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N-Substituted Hydrazones by Manganese Catalyzed Coupling of Alcohols with Hydrazine; ‘Borrowing Hydrogen’ and Acceptorless Dehydrogenation in One System

*Uttam Kumar Das, Yehoshoa Ben-David, Yael Diskin-Posner, and David Milstein**

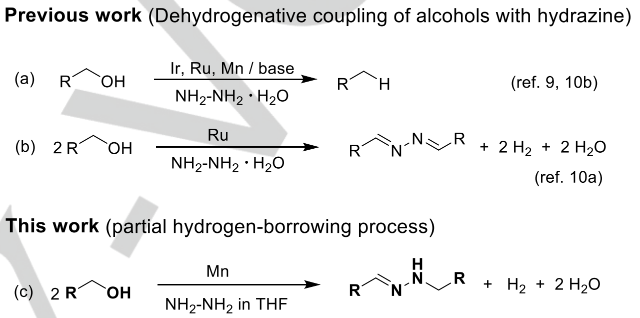
Abstract: An unprecedented one-step synthesis of N-substituted hydrazones by coupling of alcohols with hydrazine is reported. This “partial hydrogen borrowing” reaction is catalyzed by a new manganese pincer complex under mild reaction conditions, liberating water and dihydrogen as the only byproducts. Mechanistic insight, based on intermediate observation, is provided.

N-substituted hydrazones are constituents of several natural products,[1] such as Leucoagaricone,[2] Schaefferal A, Schaefferal B[3] and NG-061[4] were found in mushrooms and used as chromogens and enhancers of nerve growth. In addition, N-substituted hydrazones are important building blocks for the development of new antifungal,[5a] antimicrobial, anti-inflammatory[5b] and anticancer[5c, d] drugs for treatment of various diseases.[5]

In general, treatment of N-substituted hydrazines with aldehydes/ketones has been employed for the synthesis of N-substituted hydrazones.[6] Hydrogenation[7a] or reduction of azines in the presence of strong reducing agents in heterogeneous systems[7c] can be an alternative path to the –NH-N=CH- functionality, but selectivity is a major issue.[7] Interestingly, N-substituted hydrazones can be formed in modest yields by reaction of Grignard reagents with N_2O, although stoichiometric waste is generated.[8] Considering the important uses of this class of compounds in the pharmaceutical industry and in synthetic organic chemistry, effective catalytic waste-free procedures are desirable.

Dehydrogenative coupling of alcohols and hydrazine would be an alternative route to the synthesis of hydrazones. Although the direct use of N_2H_4 in catalysis is challenging, ruthenium and iridium catalyzed dehydrogenative coupling of alcohols with hydrazines (not leading to N-substituted hydrazones) are known (Scheme 1). In pioneering work, C. J. Li reported alcohol deoxygenation by Ru-catalyzed reaction of primary alcohols with hydrazine in presence of base (Scheme 1, a).[9] We reported dehydrogenative coupling of alcohols and hydrazine, and deoxygenation of alcohols, catalyzed by Ru-PNP[10a] and Mn-PNP[10b] pincer complexes, respectively (Scheme 1,a& b).

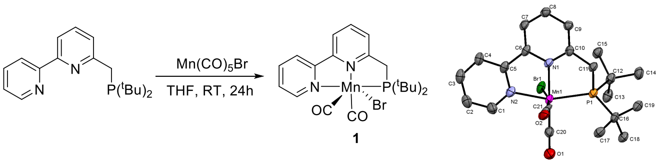
The application of earth-abundant base-metal complexes in homogeneous catalysis is of much current interest.[11] Manganese is the third most abundant metal on earth’s crust. We reported the dehydrogenative coupling of alcohols and amines to give imines, catalyzed by a pincer Mn-PNP^{tBu} complex.[12] Subsequently, several other reports on Mn catalyzed (de)hydrogenation reactions appeared.[13] Hydrogenation of multiple C-heteroatom bonds and esters using Mn pincer complexes was reported by several groups, including ours.[14] Recently, Beller reported C-alkylation of ketones,[15a] and N-methylation of amines[15b] catalyzed by Mn-PNP pincer complexes via ‘borrowing hydrogen’ strategy [16]. Substituted amine formation via ‘borrowing hydrogen’ is of much current interest.[17, 18]



Scheme 1. Reactions of alcohols with hydrazine.

To our knowledge, there is no report on dehydrogenative coupling of alcohols and hydrazine to form N-substituted hydrazones. Herein we report such a reaction, which produces N-substituted hydrazones under mild conditions. Moreover, this reaction is catalyzed by an earth abundant, new manganese pincer complex. Mechanistic insight is provided based on intermediate observation. In this reaction, both acceptorless dehydrogenative coupling of alcohols and a hydrogen borrowing process take place. We are not aware of other reports of a partial ‘hydrogen borrowing’ process.

Treatment of our previously reported ^{t}Bu-PNN ligand[19] with one equivalent of $Mn(CO)_5Br$ at room temperature in THF led to formation of the new complex Mn(^{t}Bu-PNN)$(CO)_2$Br(**1**) in 85% yield (Scheme 2). The two CO ligands of **1** give rise to bands at 1841 and 1916 cm^{-1} in the IR spectrum in a 1:1 ratio, indicating a nearly 90° C-Mn-C angle (87.5°). Single crystals of **1** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of THF at -30 °C. The structure of **1** exhibits an octahedral geometry with a meridional arrangement of the ^{t}Bu-PNN ligand. The CO ligands are orthogonal to each other, in line with the IR spectrum (Scheme 2, SI).



Scheme 2. Synthesis and molecular structure of Mn(^{t}Bu-PNN)$(CO)_2$Br (**1**) . Thermal ellipsoids are at 50% probability level. Hydrogen atoms are omitted for clarity. See Supporting Information (SI) for experimental details.

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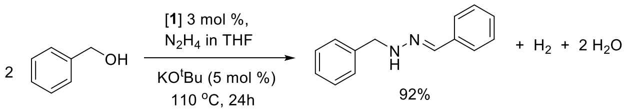


Scheme 3. Coupling of benzyl alcohol and hydrazine catalyzed by Mn(^{t}Bu-PNN)(CO)$_2$Br (**1**).

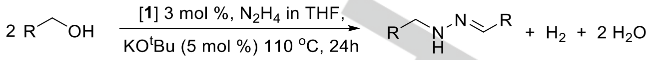
Complex **1** catalyzes in the presence of a catalytic amount of ^{t}BuOK the dehydrogenative coupling of alcohols and hydrazine to form N-substituted hydrazones with liberation of H_2 and water (Scheme 3). Thus, reaction of 0.5 mmol of benzyl alcohol, complex **1** (3 mol%) and ^{t}BuOK (5 mol%) in 1 mL of a 1M N_2H_4 solution in THF at 110°C in a closed vessel for 12 h resulted in formation of the N-substituted hydrazone (1-benzyl-2-benzylidenehydrazine) in 81% yield (Table 1, entry 1, first row). Performing the reaction in an open system under reflux, only 60% of the alcohol converted to the N-substituted hydrazone and toluene was formed as a side product after 24 h, whereas in a closed system for 24 h the product was obtained in 92% yield (Table 1, entry 1, second row). Analysis of the gas phase by GC indicated the formation of H_2. A small amount of toluene (3%) was also observed by GC-MS as a result of alcohol deoxygenation via a benzylidenehydrazine intermediate.[9, 10b]

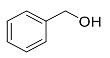
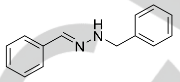
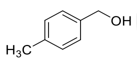
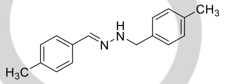
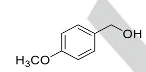
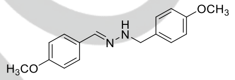
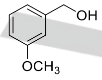
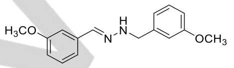
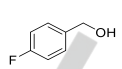
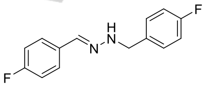
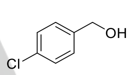
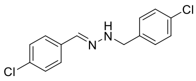
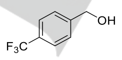
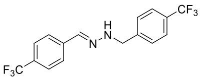
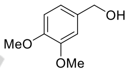
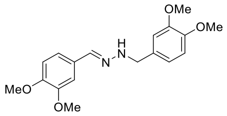
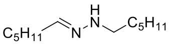
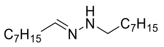
Next, the scope of this unprecedented catalytic reaction was probed with various aliphatic and aromatic alcohols. Reaction of hydrazine with 4-methylbenzyl alcohol for 24 h afforded the corresponding N-substituted hydrazone in 86% yield (Table 1, entry 2). Dehydrogenative coupling of 4-methoxybenzyl alcohol and 3-methoxybenzyl alcohol with hydrazine led to 90% and 81% yields of the corresponding hydrazones, respectively (Table 1, entries 3 and 4). The hydrazone product obtained by reaction of hydrazine with 4-methoxylbenzyl alcohol was structurally characterized by single crystal X-ray crystallography (see SI). Reaction of hydrazine with benzylic alcohols bearing electron withdrawing groups in the *para* positions (*p*-F, *p*-Cl, *p*-CF_3) afforded the corresponding products in good yields (Table 1, entries 5-7). The reaction also resulted in 79% yield of the corresponding N-substituted hydrazone by coupling of 3,4-dimethoxy benzyl alcohol and hydrazine (Table 1, entry 8).

The reaction is not limited to benzyl alcohols. Hydrazine reacts with 1-hexanol to yield 77% of 1-hexyl-2- hexylidenehydrazine (Table 1, entry 9). Similarly, 1-heptyl-2-heptylidenehydrazine was obtained in 65% yield of after 24 h reaction of hydrazine and 1-heptanol (Table 1, entry 10). The products were selectively formed as pure *E*-isomers, except for the aliphatic N-substituted hydrazones, which were formed as a 4:1 mixture of *E* and *Z* isomers (see SI). The N-substituted hydrazones are not very stable in air and convert slowly to azines by aerial oxidation.

To gain insight into the mechanism of this reaction, complex **1** was reacted with 1.1 equiv. ^{t}BuOK in pentane at room temperature, forming at -30 °C deep blue crystals of the dearomatized complex Mn(^{t}Bu-PNN*)(CO)$_2$ (**2**). The structure of **2** was confirmed by X-ray diffraction (Scheme 4, SI). Complex **2** exhibits a distorted trigonal bipyramidal geometry with two adjacent carbonyl groups (C21-Mn-C20 = 87.0°). The C1-C2 bond (1.368Å) is shorter by 0.112Å than C6-C7 (1.470Å) bond, clearly indicating a double bond character.

Table 1. Acceptorless coupling of alcohols and hydrazine catalyzed by **1**.[a]



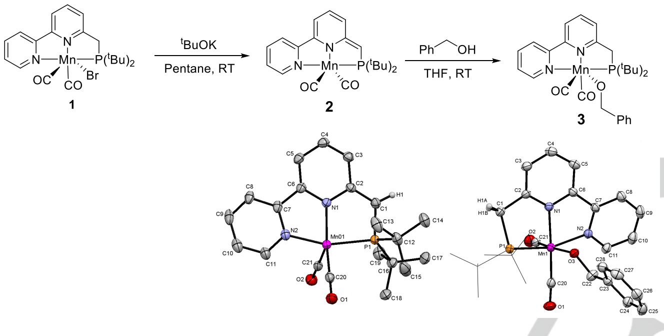
Entry	Alcohol	Product	Conv.(%)[b] (t)	Yield (%)[c]
1			84(12h) 99(24h) 90(24h)	81[d] 92 73[e]
2			99(24h)	86
3			99(24h)	90
4			95(24h)	81
5			99(24h)	81
6			97(24h)	85
7			85(24h)	74
8			88(24h)	79
9	1-hexanol		99(36h)	77
10	1-octanol		90(36h)	65

[a]Conditions: alcohol (0.5 mmol), N_2H_4 1M in THF (1 mL), **1** (0.015 mmol) and KO^{t}Bu (0.025 mmol), heated at 110 °C in a closed vessel for the indicated time. [b]Conversion determined by GC or NMR analysis using toluene or m-xylene as internal standards. [c]Yields of isolated products. [d] Average yields of two consecutive runs after 12h. [e]Yield of reaction catalyzed by pure complex **2** (3 mol %, see below) in absence of any added base, determined by GC and ^{1}H NMR analysis using m-xylene as internal standard.

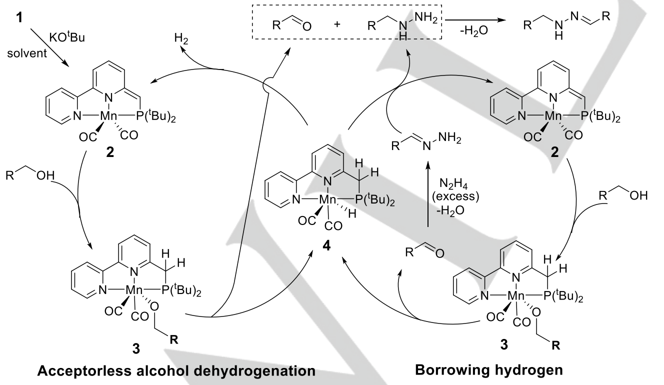
Employing the freshly prepared **2** (3 mol %) as a catalyst in the dehydrogenative coupling of benzyl alcohol and hydrazine at 110 °C resulted in the N-substituted hydrazone in 73% yield of after 24 h in absence of any added base (Table 1, entry 1, third row). However, complex **2** is somewhat unstable in solution (in absence of substrates) and slowly dissociates the ligand.

Significantly, treatment of **2** with benzyl alcohol (2.1 equiv.) in THF at room temperature resulted in instant formation of a new complex which exhibits in the ^{31}P{^{1}H} NMR spectrum one sharp signal at δ = 118 ppm, identified as the alkoxo complex **3** (Scheme

4). Complex **3** is formed by O-H activation via metal-ligand cooperation resulting in aromatization of the pincer ligand, in analogy to the previously reported formation of an alkoxy complex by reaction of a dearomatized PNP pincer Mn complex with benzyl alcohol.[12] The ^1H NMR spectrum of **3** in solution indicates the presence of a benzyl alcohol molecule H-bonded to the alkoxy ligand (see SI). Crystal stucture of **3** shows a neutral octahedral complex bearing a PNN pincer ligand, two mutually cis CO ligands and an alkoxy group (Scheme 4, see SI). Heating of **3** at 110 °C for 5h resulted in formation of the hydrido complex **4** (Scheme 5), which exhibits a Mn-H peak in the ^1H NMR spectrum at -2.3 ppm and a sharp $^{31}P\{^1H\}$ NMR signal at δ = 129 ppm. GC analysis showed quantitative formation of benzaldehyde after heating of **3**, in line with the mechanism shown in Scheme 5. It is possible that aldehyde formation from the coordinatively saturated **3** involves a non-classical alkoxide dissociation, assisted by the H-bonded alcohol molecule, followed by hydride elimination from the dissociated alkoxide, as invoked for other coordinatively saturated alkoxy complexes.[20]



Scheme 4. Synthesis of complexes **2** and **3** and their molecular structure. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms except for the vinylic C-H are omitted for clarity. See SI for experimental details.

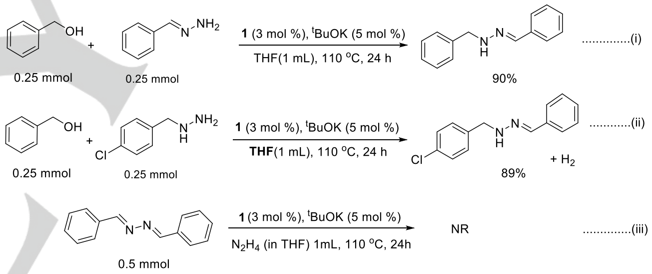


Scheme 5. Proposed mechanism.

In a separate reaction, treatment of complex **1** with an equimolar amount of $NaBHEt_3$ at RT resulted in formation of complex **4** as observed by ^1H and ^{31}P NMR spectroscopy (see SI). This *in-situ* formed hydrido complex also catalyzes the reaction between hydrazine and benzyl alcohol to form the desired product.

The catalytic cycle likely involves deprotonation of complex **1** by ^{t}BuOK to produce the active catalyst **2** which catalyzes alcohol dehydrogenation via metal-ligand cooperation (left cycle**,** Scheme 5**)**.[21] The formed aldehyde reacts with excess hydrazine to produce hydrazone,[22] which undergoes hydrogenation of the C=N bond to form the N-substituted hydrazine via a 'borrowing hydrogen' process **(**right cycle, Scheme 5**)**. The latter reacts with an additional aldehyde molecule to form the N-substituted hydrazone **(**Scheme 5**)**.

To gain more mechanistic insight, we reacted freshly prepared benzylidenehydrazine with benzyl alcohol in the presence of catalyst **1** (3 mol%) and ^{t}BuOK (5 mol%) in THF, in absence of hydrazine, resulting in 90% yield of the desired 1-benzyl-2-benzylidenehydrazine. This experiment indicates the hydrogen borrowing mechanism (Scheme 6, i). Under the same reaction conditions, 1-benzylidene-2-(4-chlorobenzyl) hydrazine was obtained in 89% yield by coupling of benzyl alcohol and 4-chlorobenzyl hydrazine with the liberation of dihydrogen **(**Scheme 6, ii**)**, indicating a dehydrogenative coupling process. No hydrogenated product was obtained when benzalazine was used as substrate under these reaction conditions, indicating that it is not an intermediate in the catalytic reaction **(**Scheme 6, iii**)**.



Scheme 6. Mechanistic experiments.

In conclusion, we have demonstrated the unprecedented formation of N-substituted hydrazones by coupling of alcohols and hydrazine. Moreover, the reaction is catalyzed by a base-metal catalyst. The reaction proceeds under homogeneous conditions, catalyzed by the new pincer catalyst Mn(^{t}Bu-PNN)(CO)$_2$Br (**1**) in the presence of catalytic amounts of ^{t}BuOK, as well as by the new dearomatized complex Mn(^{t}Bu-PNN*)(CO)$_2$ (**2**), with no added base. Uniquely, the reaction involves both acceptorless dehydrogenative coupling and 'hydrogen borrowing' in one system. A proposed mechanism is provided, supported by control experiments and observation of intermediates, formed by metal ligand cooperation.

Acknowledgements

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Keywords: manganese catalyst• partial hydrogen borrowing• N-substituted hydrazone• acceptorless alcohol dehydrogenation• hydrazine

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[23] CCDC 1580693 (complex **1**) 1580695 (complex **2**) 1589535 (complex **3**) and 1579450 (hydrazine derivative) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

COMMUNICATION

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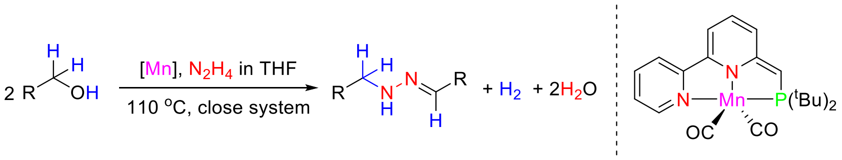
N-Substituted Hydrazones by Manganese Catalyzed Coupling of Alcohols with Hydrazine; ' Borrowing Hydrogen ' and Acceptorless Dehydrogenation in One System



An unprecedented one-step synthesis of N-substituted hydrazones by coupling of alcohols with hydrazine is reported. This “partial hydrogen borrowing” and acceptorless dehydrogenation reaction is catalyzed by a new manganese pincer complex under mild reaction conditions, liberating water and dihydrogen as the only byproducts.