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Direct Conversion of Alcohols to Alkenes by Dehydrogenative Coupling with Hydrazine/Hydrazone Catalyzed by Manganese

Uttam Kumar Das, Subrata Chakraborty, Yael Diskin-Posner, and David Milstein*

Abstract: We have developed unprecedented methodologies for the direct transformation of primary alcohols to alkenes, in the presence of hydrazine, and for the synthesis of mixed alkenes by the reaction of alcohols with hydrazones. The reactions are catalyzed by a manganese pincer complex, in absence of added base, or hydrogen acceptor, liberating dihydrogen, dinitrogen and water as the only by-products. The plausible mechanism, based on preparation of proposed intermediates and control experiments, suggests that the transformation occurs through metal ligand cooperative N-H activation of a hydrazone intermediate.

Transition metal catalyzed synthesis of alkenes is a central synthetic strategy in organic chemistry, as alkenes are essential building blocks for the construction of many important complex molecules.¹ The most common methods for the synthesis of alkenes are mainly based on C-C coupling reactions and on classical olefination of carbonyl compounds (Scheme 1).² Among others, widely used approaches are Wittig reaction,³ Julia olefination,⁴ Peterson reaction,⁵ and Tebbe olefination.⁶ In addition to stoichiometric metal-mediated coupling of carbonyl compounds,⁷ there are several reports on transition metal catalyzed olefination, such as Ir, Pd, Rh, Ru, Ni, and Cu catalyzed Wittig-type reactions with *in-situ* generated carbonyl compounds.⁸ These procedures are typically restricted to the use of stoichiometric amounts of additives and/or bases with a carbon equivalent source.

The direct transformation of alcohols to alkenes can offer an attractive 'green' route for the synthesis of C=C bonds.⁹ In several reports alcohols were used as alkylating agents towards C-C bonds formation.¹⁰ Our group reported the Wittig-type and Julia-type olefination of alcohols to form alkenes using ruthenium pincer complexes.¹¹ However, the highly desirable, green and sustainable direct catalytic transformation of alcohols themselves to alkenes using a well-defined catalyst is, to the best of our knowledge, unknown.

The application of complexes of earth abundant metals (Fe, Co, Ni, Mn) in homogeneous catalysis has attracted much recent attention.¹² Manganese offers an attractive alternative to noble metals. We reported the dehydrogenative coupling of alcohols and amines, catalyzed by the manganese complex 1 (Figure 1)¹³ and further noteworthy progress has been made by other groups in the area of homogeneous (de)hydrogenation catalysis using manganese.¹⁴ We have reported that catalyst 1 also efficiently catalyzes C-C bond

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formation via conjugate addition of non-activated nitriles at room temperature, in absence of added base.¹⁵ Several groups reported manganese catalyzed C-C bond formation reactions using alcohols for the sustainable construction of important compounds.¹⁶ We have also demonstrated that the manganese pincer complex **3** (Figure 1) is an efficient catalyst for the unprecedented α -olefination of nitriles by alcohols.¹⁷ Very recently the Kempe and Maji groups independently reported the manganese catalyzed olefination of substituted heteroarenes with alcohols.¹⁸



Coupling reaction:

$$R-X + R' \xrightarrow{Pd(0)/Base} R' \xrightarrow{R}$$

This work: Manganese catalyzed direct conversion of alcohols to alkene



Scheme 1. Prevailing methods of alkene synthesis.



Figure 1. Manganese pincer complexes explored in this study.

Direct use of hydrazine in homogeneous catalysis is a challenging task. Deoxygenation of alcohols using hydrazine, catalyzed by ruthenium and iridium complexes, was reported by Li and cowarkers.¹⁹ They also reported very interesting ruthenium catalyzed C-C bond forming reactions using carbonyl compounds and preformed substituted hydrazones as alkyl carbanion

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equivalents in the presence of base.²⁰ Our group reported dehydrogenative coupling of alcohols and hydrazine to form azines catalyzed by a Ru-PNP pincer complex, and deoxygenation of alcohols using hydrazine catalyzed by complex **3**.²¹ Very recently we have reported manganese-catalyzed coupling of alcohols and hydrazine to form N-substituted hydrazones through a 'partial hydrogen borrowing' process using complex **4** (Figure 1).²²

Inspired by the above reports we have developed a catalytic process for the direct conversion of alcohols to alkenes by dehydrogenative coupling with hydrazine/hydrazone catalyzed by a well-defined pincer complex of the earth-abundant manganese. This reaction proceeds under base free conditions and generates hydrogen, nitrogen and water as the only byproducts. To the best of our knowledge, catalytic conversion of alcohols to alkenes by reaction with hydrazine/hydrazone has not been reported.

Reaction of benzyl alcohol (0.5 mmol) in 1 mL of 1M hydrazine in THF in the presence of complex 1 (3 mol %) at 120 °C in a closed Schlenk tube resulted after 24h in 91% of alcohol conversion to form of azine in 86% yield (Table 1, entry 1). However, using complex 2 as catalyst resulted in formation of stilbene in 22% with azine in 53% yield, as measured by GC-MS and ¹H NMR (Table 1, entry 2). Under the same reaction conditions, use of complex 3 as catalyst resulted in formation of stilbene in 59% yield after 12h (Table 1, entry 3) and 91% after 24 h with 65% and 99% of alcohol conversion, respectively, as revealed by GC-MS and ¹H NMR (Table 1, entry 3 and 4). The ¹H NMR of the crude product is in accord with the E geometric isomer. Only traces of the deoxygenated product, toluene, was detected by GC-MS. Analysis of the gas phase by GC indicated formation of H₂. It is noteworthy that the reaction does not require any base or hydrogen acceptor addition. Complex 4 was not an effective catalyst for alkene formation, leading to only azine (Nsubstituted hydrazones) in 80% yield (Table 1, entry 5). Using hydrazine hydrate instead of hydrazine in THF was less effective (entry 6).

Table 1. Manganese catalyzed dehydrogenative coupling of ben	zyl
alcohol in presence of hydrazine. ^a	

Ph ^{OH}	[M N ₂ H ₄ in -2H	1n] (3 mol %) THF (1 mL), 1 ₂ , - 2H ₂ O, -N ₂	20 ⁰ C Ph alk	Ph + Ph' kene	N Ph
Entry	Cat	Time	Conv	Yield ^b of	
		(h)	(%) ^b	alkene	azine
1	1	24	91		86
2	2	24	90	22	53
3°	3	12	65	59	-
4 ^c	3	24	99	91(84) ^d	-
5	4	24	95	-	80
6 ^e	3	24	76	35(23) ^f	10
7 ^g	5	24	86	78	-
8 ^g	6	24	81	72	-
2 3 ^c 4 ^c 5 6 ^e 7 ^g 8 ^g	- 3 3 4 3 5 6	12 24 24 24 24 24 24 24	65 99 95 76 86 81	59 91(84) ^d - 35(23) ^f 78 72	- - 80 10 -

^e0.015 mmol catalyst, 0.5 mmol benzyl alcohol, 1 mL 1M N₂H₄ in THF in 50 ml Schlenk flask heated at 120 °C. ^bConv. and yield were determined using GC or NMR using *N*,*N*-dimethylaniline internal standard. ^cAverage of two runs. ^dIsolated yield. ^eReaction was in presence of hydrazine hydrate instead of N₂H₄ in THF. ^f1,2-diphenyle ethanol was the product. ^gSee mechanistic part and Scheme 3.

Table 2. Conversion	of primary	alcohols to	alkenes	catalyzed	by 3.
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	28 ОН -	[3] (3 mol %)	→ R ²	R	
En try	Alcohol	N ₂ H ₄ Pr Jettr ct120 ^O C -2H ₂ , - 2H ₂ O, -N ₂	t(h)	Conv. (%) ^b	Yield (%) ^c
1	ОН		24	99	91(84) ^d
2	МеО	H ₃ CO-CH:	24	99	90
3	Н3С ОН	H ₃ C-CH ₃	24	99	87
4	Ph	Ph-	24	99	82
5	F	FF	36	99	89
6	СІ	ci-Ci-Ci	36	99	89(81) ^d
7	Br	Br-	36	99	87
8	F ₃ C OH	F ₃ C-CF ₃	36	68	55
9	MeO OMe	Me0 OMe OMe	36	97	78(75) ^d
10	осн3	OCH3	36	95	85(80) ^d
11	N(CH ₃) ₂	N(CH ₃) ₂	36	88	77(74) ^d
12 ^e	он	N(CH ₃) ₂	36	96	17 ^f

^aConditions: 0.015 mmol catalyst, 0.5 mmol alcohol, 1 mL 1M hydrazine in THF in 50 ml Schlenk flask heated at 120 °C. ^cConversion determined by GC or NMR analysis using *N*,*N*-dimethylaniline as internal standard. ^cYield by GC or NMR analysis using *N*-*N*-dimethylaniline internal standard. ^dIsolated yields. ^eUsing 25% ^lBuOK as base. ^fMajor by-products were azine and 4-octanol.

Next, the scope of this unprecedented catalytic transformation of alcohols to alkenes was explored using various benzylic alcohols. As shown in Table 2, benzyl alcohol and substituted benzyl alcohols with electron donating or electron withdrawing groups give stilbenes in very good yields (with less amounts of deoxygenated product and/or azine as side products). Reaction of benzylic alcohols bearing electron withdrawing groups in the *para* positions (*p*-F, *p*-Cl, P-Br and *p*-CF₃) afforded the corresponding alkene products in good yields after a reaction time of 36h (Table 2, entries 5-8). The corresponding stilbenes, obtained by use of 3, 4-dimethoxybenzyl alcohol and 3-

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methoxybenzyl alcohol and hydrazine was 78% and 85%, respectively (Table 2, entries 9 and 10). Using 3-(dimethylamino)benzyl alcohol, the corresponding alkene was obtained in 77% yield (Table 1, entry 11). However, heteroaromatic alcohols and nitro substituted alcohol produce mixture of products with no alkene.

Aliphatic alcohols such as 1-butanol also underwent dehydrogenative coupling with hydrazine. However, the azine was the major product under standard conditions. Using 25% ¹BuOK as base, 17% of the alkene 4-octene, together with azine and 4-octanol were formed as determined by G.C and ¹H NMR spectroscopy (Table 2, entry 12).^{20a} See SI for details.

Scheme 2. Dehydrogenative coupling of alcohols and hydrazone to form cross alkenes catalyzed by complex **3**.^a



^a0.0075 mmol catalyst, 0.25 mmol alcohol, 0.25 mmol benzylidenehydrazine (hydrazone) in 1 mL THF in a 50 ml Schlenk flask heated at 120 °C. ^bIsolated yields. ^oYield was determined by GC and NMR using *N*,*N*-dimethylaniline as internal standard (see SI)

The synthesis of mixed alkenes from the coupling of hydrazone and alcohols is also an attractive process. Recently Li and coworkers reported very interesting Ru-catalyzed cross alkene synthesis from carbonyl compounds and preformed hydrazone.23 However, stoichiometric amounts of additives and base were used. We now report the first example of a manganese-catalyzed coupling of alcohols and hydrazone to form mixed alkenes. The reaction is catalyzed by 3. Heating a THF solution of benzylidenehydrazine (0.25 mmol) and alcohol (0.25 mmol) with 3 (3 mol %) at 120 °C resulted in formation of mixed E-alkene in good yield as determined by G.C and ¹H NMR spectroscopy. To explore the scope of the cross coupling reaction, different alcohols were examined, producing mixed alkene products in acceptable yields (Scheme 2). In most of the cases the secondary alcohol (easily separated) was a side product obtained from the cross coupling of hydrazone and the primary alcohol as described by Li (see SI). 20a However reaction of aliphatic hydrazones with alcohols yields azines and no mixed alkenes.

Regarding the mechanism, we believe that the amido complex **5** (Scheme 3) is involved in the catalytic cycle.¹⁴⁹ Indeed, when freshly prepared **5** (3 mol %) was employed as catalyst in the dehydrogenative coupling of benzyl alcohol, stilbene was obtained in 78% yield after 24 h (Table 1, entry 7). Significantly, treatment of **5** with benzylidenehydrazine (1 equiv.) in THF at room temperature

resulted in formation of a new complex **6** (Scheme 3, a), which exhibited two doublet signals in ³¹P{¹H} NMR at δ = 59.8 (²J_{PP} = 129 Hz) and 89.5 (²J_{PP} = 129 Hz) ppm, indicating N-H activation at room temperature. Abstraction of the acidic -NH from benzylidenehydrazine by the basic amido moiety of complex **5** generates the N-H activated Mn(ⁱPr-PN^HP)(NHN=CHPh)(CO)₂ complex (**6**), which was structurally characterized by NMR, IR spectroscopy and X-ray crystallography (Figure 2, see also SI). This represents a rare direct N-H activation of hydrazone by MLC (MLC=Metal Ligand Cooperation).²⁴ To further support these assignments, benzaldehyde was reacted with complex **6** in THF at 120 °C and leading to formation of stilbene in 83% yield as well as complex **5** after 16h (Scheme 3, b). Benzyl alcohol was converted to stilbene in 72% yield using complex **6** as catalyst (Table 1, entry 8).



Scheme 3. (a) Hydrazone N-H bond activation by **5**. (b)Reaction of **6** with benzaldehyde to form stilbene. (c) Water activation by **5**.



Figure 2. Structure of complex **6**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity except N-H protons.



Scheme 4. Proposed mechanism

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Considering our experimental findings, and our recent reports on Mn-catalyzed dehydrogenative coupling of alcohols and hydrazine,²¹ and deoxygenation of primary alcohols catalyzed by 3,²⁰ we propose a plausible catalytic cycle (Scheme 4). Hydrogen liberation from 3 forms complex 5 which undergoes O-H activation by MLC to generate the alkoxy intermediate A.²⁰ Hydride elimination from the alkoxy ligand leads to formation of an aldehyde which reacts with excess hydrazine to produce hydrazone.21,22 Reaction of the generated hydrazone with complex 5 forms the N-H activated complex 6, which reacts with the aldehyde to produces olefin via a concerted pathway, without use of any base or additives, forming the intermediate manganese hydroxo complex 7 and N2 gas.23 Complex 7 then releases water, regenerating the active catalyst 5. It is noteworthy that in a separate experiment it was observed that complex 5 can reversibly add H₂O/D₂O (Scheme 3, c and SI).

In conclusion, unprecedented base-metal catalyzed direct transformation of alcohols to alkenes by acceptorless dehydrogenative coupling of alcohols with hydrazine, as well as dehydrogenative coupling of alcohols with hydrazones to form mixed alkenes is demonstrated. Moreover, the reaction is catalyzed by a complex of an earth abundant metal (Mn). This E-alkene formation proceeds in absence of added bases, or hydrogen acceptors, using the manganese pincer catalyst (ⁱPr-PN^HP)Mn(H)(CO)₂. A plausible mechanism is provided, based on preparation of postulated intermediates and demonstration of steps though to be involved in the catalytic cycle, including N-H activation by amido-amine metal-ligand cooperation.

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Direct Conversion of Alcohols to Alkenes by Dehydrogenative Coupling with Hydrazine/Hydrazone Catalyzed by Manganese



Unprecedented methodologies for direct transformation of primary alcohols to alkenes by acceptorless dehydrogenative coupling of alcohols with hydrazine, and dehydrogenative coupling of alcohols with hydrazones to form mixed alkenes, are demonstrated. These reactions are catalyzed by a manganese pincer complex, in absence of added base, or hydrogen acceptor, liberating dihydrogen, dinitrogen and water as the only by-products.