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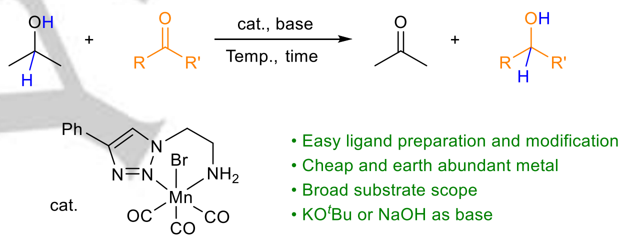
Aminotriazole Mn(I) Complexes as Effective Catalysts for Transfer Hydrogenation of Ketones

Oriol Martínez-Ferraté,[a], [b] Christophe Werlé,[a] Giancarlo Franciò,[b] and Walter Leitner*[a], [b]

Abstract: A catalytic system based on complexes comprising abundant and cheap manganese together readily available aminotriazole ligands is reported. The new Mn(I) complexes are catalytically competent in transfer hydrogenation of ketones with 2-propanol as hydrogen source. The reaction proceeds under mild conditions at 80 °C for 20 h with 3% of catalyst loadings using either KO^{t}Bu or NaOH as base. Good to excellent yields were obtained for a wide substrate scope with broad functional group tolerance. The observed effects of substitution pattern in the ligand are consistent with an out-sphere mechanism for the H-transfer.

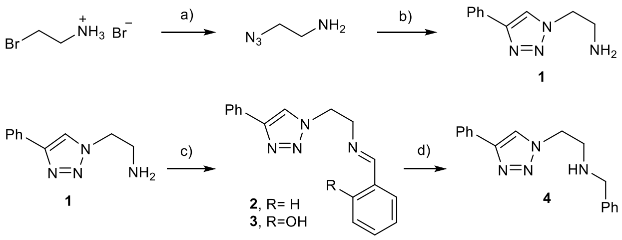
The concept of *Green Chemistry* has stimulated numerous new research directions in the chemical sciences.[1] Homogeneous catalysis can impact directly on several of its twelve principles and thus plays a major role in the development of more sustainable chemical processes. Traditionally, homogeneous catalysts are often based on transition metals from the platinum group, which are comparably rare elements, whose mining generates large amounts of waste, and is often associated with high costs.[2] Over the last two decades, first row metals emerged as potentially greener alternatives exhibiting catalytic activity for a wide range of chemical transformations (*i.e.* reductions, oxidations, or C–C bond formation).[3] Despite its high abundancy, non-toxicity, and its biocompatibility, the application of manganese catalytically active metal is still limited, even when compared to other third-row metals such as iron or cobalt.[4]

In 2016, the groups of Milstein and Beller independently reported on the use of Mn(I) complexes in transformations typically associated with noble metals. They respectively showed the aptitude of Mn(I) to catalyze the dehydrogenative condensation of alcohols and amines to imines[5] and that Mn complexes are catalytically competent in hydrogenation reactions.[6] Since then, manganese (I) complexes have been applied in indirect reduction of carbon dioxide,[7] N alkylation with alcohols,[8] hydrogenation reactions (nitriles, esters, amides, and carbonyls),[9] transfer hydrogenation,[10] among others.[11] In most of the cases, manganese is coordinated to a pincer ligand with nitrogen and/or phosphorus as donors.[12] Interestingly, the transfer hydrogenation reaction can be carried out also with bidentate nitrogen ligands.[13] The use of picolylamine as ligand resulted in a highly active catalyst that performs comparably to well-known Ruthenium-based systems (Scheme 1).[13b,14] Based on this literature precedence, we envisaged triazole derivatives as attractive alternative N-donor units to pyridine compounds to be used as bidentate ligands for Mn-catalysis.[15] The synthesis of triazoles takes advantage of the modularity of Cu-catalyzed azide-alkyne cycloaddition (click chemistry), an extremely powerful synthetic tool when it comes to generate molecular complexity.[16] Thus, a range of structurally different ligand frameworks becomes accessible *via* a robust atom- and step-economic synthetic method.[17]



Scheme 1. Advantages of aminotriazole Mn(I) complex as catalyst in transfer hydrogenation.

In this paper, we report the synthesis of new amino- and iminotriazole ligands from low-cost and readily available organic precursors as well as the preparation of corresponding manganese (I) complexes, and their application in the transfer hydrogenation of ketones. The best ligand/metal combination was found to effect reduction of a broad range of functionalized ketones under mild conditions in good to excellent yields using ^{i}PrOH as hydrogen donor and various bases including in particular KO^{t}Bu and NaOH as co-catalyst.



Scheme 2. Reagents and conditions: a) H_2O, 80 ºC, 16 h, quant.; b) phenylacetylene, $CuSO_4 \cdot 5H_2O$, MeOH:H_2O. r.t., 1 h, 71% c) aldehyde, $MgSO_4$, THF, 60 ºC, 16h, quant; d) $NaBH_4$, EtOH, 75 ºC, overnight, 95%.

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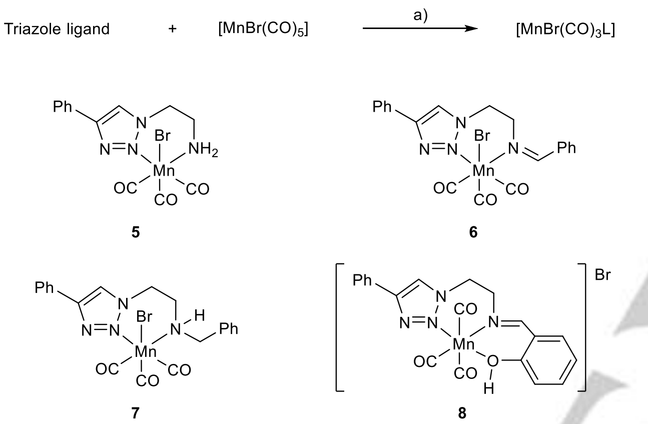
The different aminotriazole based ligand frameworks **1**–**4** were prepared as depicted in Scheme 2 following modified reported procedures in the individual steps. Triazole **1** was readily synthesized starting from commercially available 2-bromoethylamine hydrobromide. The first step involved the nucleophilic substitution of the bromide using sodium azide in water leading to the corresponding 2-azidoethylamine after basic work up. The resulting azide was then reacted with phenylacetylene in presence of catalytic amounts of copper sulfate in to give **1** in 71% overall yield

Triazoles **2**–**4** with various substitution patterns at the amino group were considered to investigate how the modification of the electronic properties (sp^3 *vs.* sp^2 nitrogen), steric hindrance (H *vs.* benzyl) and denticity of the ligand (bidentate *vs*. tridentate) would impact the catalytic efficiency of the complex. Triazoles **2** and **3** could be synthesized in quantitative yields by simple condensation of **1** with the corresponding aldehyde in THF at 60 ºC for 16 hours. The reduction of imine derivative **2** using sodium borohydride led to the secondary amine **4** in 95% yield.



Scheme 3. Synthesis of the Manganese (I) complexes. Reagents and conditions: a) toluene, 100 ºC, 16 h.

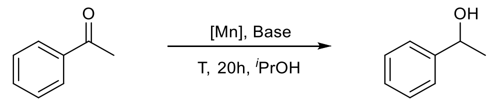
The coordination of the different triazoles to manganese was performed using bromopentacarbonylmanganes(I) as a precursor in dry toluene at 100 ºC for 16 hours (Scheme 3). Thereby, complexes **5**–**8** could be isolated with high yields ranging between 81% to 87%. Nuclear magnetic resonance spectroscopy confirmed the coordination of the ligand to the d^6 Mn(I) centers and high-resolution mass spectrometry confirmed the formation of neutral manganese complexes for **5**, **6**, and **7** with the bromide atom coordinated to the metal center. Complex **8** exhibits a cationic form due to displacement of the bromide by the phenolic side arm. Complexes **5**–**8** were found stable under atmospheric conditions in the solid state. However, once in solution they were found to decompose rapidly in the presence of oxygen.

The catalytic activity of the newly synthesized complexes was investigated in the transfer hydrogenation of ketones, a reaction with large synthetic utility on laboratory and industrial scale. Using acetophenone as benchmark substrate and complex **5** as representative catalyst the influence of key reaction parameters was investigated as summarized in Table 1. Reactions were carried out in ^{i}PrOH as solvent and hydrogen donor using KO^{t}Bu as base under standard conditions. The variation of the metal:base ratio (entries 1–4) showed that the presence of base is mandatory to reduce acetophenone to 1-phenylethanol. Only 6% of yield was obtained using an 1:1 ratio, whereas around 30% of yield could be obtained when using 1:2 and 1:4 ratios, (entries 3 and 4). Once the metal:base ratio was optimized, the catalyst loading was screened showing an almost linear relationship between catalyst loadings and yield (entries 3, 5 and 6). Optimal conditions were reached using 3 mol% of catalyst loadings leading to 90% of product. Upon decreasing the temperature (80→60 °C) yields dropped considerably (90→52%) (entry 7). Next, several bases, organic and inorganic were investigated as additives (entries 8–12). While NEt_3 was not effective, lithium bis(trimethylsilyl)amide (LiHMDS) and potassium acetate and resulted in moderate to good yields (55% and 72%, respectively. Interestingly, sodium hydroxide was found to perform almost as well as KO^{t}Bu with 89% yield, providing a cost-effective alternative for potential scale-up.

After optimization of the reaction conditions, the aptitude of the different manganese **5**-**8** complexes to undergo the desired reaction was investigated (entries 6, 13–15). Low yields (2%) were obtained when using catalyst **8**. This may reflect the presence of the phenol group in the coordination sphere of Mn. In the presence of base, it can be deprotonated forming a very stable chelating phenolate that prevents entry into the catalytic cycle. Interestingly, complexes **6** and **7** exhibit very different catalytic activities (entry 13 *vs*. 14). Only 15% of yield was obtained in presence of the imino moiety whereas yields up to 83% are observed for the complex bearing an amino moiety. These results strongly suggest an out-sphere mechanism where the proton of amino-ligand is directly involved in the reduction step.

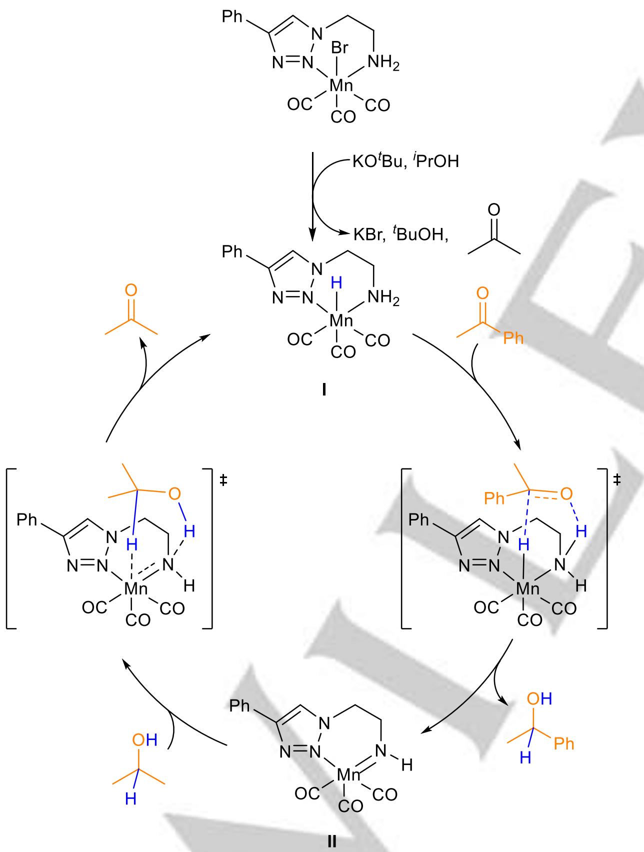
Taken together, the results summarized in Table 1 together with previous reports from the literature[10b] are consistent with a reaction mechanism as suggested in Scheme 4. First, the active manganese hydride **I** could be generated in presence of ^{i}PrOH and the base. Then, an outer-sphere mechanism can transfer the hydride from the Mn center and the H^+ from the NH unit (either concerted or step-wise) to the ketone, resulting in the reduction of the substrate and formation of **II**. The proton transfer may be assisted by the conjugated acid of the base additive, which might explain their influence on yield. Reaction of **II** with ^{i}PrOH under dehydrogenation to acetone can regenerate the active species **I**.

Table 1. Optimization of reaction condition for acetophenone transfer hydrogenation.



Entry	[Mn] (mol%)	Base (mol%)	T (°C)	Yield[a] (%)
1	**5** (1)	–	80	0
2	**5** (1)	KO^{t}Bu (1)	80	6
3	**5** (1)	KO^{t}Bu (2)	80	33
4	**5** (1)	KO^{t}Bu (4)	80	30
5	**5** (2)	KO^{t}Bu (4)	80	66
6	**5** (3)	KO^{t}Bu (6)	80	90
7	**5** (3)	KO^{t}Bu (6)	60	52
8	**5** (3)	AcOK (6)	80	72
9	**5** (3)	LiHMDS (6)	80	55
10	**5** (3)	Et_3N (6)	80	8
11	**5** (3)	K_3PO_4 (6)	80	44
12	**5** (3)	NaOH (6)	80	89
13	**6** (3)	KO^{t}Bu (6)	80	15
14	**7** (3)	KO^{t}Bu (6)	80	83
15	**8** (3)	KO^{t}Bu (6)	80	2

0.5 mmol acetophenone, 2 mL of ^{i}PrOH. [a] Quantified by ^{1}H NMR using mesitylene as an internal standard.



Scheme 4. Proposed mechanism for the transfer hydrogenation of ketones promoted by manganese aminotriazole complexes.

Having established complex **5** as the most effective catalyst for the benchmark ketone acetophenone, the substrate scope of Mn-aminotriazole transfer hydrogenation reaction was explored under the standard reaction conditions using KO^{t}Bu base co-catalyst.

Gratifyingly, catalyst **5** proved to be very versatile for the reduction of aromatic, aliphatic and cyclic ketones tolerating a broad range of functional groups (Table 2). Entry 2–3 show that even higher yields can be obtained in the presence of *ortho* substituents on the phenyl ring. *Ortho*-methoxy acetophenone was reduced with 92% yield (entry 2), and nearly quantitative yield of the alcohol was obtained with the electron withdrawing fluorine substitutent (entry 3). In contrast, 2-nitroacetophenone could be reduced in only 31% yield. This reflects mainly the low solubility of this compound in 2-propanol leading to a heterogeneous reaction mixture. *Para*-substituted acetophenone derivatives were also explored and similar trends were observed (entries 5–8). For instance, 99% yields were obtained in presence of *para*-methoxy or *para*-chloro groups, and the yield amounted still to 80% when a phenoxy group was present in *para*-position. Again, the analogous *p*-nitroacetophenone remained almost unreacted with only 19% of yield due to the same solubility reasons mentioned above (entry 8). Disubstituted 3,4-dimethoxiacetophenone was converted to the corresponding alcohol also in very good yield of 80% (entry 9). The phenolic substrate 3-hydroxy-4-methoxyacetophenone was not reduced under these reaction conditions again probably due to its low solubility (entry 10).

Excellent results were obtained with 1-acetonaphthone and 2-acetonaphthone with yields over 99% (entries 11–12) further demonstrating the good tolerance of catalyst **5** against steric hindrance for the aromatic ketones. Moderate yields were obtained when 2-acetylfuran was reduced (entry 13). Substituting the methyl group with different aliphatic chains resulted also in high reactivity of the ketones allowing quantitative reduction to the target alcohols (entries 14–15). Benzylidene acetone was hydrogenated at the C=C and C=O double bonds converting it to the saturated alcohol also in high yield (entry 17). In sharp contrast, the ketone functionality was reduced exclusively in furfuryl acetone, indicating again a different behavior of the heteroaromatic group (entry 16). Benzophenone derivatives were hydrogenated with good to excellent yields 78–99% (entries 18–20). Benzoin, however, remained almost unreduced giving low yields of the diol. This may be attributed to deactivation of the catalyst through a strong catalyst/substrate interaction, indicated by an instantaneous color change from yellow to purple upon benzoin addition. No well-defined species could be isolated or characterized.

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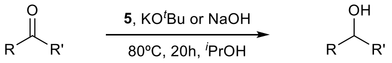
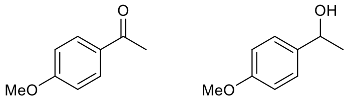
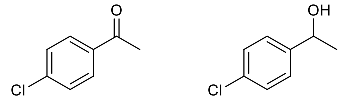
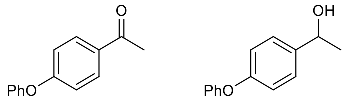
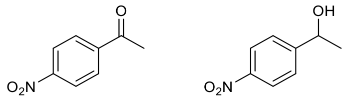
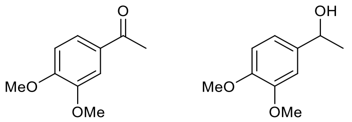
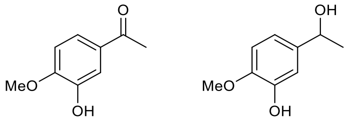
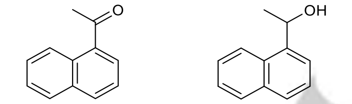
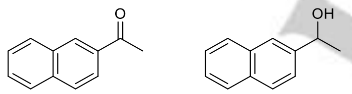
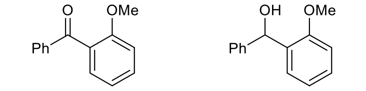
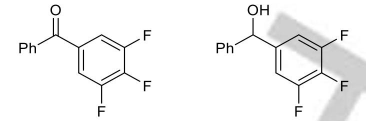
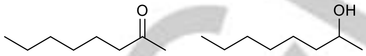
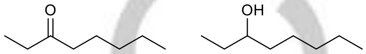
Table 2. Substrate scope in transfer hydrogenation of ketones catalyzed by Mn-complex **5**.



Entry	Substrate	Product	Yield (%)
1			90[a] 89[b]
2			92[a] 73[b]
3			98[a] 99[b]
4			31[a] 1[b]
5			99[a] 75[b]
6			99[a] 50[b]
7			80[a] 75[b]
8			19[a] 1[b]
9			78[a] 57[b]
10			2[a] 5[b]
11			96[a] 60[b]
12			91[a] 68[b]
13			65[a] 60[b]
14			99[a] 99[b]
15			99[a] 57[b]
16			85[a] 26[b]
17			88[a] 25[b]
18			92[a] 96[b]
19			78[a] 51[b]
20			99[a] 99[b]
21			6[a] 3[b]
22			68[a] 23[b]
23			63[a] 27[b]
24			66[a] 27[b]
25			0[a] 0[b]
26			75[a] 0[b]
27			47[a] 40[b]
28			76[a] 73[b]
29			74[a] 14[b]

0.5 mmol substrate, 3% mol of **5**, 6% mol base, 2 mL of ^{i}PrOH, 80ºC, 20h. Quantified by ^{1}H NMR using mesitylene as internal standard. [a] KO^{t}Bu as a base. [b] NaOH as a base.

For aliphatic ketones the yields were somewhat lower than for aromatic ketones. This is most obvious in the direct comparison of cyclohexyl methyl ketone (entry 26, 75%) yield with acetophenone *(*entry 1, 90% yield). 2-octanone and 3-octanone were reduced with comparable yields (68 *vs.* 63%), showing a negligible impact of the relative position of the ketone. More sterically demanding *tert*-butyl metylketone could be reduced also in 66% yield. However, the most crowded di-*tert*-butyl ketone showed no reaction (entry 25). Cyclopentenone was hydrogenated in moderate yield (entry 27, 47%) while six membered ring ketones reacted more smoothly (entry 28, 76% and entry 29, 74%).

For all substrates, the same protocol was applied substituting KO^{t}Bu with NaOH as co-catalysts. For a range of substrates, sodium hydroxide constitutes a potential alternative. In particular this is the case for acetophone (entry 1), *ortho*- (entries 2–3) and *para*- (entries 5, 7, 9) substituted phenyl rings, 2-acetylfuran (entry 13), propiophenone (entry 14), benzophenone derivatives (entries 18–20) and cyclic ketones (entries 27–28). Generally, however, KOtBu shows a broader application profile in particular including aliphatic ketones.

In conclusion, we have demonstrated that aminotriazole ligands are promising lead structures for the development of efficient manganese (I) catalyst for transfer hydrogenation of ketones. Good to excellent yields could be achieved for a large substrate scope spanning from aromatic ketones to aliphatic ketones in presence of different functional groups. *Iso*-propanol can be used as hydrogen donor together with different bases including even NaOH as co-catalyst in certain cases. The catalytic results obtained with a systematic series of ligands suggest an out-sphere hydrogen transfer involving the amino function as proton source. Further mechanistic studies are currently ongoing to elucidate the detailed catalytic cycle.

Experimental Section

General procedure for the catalytic transfer hydrogenation: Isopropanol (2 mL) was added to a mixture of complex **5** (6.1 mg, 0.015 mmol), considered ketone (0.5 mmol), base (0.003 mmol), and mesitylene (0.5 mmol, 70 μL). The reaction mixture was stirred at 80 °C for 20 h. After this time, the reaction was cooled to room temperature. A sample of 0.2 mL of the mixture was added to 0.6 mL of $CDCl_3$, filtered over celite, and ^{1}H-NMR was recorded to determine the yield using the peak of mesitylene as internal standard.

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Keywords: Catalysis • Manganese Complexes • Reduction of ketones • Transfer Hydrogenation • Triazole Ligands

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Layout 2:

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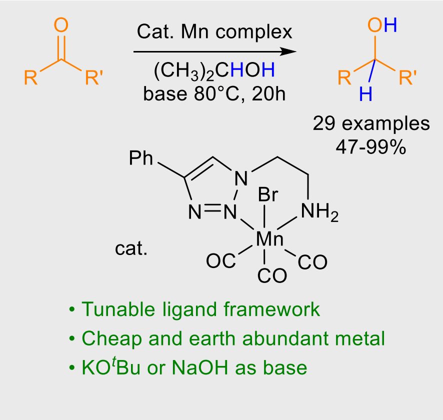

Manganese transfer: Aminotriazole structures are presented as readily accessible ligands for the synthesis of Mn(I) complexes. Three new ligands and four new Mn(I) complexes were prepared allowing to deduce favourable structural features for their use as catalysts in transfer hydrogenation of ketones. The catalyst shown is capable of reducing a broad scope of substrates with high functional group tolerance in high yields under mild conditions using either KO^{t}Bu or NaOH as base co-catalysts.

*Dr. Oriol Martínez-Ferraté, Dr. Christophe Werlé, Dr. Giancarlo Franciò, and Prof. Dr. Walter Leitner**

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