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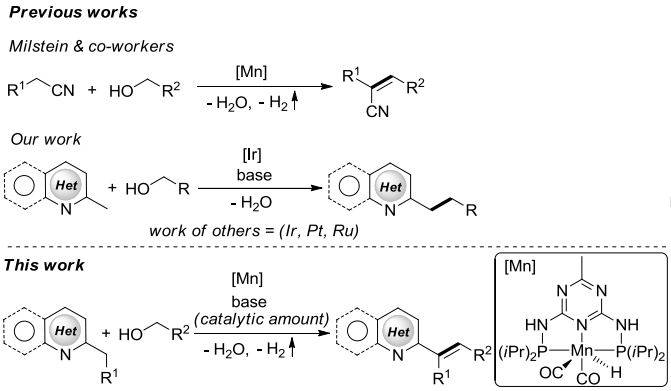
Manganese-catalyzed Dehydrogenative Alkylation or *α*-Olefination of Alkyl-*N*-Heteroaromatics by Alcohols

*Guoying Zhang, Torsten Irrgang, Thomas Dietel, Fabian Kallmeier, and Rhett Kempe**

***Abstract**: Catalysis involving earth-abundant transition metals is an option to help save our rare noble metal resources and is especially interesting if novel reactivity or selectivity patterns are observed. We report here on a novel reaction: the dehydrogenative alkylation or α-olefination of alkyl-N-heteroaromatics by alcohols. Manganese complexes developed in our laboratory catalyze the reaction efficiently. Fe and Co complexes stabilized by such ligands are essentially inactive. Hydrogen is liberated during the reaction and bromo or iodo functional groups and olefins can be tolerated. A variety of alkyl-N-heteroaromatics can be functionalized, and benzyl and aliphatic alcohols undergo the reaction.*

Noble metals are rare and used in a variety of key technologies, for example, catalysis. The replacement of noble metals by earth-abundant transition metals, such as Mn, Fe or Co, is a possible strategy to reduce the use of noble metals, especially in homogeneous catalysis, where reusability of the active metal is challenging. The use of earth-abundant metals may also permit the discovery of new selectivity patterns in known reactions or the development of novel catalytic transformations. Manganese complexes have been used successfully in hydrogenation and dehydrogenation catalysis since early 2016.[1] Despite significant progress in the (transfer) hydrogenation of ketones,[2] esters,[3] amides[4] and CO_2,[5] and dehydrogenative coupling,[6] dehydrogenative condensation,[7] and borrowing hydrogen/hydrogen autotransfer,[8] only rare examples of novel catalytic transformations, not yet observed with other transition metals, have been reported.[9] Olefins are highly important compounds since they are used broadly as starting materials for the synthesis of fine and bulk chemicals.[10] Aryl-substituted olefins and especially those linked to *N*-heteroaromatics find applications as pharmaceuticals and agrochemicals or are important intermediates for their synthesis.[11] Polyaryl vinylenes are conducting polymers and have applications in material science, for instance, as emissive layers in organic light-emitting diodes.[12]



Scheme 1. State of the art and the reaction described here. Top: Mn-catalyzed *α*-olefination of nitriles using primary alcohols by Milstein and co-workers and our Ir catalyzed alkylation of methyl-*N*-heteroaromatics by alcohols and work of others using different noble metal catalysts. Bottom: The Mn-catalyzed dehydrogenative alkylation or *α*-olefination of alkyl-*N*-heteroaromatics by alcohols disclosed here (R^1 and R^2 are H, alkyl or aryl substituents).

We have developed the alcohol-based alkylation of methyl-*N*-heteroaromatics (Scheme 1, middle),[13,14] have contributed to the development of Mn-based (de)hydrogenation catalysis[2b,7g,7e] and became interested in a Mn complexes mediate dehydrogenative version of our catalytic alkylation of methyl-*N*-heteroaromatics by alcohols.[9a]

Herein, we report on the dehydrogenative alkylation or α-olefination of alkyl-*N*-heteroaromatics by alcohols. (*E*)-Diaryl or -alkyl-aryl olefins are formed selectively in this novel transformation and dihydrogen is liberated. Manganese complexes stabilized by PN_5P ligands mediate the reaction with low catalyst loadings (0.5 mol%). Fe and Co complexes stabilized by such ligands are essentially inactive. We can tolerate bromo and iodo functional groups and C-C double bonds, despite the liberation of hydrogen during the reaction. A variety of alkyl-*N*-heteroaromatic compounds can undergo the reaction, and benzyl and aliphatic alcohols have been employed successfully.

The reaction between 2-methylquinoline (**1a**) and benzyl alcohol (**2a**) to (*E*)-2-styrylquinoline (**3aa)** was thoroughly investigated to develop broadly applicable reaction conditions. After finding initial reaction conditions applying precatalyst **B** (see Table 1 for its structure), different Mn complexes stabilized by PN_5P ligands were tested to find the most active precatalyst (Table 1, complexes **A**–**F**). The Mn complex stabilized with a triazine-based ligand bearing a methyl substituent in the *para*-position (**B**) gave the highest yield of **3aa** (Table 1, entry 2) and an olefin to alkane ratio of 20:1. NMR analysis of the desired product indicated that the (*E*)-isomer was formed. Only traces of the C=C hydrogenation product 2-phenethylquinoline **4aa**, along with traces of another product, most likely the (*Z*)-isomer, were detected by GC-MS. Only low amounts (<5 %) of the desired product **3aa** were obtained for iron (**G-I**) and cobalt (**J**) complexes stabilized by the same ligands as **B** or **C** (Table 1, entries 7-10). As anticipated, control reactions

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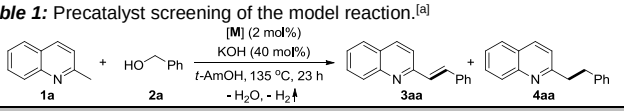
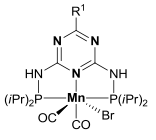
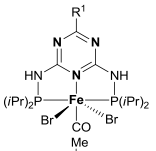
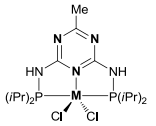
demonstrated that only a trace amount of the α-olefination product was obtained in the absence of a ligand or Mn precatalyst (Table 1, entries 11-12). The best yield of **3aa** was obtained after final optimization of the reaction parameters (solvent, solvent ratio, base, base amount, substrate ratio and reaction temperature; see the Supporting Information for details) with **B** as the most active precatalyst. We used 0.5 mol% of precatalyst **B**. The reaction was carried out in a solvent mixture of *t*-AmOH (2 mL) and toluene (1 mL) with 0.4 equivalents KOH as the base and an excess of **1a** (2 equivalents) with respect to **2a**.

Table 1: Precatalyst screening of the model reaction.[a]

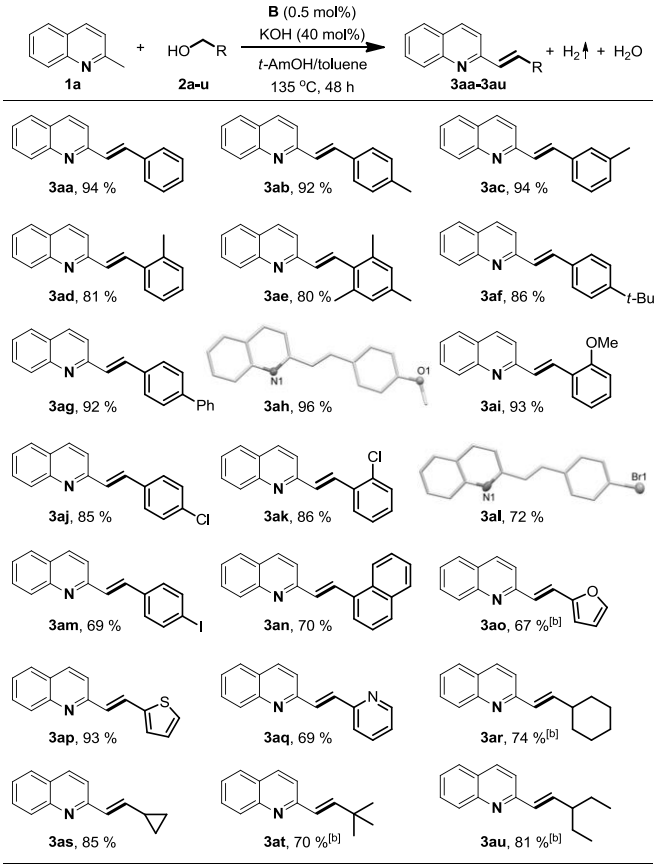


Entry	Precatalyst [M]			3aa[%]	3aa:4aa
1		R^1 = H	**A**	66	>20:1
2		R^1 = Me	**B**	79 (96[b])	>20:1
3		R^1 = C_6H_5	**C**	76	8:1
4		R^1 = 4-CF_3(C_6H_4)	**D**	70	13:1
5		R^1 = NHC_3H_5	**E**	67	>20:1
6		R^1 = NEt_2	**F**	54	3:1
7		R^1 = Me	**G**	<5	-
8		R^1 = C_6H_5	**H**	<5	-
9		M = Fe	**I**	0	-
10		M = Co	**J**	<5	-
11	$[Mn(CO)_5Br]$			traces	-
12	Precatalyst free			traces	-

[a] Reaction conditions: 2 mol% precatalyst (0.02 mmol), KOH (0.4 mmol, 22 mg), **1a** (3 mmol, 405 µL), **2a** (1 mmol, 104 µL), *t*-AmOH (2 mL), 135 °C (extern temperature), 23 h. Yield of **3aa** and the ratio of **3aa**:**4aa** determined by GC-analysis using *n*-dodecane as an internal standard. [b] 0.5 mol% precatalyst (0.005 mmol), KOH (0.4 mmol, 22 mg), **1a** (2 mmol, 270 µL), **2a** (1 mmol, 104 µL), *t*-AmOH (2 mL) and toluene (1 mL), 48 h.

We could apply a wide range of alcohol substrates using our optimized conditions allowing the preparation of (*E*)-disubstituted 2-vinylquinoline derivatives (Table 2). Again, only traces of the C=C hydrogenation or (*Z*)-disubstituted by-products were observed. X-ray crystal-structure analyzes of **3ah** and **3al** (Table 2) were performed and underline the formation of the thermodynamically more stable (*E*)-isomers.[18] Yields of isolated products higher than 90 % could be obtained for seven out of 21 examples. Both electron-rich and -deficient alcohols could be employed efficiently in our protocol (**3aa**-**3am**). A series of functional groups were compatible with the present catalytic system for alcohols. Halide groups particularly, even iodo, survived well in the standard procedure, leading to corresponding products **3aj**-**3am**, which can be used for further transformations involving oxidative addition of an aryl-X bond (X = Cl, Br, I). Alcohols carrying a hetero aromatic group (**2o**-**2q**) able to bind to metal complexes and, thus, able to poison catalysts, were linked successfully to **1a** with this catalytic system. The corresponding olefination products were obtained with moderate (**3ao**, **3aq**) to excellent (**3ap**) yields. We next turned our attention to the more challenging aliphatic alcohols. Cyclohexylmethanol (**2r**) and cyclopropylmethanol (**2s**) were initially surveyed and the reaction proceeded smoothly to give the desired adducts **3ar** and **3as** in 74 and 84 % yields, respectively. Similar results were obtained in the reactions of 2,2-dimethylpropan-1-ol (**2t**) and 2-ethylbutan-1-ol (**2u**) to deliver the α-olefination adducts efficiently in high yields. A gram-scale reaction was successfully realized with 0.5 mol % of Mn precatalyst **B**, affording **3aa** in 87 % (2.0 g) yield (see Supporting Information for details).

Table 2. α-Olefination of 2-methylquinoline (**1a**) with various primary alcohols.[a]



[a] Reaction conditions: 0.5 mol% precatalyst **B** (0.005 mmol), KOH (0.4 mmol, 22 mg), **1a** (2 mmol, 270 µL), **2a-u** (1 mmol), *t*-AmOH (2 mL) and toluene (1 mL), 135 °C (extern temperature), 48 h, Yield of isolated product. [b] 2 mol% precatalyst **B** (0.02 mmol).

Having demonstrated that the dehydrogenative process is compatible with a wide range of primary alcohols, investigation of the scope regarding the alkyl-*N*-heteroaromatics was undertaken (Table 3). Several methyl-*N*-heteroaromatics **1b-c** derived from 2-methylquinoline were effective substrates to react with benzyl alcohol smoothly to provide the desired products **3ba** and **3ca** in 95 and 86 % yields, respectively. However, 1-methylisoquinoline was less reactive and the olefination adduct **3da** was obtained in only moderate isolated yield. It is worth noting that 2-methyl benzoxazole (**1e**) derivative could also be used in the present reaction, affording **3ea** in good isolated yield. Furthermore, when **1f-1h** were subjected to this procedure, the corresponding olefination products **3fa-3ha** were isolated in yields of 60, 80 and 81 %, respectively, which revealed that a variety of *N*-heteroaromatics could function as useful substrates for our olefination reaction. In order to further explore the synthetic potential of this process, a series of typical functional groups of the primary alcohols, such as methyl, chloro, bromo and thienyl, were subjected to reaction with 2-methylpyrazine under the standard reaction conditions, affording the corresponding products **3hb-3hp** in good to excellent yields. Selective mono or double olefination of substrates containing two methyl groups is possible as well albeit only moderate isolated yields were obtained (**3ka** and **3kaa**). In addition, secondary carbon atoms can be olefinated (**3is** and **3ja**). Secondary alcohols could not be employed successfully.[9c] The practice and convenience of this novel method to (*E*)-disubstituted alkenes can be readily applied in the synthesis of (*E*)-alkene-containing functional compounds (Scheme 2). As exemplified by

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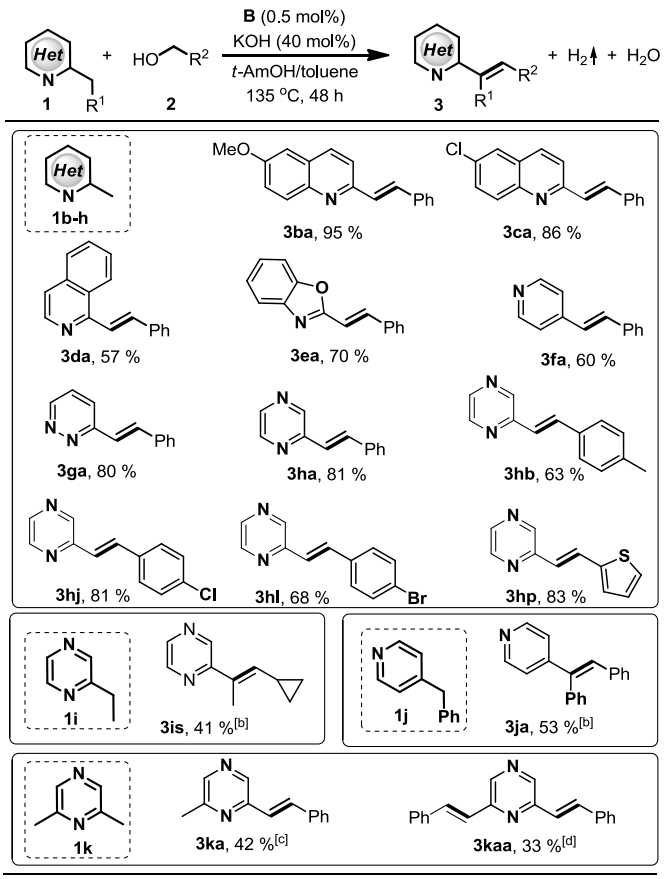
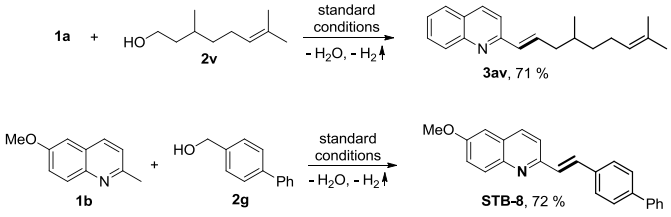
reaction of citronellol (**2v**), the corresponding product **3av** could be obtained in 71 % yield, while the internal double bond remained intact. With the newly developed catalytic system, **STB-8**[15] was prepared in acceptable yield by *α*-olefination of **1b** with **2g** under the standard conditions.

Table 3. *α*-Olefination of alkyl-*N*-heteroaromatics with various alcohols.[a]



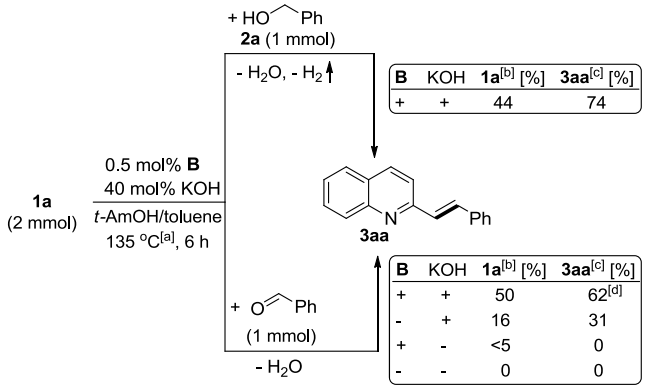
[a] Reaction conditions: 0.5 mol% precatalyst **B** (0.005 mmol), KOH (0.4 mmol, 22 mg), **1** (2 mmol), **2** (1 mmol), *t*-AmOH (2 mL) and toluene (1 mL), 135 °C (extern temperature), 48 h, Yield of isolated product. [b] 5 mol% precatalyst **B** (0.05 mmol), KOH (1 mmol). [c] toluene (2 mL). [d] 2 mol% precatalyst **B** (0.02 mmol), **1** (1 mmol), **2** (2 mmol), toluene (2 mL).



Scheme 2. Olefination reactions employing a natural product and synthesis of imaging agent (**STB-8**) for Alzheimer's disease *β*-amyloid plaques.

Several 6-h experiments between **1a** and benzaldehyde were carried out in the presence and absence of Mn complex **B** or KOH (Scheme 3) to gain insight into the reaction mechanism. Benzaldehyde reacts with **1a** in the presence of base and **B** to give rise to **3aa** in 62 % yield (Scheme 3, bottom). However, **3aa** can only be obtained in 31 % yield in the absence of the Mn catalyst under the same reaction conditions. These results indicated that the Mn catalyst, in addition to the catalytic dehydrogenation step, is also involved in the C-C bond forming condensation step. Benzaldehyde could not be transformed into the product at all in the absence of KOH.

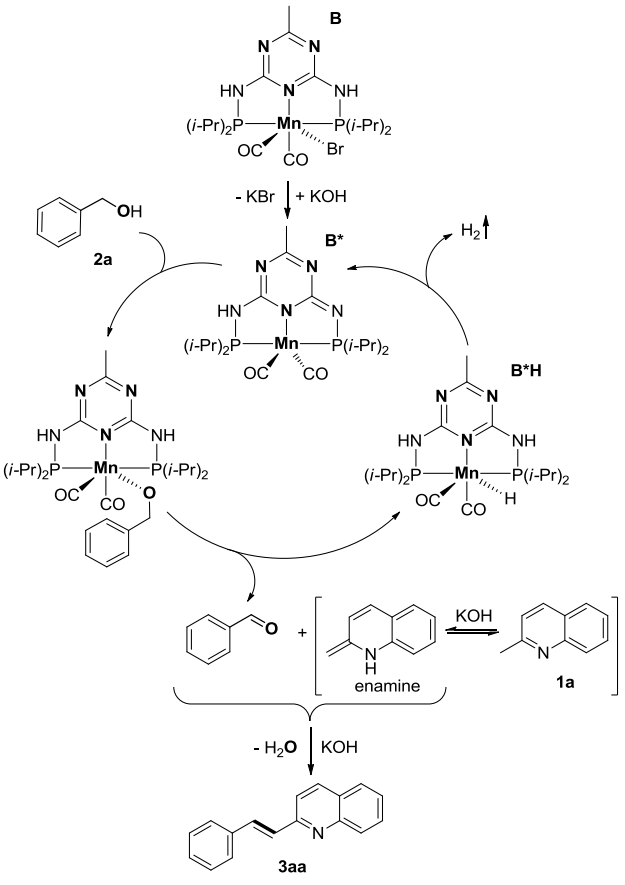
Scheme 3: Mechanistic investigations.



[a] Extern temperature. [b] (Conversion) and [c] (Yield) were determined by GC-analysis using *n*-dodecane as an internal standard. [d] A significant amount of the alkylation product (**4aa**) was identified as by-product via GC-MS.

The catalyst **B*H** is generated by salt elimination and hydrogen addition or via alcohol dehydrogenation under catalytic conditions (see SI). Thus, we conclude that **B*H** is a key intermediate of the proposed catalytic cycle (Scheme 4). In addition, alkoxy intermediates, as isolated by Liu[8e] or Milstein and coworkers,[9d] are proposed. A time conversion plot (see SI) indicates that aldehyde concentration is low at all times. **B*H** is not able to olefinate under base free condition and the base is needed for the dehydrogenation step.[7f] Neither **B*** nor **B*H** react with 2-methylquinoline **1a** to activate it, which indicates a different mechanism as observed by Milstein and coworkers.[9a]

Scheme 4: Proposed catalytic cycle.



In summary, we have developed a novel and efficient protocol for the Mn-catalyzed dehydrogenative alkylation or α-olefination of alkyl-*N*-heteroaromatics by alcohols. A broad range of (*E*)-disubstituted alkenes have been synthesized. Ten of the 38 synthesized examples are novel compounds. The olefination reaction is catalyzed efficiently by a PN_5P-pincer complex (triazine backbone) with a low catalyst loading of 0.5 mol%. The presence of a catalytic amount of base is crucial. Co and Fe complexes stabilized by the same ligands as the most active Mn catalyst are nearly inactive in our dehydrogenative alkylation reaction. Existing synthesis protocols for olefination reactions are divers. Classic carbonyl compound based olefination reactions such as Wittig,[16] Horner-Wadsworth-Emmons,[17] Peterson,[18] Julia[19] or McMurry[20] are important methodologies but require expensive pre-functionalization and partially the involvement of toxic reagents. Catalytic transformations like Heck reaction[21] or olefin metathesis[22] are very important too, but employ olefins already as starting materials. In addition, the Heck reaction, which forms very similar products compared to our olefination, proceeds via Aryl-X activation with X being, for instance Cl, Br as well as I and, thus, such functionalities are difficult to tolerate. We could demonstrate the tolerance of all of them in our olefination reaction.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alcohols · alkyl-*N*-heteroaromatics · dehydrogenation · manganese · olefination

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Angewandte Communications

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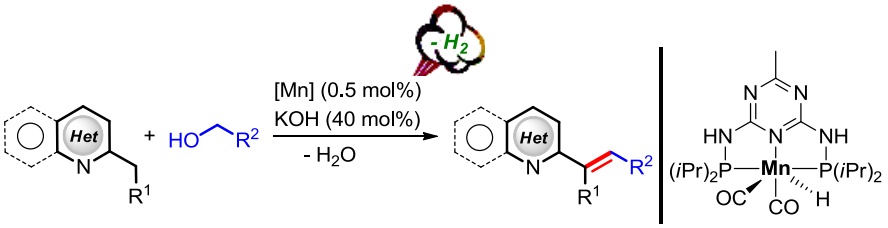
α-Olefination

Guoying Zhang, Torsten Irrgang, Thomas Dietel, Fabian Kallmeier, and Rhett Kempe* _____ **Page – Page**

Manganese-catalyzed Dehydrogenative Alkylation or *α*-Olefination of Alkyl-*N*-Heteroaromatics by Alcohols



The manganese complex (shown right) catalyzes the *α*-olefination of alkyl-*N*-heteroaromatics by alcohols via liberation of hydrogen efficiently in the presence of a catalytic amount of an inexpensive base. Reported noble metal catalysts mediate C-C single bond formation, non-dehydrogenative coupling.