was detected after 48 h (Table 2 entry a, second row). A similar result was obtained when azobenzene was hydrogenated using complex **6** in absence of added base under the conditions described in Table 2. These experiments suggest that complexes **5** and **6** are involved in the catalytic cycle. To get further insight into the reaction mechanisms we performed a reaction

Table 3. Manganese catalyzed hydrogenation of unsymmetrical azobenzene derivatives.[a]



[a] Reaction condition: Complex **4** (0.03 mmol), ^{t}BuOK (0.03 mmol), azo derivative (1 mmol), H_2 (30 bar), THF (2 mL), 130 °C (bath temperature), reaction time: 48 h.
[b] Conversion of azo derivatives were determined by GC–MS using mesitylene as an internal standard.
[c] All isolated yields were in brackets.



Scheme 4. Mechanistic reactions.

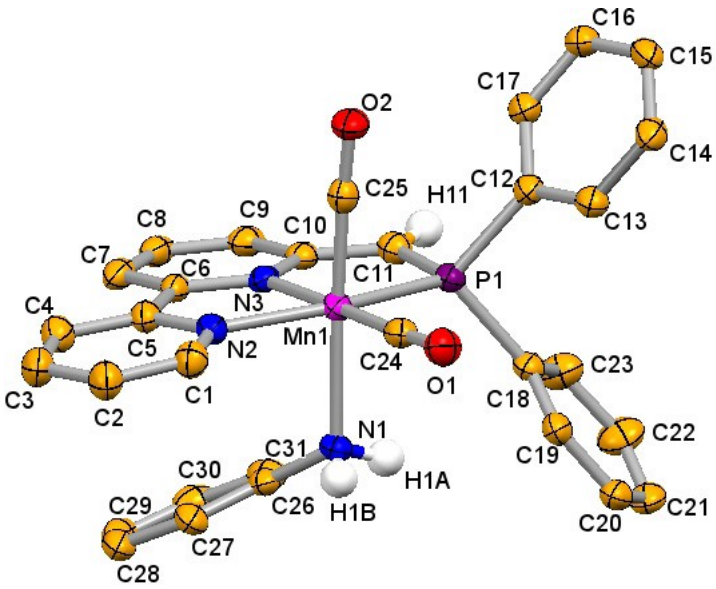
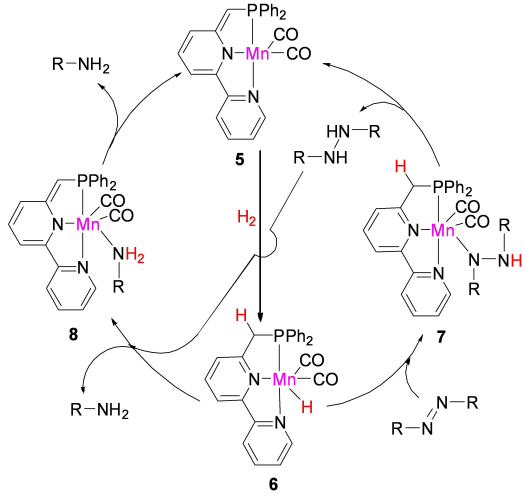


Figure 1. Molecular structure of Mn(^{Ph}PNN*)(CO)$_2$(PhNH$_2$) (**8**) complex (CCDC-2051750). Thermal ellipsoids are drawn at 50% probability level. Selected hydrogens are omitted for clarity.

of complex **6** with 1.1 equimolar amount of azobenzene at room temperature. ^{31}P NMR spectroscopy in THF showed no conversion of complex **6** but heating the mixture at 120 °C resulted in almost complete consumption of complex **6** and formation of a new manganese complex **8** (71 ppm), complex **5** and 1,2-diphenylhydrazine was detected by GC-MS (Scheme 4b). A separate reaction between complex **6** and 1,2-diphenylhydrazine also produced complex **8** at 120 °C and aniline (Scheme 4c). Complex **8** was also obtained from the reaction between complex **5** and 1,2-diphenylhydrazine at 120 °C after 2 h of reaction time with azobenzene as organic product (Scheme 4d).

Complex **8** was isolated from a reaction of complex **5** and aniline (1:1.5) at room temperature. Single crystals of complex **8** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of THF at −30 °C. The aniline complex **8** was also characterized by IR, NMR, and single crystallography (see SI). Crystal stucture of complex **8** showed a neutral octahedral manganese complex bearing a dearomatized ^{Ph}PNN pincer ligand (C10–C11 = 1.401(6) Å), two mutually cis CO ligands (C–Mn–C = 86.04°) and an axial aniline ligand (Figure 1, see SI).

Considering our experimental findings in manganese catalyzed hydrogenation of urea and carbamate derivatives[17a] and previous reports on ruthenium catalyzed hydrogenation of azobenzene[7] we propose a catalytic cycle as depicted in Scheme 5. Reaction of the pre-catalyst **4** with the base generates the dearomatized complex **5**, which forms the hydride complex **6**



Scheme 5. Proposed mechanism for the manganese catalyzed hydrogenation of azobenzene.

under hydrogen pressure. In presence of azobenzene, complex **6** converts to complex **7**. Complex **7** converts to complex **5** by releasing 1,2-diphenylhydrazine involving metal ligand cooperation (MLC). In the presence of 1,2-diphenylhydrazine complex **6** converts to complex **8** releasing one mole of aniline. Complex **8** regenerates complex **5** after releasing another aniline molecule to complete the catalytic cycle.

In conclusion, the homogeneous hydrogenation of N=N bond is made possible using, for the first time, a catalyst based on an earth-abundant-metal, the man-

ganese complex **4**. Our mechanistic investigations suggest that the hydrogenation reaction proceeds via metal-ligand cooperativity involving N=N and NH-NH bond hydrogenation of the azo derivatives by a manganese hydride complex intermediate. Interestingly the dearomatized complex **5** catalyzes the same reaction without any added base. Overall, this methodology presents a green route for the hydrogenation of the non-polar N=N bond using a complex of a metal that is relatively cheap and abundant.

Experimental Section

General procedure for the catalytic hydrogenation of azobenzene derivatives (Table 2 and 3**)**: In a N_2 glove box, 16 mg (0.03 mmol) of complex **4** and 3.5 mg (0.03 mmol) of ^{t}BuOK in 2 mL of THF were added to a 20 mL vial. To this suspension, 1 mmol of the azo compound and mesitylene (1 mmol, 120 mg, internal standard) were added and placed in a 25 mL steel autoclave fitted with a Teflon sleeve. The autoclave was pressurized with H_2 (30 bar, amount of hydrogen gas was approximately 30 mmol) and heated at 130 °C for 48 h, after which the steel autoclave was cooled in an ice-bath for 30 min and the H_2 was vented off carefully. The cold solution was then filtered through Celite, and the solution was analyzed by GC-MS. The conversion of azo compounds and the yields of amines and alcohols were determined by GC-MS with respect to the internal standard (mesitylene). Isolation of products were done by column chromatography.

The X-ray crystal structure: The X-ray crystallographic coordinates for the structure reported (complex **8**) in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number 2051750. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/data_request/cif

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