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Molybdenum-Catalyzed Dehydrogenative Synthesis of Imines from Alcohols and Amines

Kobra Azizi and Robert Madsen*[a]

Abstract: A molybdenum N-heterocyclic carbene catalyst has been developed for the synthesis of imines from primary alcohols and amines with the liberation of dihydrogen. The catalyst is generated in situ from molybdenum hexacarbonyl, 1,3-dicyclohexylimidazolium chloride and potassium *tert*-butoxide and is further stabilized by the phosphine ligand dppe. Imines are formed in moderate to good isolated yields and a variety of alcohols and amines can be employed in the reaction including anilines. The transformation constitutes the first example of a homogeneous molybdenum-catalyzed acceptorless dehydrogenative coupling with alcohols and is believed to proceed by formation of a *cis*-coordinated molybdenum bis-N-heterocyclic carbene complex, which performs an oxidative addition to the alcohol, β-hydride elimination and reductive elimination of dihydrogen.

Introduction

Since the turn of the century, acceptorless dehydrogenation of alcohols has been developed as an atom-economical method for the synthesis of imines, amides, esters, heterocycles and various aldol condensation products.[1] In these reactions, the alcohol is dehydrogenated to the corresponding carbonyl compound, which then undergoes further transformations in the same pot. The reactions do not require any stoichiometric additives or oxidants and only releases dihydrogen (and water) as the byproduct(s). The most commonly used catalysts have been complexes based on the platinum-group metals ruthenium and iridium.[1] Our group has developed the ruthenium N-heterocyclic carbene complex [$RuCl_2$*i*Pr(*p*-cymene)] for the dehydrogenations and investigated the reaction mechanisms.[2] We have also shown that the iridium complex IrCl(CO)(BINAP) is able to perform a consecutive dehydrogenation and decarbonylation reaction of primary alcohols.[3] However, recently attention has shifted towards earth-abundant metals where a number of complexes based on iron, cobalt and manganese have been developed as catalysts for alcohol dehydrogenations.[4] Furthermore, these transformations have also been achieved with nickel and copper catalysts in several cases.[5] Notably, homogeneous catalysts based on molybdenum have to the best of our knowledge not been employed for the acceptorless dehydrogenation of alcohols.[6]

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Molybdenum is an essential trace element for all living organisms and constitutes a relatively non-toxic metal.[7] Molybdenum is a rather inexpensive transition metal where the major application is found in the production of steel.[8] In homogeneous catalysis, molybdenum has been used for a variety of reactions ranging from olefin metathesis and allylic alkylations to oxidation of different functional groups with hydroperoxides.[9] Several low-valent molybdenum complexes have been developed as catalysts for the hydrogenation of alkenes, ketones, imines and nitriles with dihydrogen.[10] Furthermore, molybdocene hydrides have been shown to catalyze the transfer hydrogenation of ketones with alcohols[11] while molybdenum sulfide clusters have been used for the reductive amination between aldehydes and nitrobenzenes under a dihydrogen atmosphere.[12] Based on these results, we speculated that homogeneous molybdenum complexes would be able to catalyze the acceptorless dehydrogenation of alcohols.

Herein, we describe the development of a molybdenum-catalyzed protocol for the dehydrogenative synthesis of imines from alcohols and amines. Imines are key intermediates in organic synthesis and the direct preparation from alcohols constitutes an environmentally benign route from inexpensive starting materials.[13]

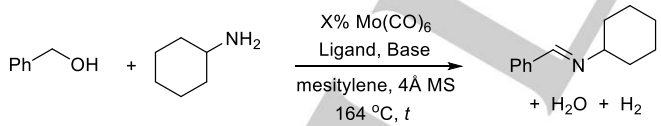
Results and Discussion

The initial experiments were performed with benzyl alcohol and cyclohexylamine as the substrates and focused on the low-valent molybdenum complex $Mo(CO)_6$ as the catalyst. Interestingly, refluxing this mixture in mesitylene produced the corresponding imine in 50% yield (Table 1, entry 1). Traces of the secondary amine *N*-benzylcyclohexylamine was also observed, but not further quantified. Unfortunately, no improvements were observed by adding a phosphine (PCy_3, PPh_3, dppe) or an amine (pyridine, DABCO, phenanthroline, 2,2'-bipyridine) as a ligand for the reaction (results not shown). Instead, several N-heterocyclic carbene ligands were investigated based on the previous experience in the group.[2] The carbenes were generated in situ from the corresponding imidazol(in)ium salts by deprotonation with potassium *tert*-butoxide. A total of 14 different salts were investigated containing different wingtip groups and counter ions (Figure 1). Notably, with 1,3-dicyclohexylimidazolium chloride (**A**) the yield increased to 62% with 5% of $Mo(CO)_6$ and the reaction was now completely selective for the imine with no concomitant formation of the secondary amine (entry 2). A slightly lower yield was obtained with the analogous benzimidazolium salt **B** (entry 3) and the same was observed with imidazolium salts **C** – **H** containing different substituents or counter ions (entries 4 – 9).

With methyl-substituted salts **I** and **J** traces of the secondary amine was also detected (entries 10 and 11). Imidazolinium salts **K** – **N** were not good carbene precursors since they all afforded the secondary amine as a byproduct in addition to moderate yields of the imine (entries 12 – 15). Therefore, imidazolium salt **A** was selected for general use with potassium *tert*-butoxide as the base (entry 16) which gave higher yields than by deprotonating with sodium hydride or sodium *tert*-butoxide (entries 17 and 18). The role of the base is only to generate the carbene in situ and not to promote the imination. When the corresponding carbenes of salts **D** and **G** were prepared separately and included in the reaction in the absence of a base, the imine was formed in 54 and 48% yield, respectively (entries 19 and 20).

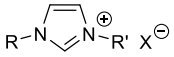
Further optimization of the reaction was performed by reinvestigating the influence of different phosphine and amine ligands. No improvement was observed by adding 20% of pyridine, DABCO, $P(Cyp)_3$, PPh_3, $P(o\text{-tolyl})_3$, $P(t\text{Bu})_3$ or 10% of BINAP or dppp (results not shown). However, with 20% of PCy_3 the yield improved to 91% (entry 21) indicating that additional stabilization by a phosphine ligand can be beneficial. Changing the solvent to toluene or decreasing the amount of **A** gave significantly less imine formation (entries 22 and 23). Furthermore, two equivalents of phosphine per equivalent of molybdenum seems necessary since lower or higher amounts of PCy_3 also decreased the yield (entries 24 and 25). Therefore, bidentate phosphine ligands were considered again and with 10% of dppe the yield increased to 96% (entry 26). The yield was reduced when lower amounts of dppe, the carbene or $Mo(CO)_6$ were employed (entries 27 – 29). As a result, it was decided to use 10% of $Mo(CO)_6$, 20% of the carbene from imidazolium salt **A** and 10% of dppe in refluxing mesitylene as the optimum protocol for the molybdenum-catalyzed dehydrogenative synthesis of imines. All the reactions after 60 h in Table 1 showed full conversion of benzyl alcohol. For comparison, imination reactions catalyzed by ruthenium, osmium, cobalt and manganese catalysts have typically used a 0.2 – 5% loading at 110 – 140 °C for 18 – 60 h.[2d,14]

Table 1. Optimizing molybdenum-catalyzed alcohol dehydrogenation.[a]

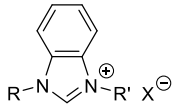


Entry	X	Ligand	Base	*t* [h]	Yield [%][b]
1	10	-	-	60	50[c]
2	5	10% **A**	10% KO*t*Bu	45	62
3	5	10% **B**	10% KO*t*Bu	45	57
4	5	10% **C**	10% KO*t*Bu	45	48
5	5	10% **D**	10% KO*t*Bu	45	43
6	5	10% **E**	10% KO*t*Bu	45	44
7	5	10% **F**	10% KO*t*Bu	45	47
8	5	10% **G**	10% KO*t*Bu	45	46
9	5	10% **H**	10% KO*t*Bu	45	55
10	5	10% **I**	10% KO*t*Bu	45	54[c]
11	5	10% **J**	10% KO*t*Bu	45	37[c]
12	5	10% **K**	10% KO*t*Bu	45	41[c]
13	5	10% **L**	10% KO*t*Bu	45	38[c]
14	5	10% **M**	10% KO*t*Bu	45	40[c]
15	5	10% **N**	10% KO*t*Bu	45	57[c]
16	10	20% **A**	20% KO*t*Bu	60	76
17	10	20% **A**	20% NaH	60	62
18	10	20% **A**	20% NaO*t*Bu	60	68
19	5	10% **D**[d]	-	45	54
20	5	10% **G**[d]	-	45	48
21	10	20% **A** + 20% PCy_3	20% KO*t*Bu	60	91
22[e]	10	20% **A** + 20% PCy_3	20% KO*t*Bu	60	40
23	10	10% **A** + 20% PCy_3	10% KO*t*Bu	60	64
24	10	20% **A** + 10% PCy_3	20% KO*t*Bu	60	78
25	10	20% **A** + 40% PCy_3	20% KO*t*Bu	60	67
26	**10**	**20% A + 10% dppe**	**20% KOtBu**	**60**	**96**
27	10	20% **A** + 5% dppe	20% KO*t*Bu	60	77
28	10	10% **A** + 10% dppe	10% KO*t*Bu	60	84
29	5	10% **A** + 5% dppe	10% KO*t*Bu	60	65

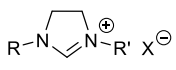
[a] Reaction conditions: Benzyl alcohol (1 mmol), cyclohexylamine (1 mmol), $Mo(CO)_6$, ligand, base, mesitylene (4 mL), 4Å MS (150 mg), reflux. [b] GC yield. [c] Traces of *N*-benzylcyclohexylamine was also formed. [d] As the free carbene. [e] Toluene was used instead of mesitylene.



A: R = R' = Cy, X = Cl
C: R = R' = Cy, X = BF_4
D: R = R' = *i*Pr, X = Cl
E: R = R' = *i*Pr, X = BF_4
F: R = R' = *t*Bu, X = BF_4
G: R = R' = Mes, X = Cl
H: R = R' = dipp, X = Cl
I: R = R' = Me, X = Cl
J: R = Me, R' = Bu, X = BF_4
(dipp = 2,6-diisopropylphenyl)



B: R = R' = Cy, X = Cl

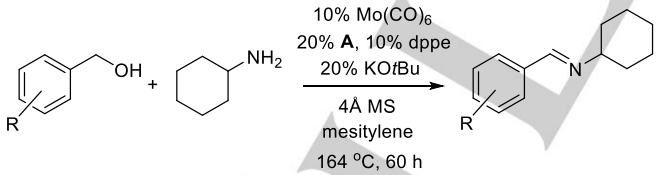


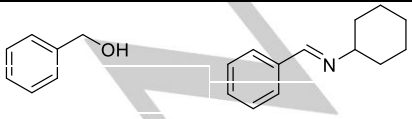
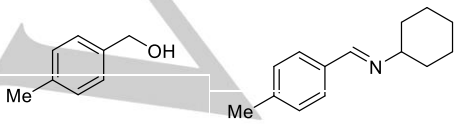
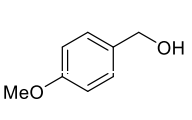
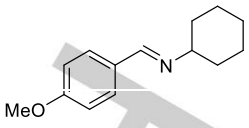
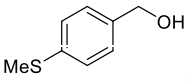
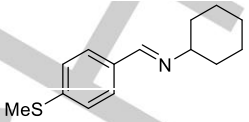
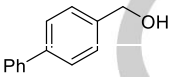
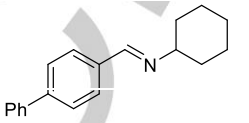
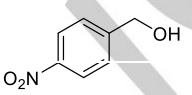
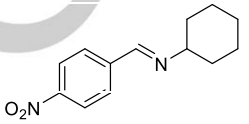
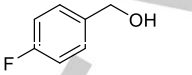
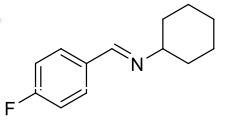
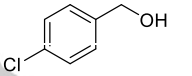
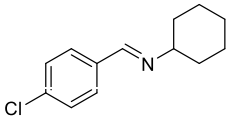
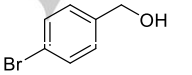
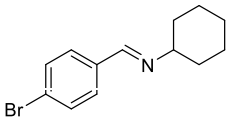
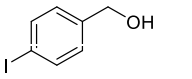
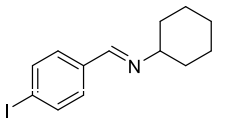
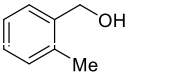
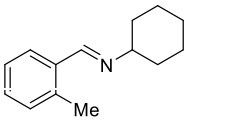
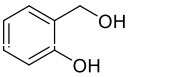
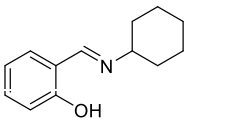
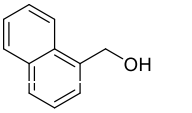
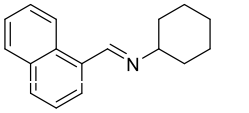
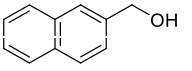
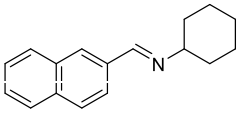
K: R = R' = *i*Pr, X = BF_4
L: R = R' = *t*Bu, X = BF_4
M: R = R' = Mes, X = BF_4
N: R = R' = dipp, X = Cl

Figure 1. Imidazol(in)ium salts as ligand precursors.

The procedure was then subjected to a variety of primary alcohols and amines to explore the substrate scope and limitations of the transformation. Cyclohexylamine was first reacted with different alcohols and the corresponding imines were purified by flash chromatography (Table 2). This produced the product from benzyl alcohol in 89% isolated yield (entry 1). The influence of various groups in the *para* position of benzyl alcohol were subsequently investigated where the *p*-methyl- and *p*-methoxy-substituted substrates afforded 80% and 87% yield, respectively (entries 2 and 3). *p*-Methylthiobenzyl alcohol gave 70% yield of the imine while *p*-phenylbenzyl alcohol furnished 62% yield (entries 4 and 5). In the latter case, small amounts of the starting alcohol could still be observed after the reaction. *p*-Nitrobenzyl alcohol afforded the product in 58% yield after an extended reaction time (entry 6) and traces of several byproducts could be observed due to competing reduction of the nitro group. The four *p*-halobenzyl alcohols gave 37 – 79% yield (entries 7 – 10) where no dehalogenation could be detected with the chloro and the bromo substrate. However, with *p*-iodobenzyl alcohol the transformation was accompanied by both dehalogenation, reduction of the imine to the secondary amine and deoxygenation to *p*-iodotoluene leading to a low yield of 37% (entry 10). The *ortho*-substituted substrates *o*-methyl- and *o*-hydroxybenzyl alcohol produced the corresponding imines in 70% and 32% yield, respectively (entries 11 and 12). The phenolic moiety clearly impaired the reaction since several byproducts were observed in addition to unreacted starting alcohol. The two naphthalenemethanols gave the products in 75% and 80% yield (entries 13 and 14) and in both cases a slight amount of methylnaphthalene was observed indicating that some deoxygenation of the alcohol is also occurring in these cases. Aliphatic primary alcohols such as hexan-1-ol and 2-phenylethanol were also subjected to the reaction conditions, but in these cases no conversion of the alcohol was observed.

Table 2. Imine formation from different alcohols and cyclohexylamine.[a]

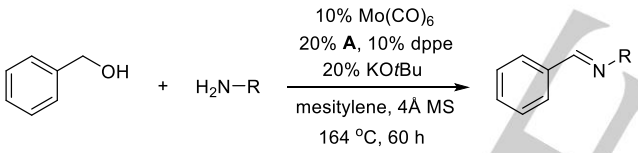


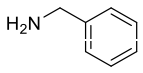
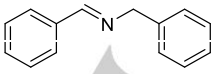
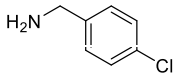
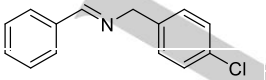
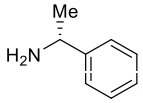
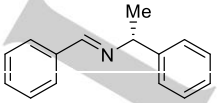
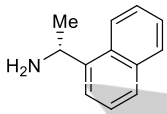
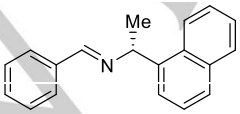
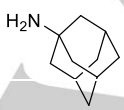
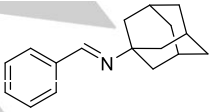
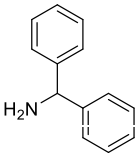
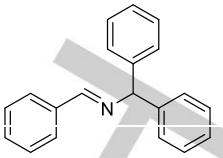
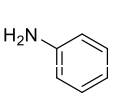
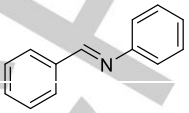
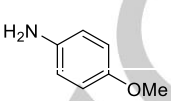
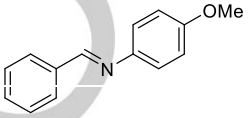
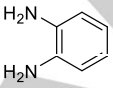
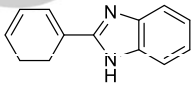
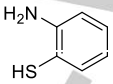
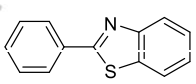
Entry	Alcohol	Product	Yield [%][b]
1			89
2			80
3			87
4			70
5			62
6[c]			58
7			79
8			65
9			68
10			37
11			70
12			32
13			75
14			80

[a] Reaction conditions: Alcohol (1 mmol), cyclohexylamine (1 mmol), $Mo(CO)_6$ (0.1 mmol), **A** (0.2 mmol), dppe (0.1 mmol), KO*t*Bu (0.2 mmol), mesitylene (4 mL), 4Å MS (150 mg), reflux, 60 h. [b] Isolated yield. [c] Reaction time 72 h.

Next, different amines were submitted to the reaction with benzyl alcohol to study the influence of this substrate in the transformation (Table 3). Benzylamine afforded the imine in 88% yield (entry 1) while the corresponding *p*-chloro compound only gave 15% yield due to competing dehalogenation, secondary amine formation and self-condensation into *N*-(*p*-chlorobenzylidene) *p*-chlorbenzylamine (entry 2). Optically active (*R*)-1-phenylethylamine and (*R*)-1-(1-naphthyl)ethylamine furnished the products without any sign of racemization although a longer reaction time was necessary in the latter case (entries 3 and 4). The sterically hindered amines 1-adamantylamine and benzhydrylamine afforded the imines in moderate yields (entries 5 and 6) and traces of benzyl benzoate could be observed as a byproduct in both cases. The reaction was also applicable to aromatic amines where aniline and *p*-anisidine gave 73% and 70% yield, respectively (entries 7 and 8). Full conversion of benzyl alcohol was observed in all the reactions in entries 1 – 8. With *o*-phenylenediamine and *o*-aminothiophenol additional dehydrogenation took place to furnish the corresponding benzimidazole and benzthiazole in 65% and 54% yield, respectively (entries 9 and 10). *o*-Aminophenol, on the other hand, was completely unreactive which again shows the impeding effect of the phenol moiety. Even with one equiv. of potassium *tert*-butoxide *o*-aminophenol only afforded a trace amount of 2-phenyl benzoxazole.

Table 3. Imine formation from benzyl alcohol and different amines.[a]



Entry	Amine	Product	Yield [%][b]
1			88
2			15
3			65
4[c]			58
5			52
6[c]			45
7			73
8			70
9			65
10			54

[a] Reaction conditions: Benzyl alcohol (1 mmol), amine (1 mmol), $Mo(CO)_6$ (0.1 mmol), **A** (0.2 mmol), dppe (0.1 mmol), KO*t*Bu (0.2 mmol), mesitylene (4 mL), 4Å MS (150 mg), reflux, 60 h. [b] Isolated yield. [c] Reaction time 72 h.

No benzaldehyde was detected by GCMS in any of the experiments in Table 1 and 3. In the absence of an amine, benzyl alcohol was converted into benzyl benzoate in 45% GC yield with the optimized protocol. Under the same conditions, 1-phenylethanol gave 73% conversion into acetophenone after 60 h with no sign of any byproducts. When $PhCD_2OH$ was reacted with $BnNH_2$ (as in Table 3, entry 1), the product was a mixture of PhCD=NBn and PhCH=NBn in a 1:4 ratio according to ^1H NMR. The result is not due to an exchange with the solvent since the ratio was the same in both mesitylene and mesitylene-d_{12}. The scrambling in the benzylic position implies that the dehydrogenation to the aldehyde is a reversible reaction and that it involves a molybdenum dihydride species. We have previously observed the same scrambling and dihydride pathway in our mechanistic analysis of the ruthenium-catalyzed alcohol dehydrogenation.[2c,d]

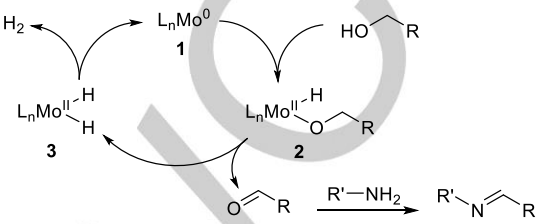
The gas evolution was measured by connecting the Schlenk tube from the reaction in Table 1, entry 26 to a burette filled with water.[3a] Under these conditions, the transformation with 1 mmol of benzyl alcohol produced the imine in 67% GC yield and 0.57 mmol (14 mL) of gas was collected indicating the release of one equivalent of dihydrogen. Essentially the same lower yield of the imine was obtained when the reaction was performed in a closed vial, which illustrates the importance of removing the gaseous co-product from the reaction with a stream of nitrogen in order to obtain the yield in Table 1, entry 26. The identity of the liberated gas was confirmed by trapping the released substance in a sealed two-chamber system.[3a,15] A Schlenk tube with the reaction mixture was connected to another tube with diphenylacetylene and Pd/C in methanol. After running the dehydrogenation for 36 h, a GC sample from the second tube

showed the formation of stilbene as a 16:1 mixture of the *Z* and the *E* isomers. In addition, a NMR sample was taken from the reaction that was run in a closed vial. The sample was transferred to benzene-d_6 in a closed NMR tube which gave rise to a broad singlet a 4.47 ppm in the NMR spectrum corresponding to H_2.[16] This signal could not be detected when NMR samples were taken from reactions that were run under a flow of nitrogen.

A small trace of *tert*-butyl formate was detected in the imination which is due to a reaction between coordinated carbon monoxide and *tert*-butoxide.[17] No other byproducts from the release of the CO ligands could be detected. A ^{13}C NMR spectrum of $Mo(CO)_6$ in toluene-d_8 showed a signal at 201 ppm. A small singlet from the CO ligands could also be observed at 203 ppm when $Mo(CO)_6$, **A**, dppe and KO*t*Bu were stirred in mesitylene for 2 h at 50 °C. However, no CO signal could be detected upon further stirring this mixture at 100 °C for an additional 2 h. The same was observed when benzyl alcohol and cyclohexylamine were also added to the mixture indicating that a majority of the CO ligands are readily released at the beginning of the transformation.

No imine was formed in the absence of $Mo(CO)_6$ under the conditions in Table 1, entry 26. The presence of trace metal impurities have been a serious concern in several metal-catalyzed reactions or transformations presumed to be metal-free.[18] Especially, some reactions believed to be catalyzed by iron or manganese have turned out to be mediated by trace amounts of another metal most likely copper or palladium.[19] Therefore, it was decided to analyze $Mo(CO)_6$ by inductively coupled plasma mass spectrometry (ICP-MS) for traces of elements known to perform alcohol dehydrogenations. However, none of these metals could be detected beyond their detection limit of typically 1 ppm. Consequently, we do not believe that the findings in Table 1 – 3 are due to traces of another element since alcohol dehydrogenations are not known to occur with extremely low loadings of catalyst.

The transformation is presumed to proceed through the formation of a molybdenum bis-N-heterocyclic carbene intermediate. $Mo(CO)_6$ is known to react with two equivalents of N-heterocyclic carbenes (or precursors) at about room temperature to afford *cis*-$Mo(CO)_4(NHC)_2$ species as the thermodynamically most stable products.[20] In fact, *trans*-$Mo(CO)_4(NHC)_2$ complexes will isomerize thermally to the corresponding *cis* compounds[21] and $Mo(CO)_5(NHC)$ complexes will split upon heating to *cis*-$Mo(CO)_4(NHC)_2$ and $Mo(CO)_6$.[22] Likewise, further displacement of CO ligands in these complexes with phosphines can occur at elevated temperature[20] making $Mo(CO)_2(ICy)_2$dppe the most likely compound formed initially in the reaction. The coordination of water and alcohols to the related molybdenum(0) complex $Mo(CO)_3(PCy_3)_2$ has been studied previously, and with water it has been debated whether an oxidative addition occurs to form a hydrido-hydroxo complex.[23] The oxidative addition in known to occur with thiols where $Mo(N_2)_2(dppe)_2$ was shown to react with RSH to form $MoH(SR)(dppe)_2$ complexes.[24] If this oxidative addition also takes place with an alcohol (e.g. at elevated temperature) a hydrido-alkoxo species **2** will be formed (Scheme 1). β-Hydride elimination from this intermediate will afford the carbonyl compound and dihydrido complex **3**. Reductive elimination of dihydrogen from the latter will then regenerate the starting complex **1** with an available coordination site. Dihydrogen is known to be a weak ligand for molybdenum(0) complexes such as $Mo(CO)(dppe)_2$ and the coordination to molybdenum has been studied in detail showing a very small difference between η^2-dihydrogen and dihydride bonding.[25]



Scheme 1. Proposed mechanism.

The mechanistic proposal in Scheme 1 receives further support from a reported stoichiometric reaction at room temperature between benzyl alcohol and the complex $Mo(N_2)_2(dppe)_2$.[26] This transformation produced one equivalent of benzene (due to aldehyde decarbonylation), one equivalent of dihydrogen gas, and a total of one equivalent of molybdenum complexes $Mo(CO)(N_2)(dppe)_2$, $Mo(CO)_2(dppe)_2$ and $MoH_4(dppe)_2$ in a 5:4:2 ratio.[26] This experiment shows that molybdenum(0) compounds are capable of dehydrogenating alcohols and liberate both hydrogen gas and form hydrido molybdenum species.

Conclusions

In summary, we have described the first homogeneous molybdenum catalyst system for acceptorless dehydrogenation of alcohols and applied the reaction to the synthesis of imines. The catalyst is generated in situ from $Mo(CO)_6$ with two equivalents of 1,3-dicyclohexylimidazol-2-ylidene and one equivalent of dppe. The catalytically active species is believed to be a molybdenum(0) complex with *cis* coordination of the two carbenes.

Experimental Section

General Information: All commercially available reagents were purchased from Sigma-Aldrich or Stem Chemicals and were not further purified. Mesitylene was stored over activated 4Å molecular sieves and degassed with N_2 before being used. Gas chromatography was performed on a Shimadzu GCMS-QP2010S instrument fitted with an Equity 5, 30 m × 0.25 mm × 0.25 μm column. Flash column chromatography separations were performed on silica gel 60 (40 – 63 μm). NMR spectra were recorded on a Bruker Ascend 400 spectrometer. Chemical shifts were measured relative to the signals of residual $CHCl_3$ (δ_H = 7.26 ppm) and $CDCl_3$ (δ_C = 77.16 ppm). Analysis for trace metals

by ICP-MS was performed by ALS Scandinavia AB and had a detection limit of 0.5 ppm for Co, 1 ppm for Pd, Pt, Ir, Rh, Ru, and Os, 4 ppm for Ni, 5 ppm for Mn, 10 ppm for Cu and 20 ppm for Fe.

General Procedure: $Mo(CO)_6$ (26.4 mg, 0.10 mmol), 1,3-dicyclohexylimidazolium chloride (53.6 mg, 0.20 mmol), 1,2-bis(diphenylphosphino)ethane (39.8 mg, 0.10 mmol), KO*t*Bu (22.4 mg, 0.20 mmol) and pre-activated 4Å molecular sieves (150 mg) were placed in an oven-dried tube (20 mL). The tube was placed in a Radley carousel on a hotplate, subjected to vacuum and then filled with N_2 (repeated 3 times). Freshly degassed mesitylene (4 mL) was injected into the mixture, which was then heated to 164 °C under a N_2 atmosphere. After 10 min at this temperature, the alcohol (1 mmol), the amine (1 mmol) and tetradecane (0.5 mmol, internal standard) were added and the reaction was refluxed for 60 h. The mixture was cooled down and the solvent was removed under vacuum at 60 °C. The residue was purified by silica gel column chromatography (98/2 hexane/Et_3N) to obtain the desired product.

Acknowledgements

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Keywords: Alcohols • Dehydrogenation • Homogeneous catalysis • Imines • Molybdenum

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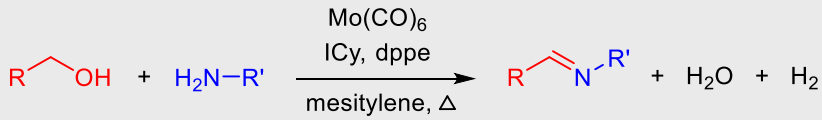

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Molybdenum-Catalyzed Dehydrogenative Synthesis of Imines from Alcohols and Amines

Now with molybdenum: A homogeneous molybdenum catalyst has been developed for the acceptorless dehydrogenative synthesis of imines from alcohols and amines. The catalyst is generated in situ from molybdenum hexacarbonyl, 1,3-dicyclohexylimidazol-2-ylidene and 1,2-bis(diphenylphosphino)ethane.