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Reductive Cleavage of Amides to Alcohols and Amines Catalyzed by Well-Defined Bimetallic Molybdenum Complexes

Sebastian Krackl, Chika I. Someya, and Stephan Enthaler*[a]

The selective reduction of carboxylic acid derivatives is one of the most important transformations in academic and industrial research. Such transformations afford countless building blocks for use in, for example, the production of pharmaceuticals, agrochemicals, or fine chemicals. Among those carboxylic acid derivatives, the reduction of amides is of great interest and is still a challenging task in organic chemistry.[1] Besides reduction with metal hydrides (e.g., $NaBH_4$, $LiAlH_4$), the application of transition-metal catalysts offers an efficient and versatile strategy.[1,2] Indeed, various catalysts are efficient for the cleavage of the C–O bond under reductive conditions to obtain the corresponding amine (Figure 1). Currently, well-established methodologies

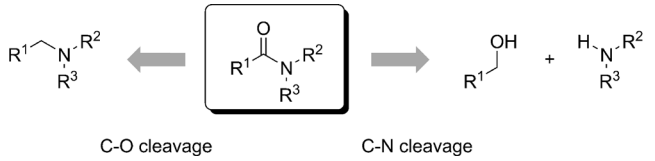
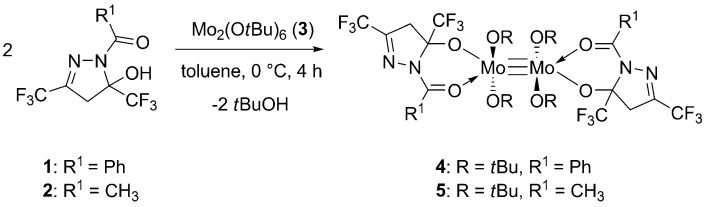


Figure 1. General pathways for the reduction of amides.

are based on the combination of transition metals and hydrosilanes as the reductants.These procedures are able to realize excellent yields and chemoselectivities, which underlines their high applicability.[3] On the other hand the reductive cleavage of the C–N bond of organic amides is more sophisticated and generates primary alcohols and amines as products, which are excellent synthons in organic chemistry (Figure 1). It is worth noting that the procedure for a reductive cleavage of the C–N bond will also be more useful for protection/deprotection chemistry or peptide chemistry. However, only a few protocols have been described so far, that accomplish this transformation with stoichiometric amounts of reductants.[4] Recently, the groups of Milstein and Ikariya reported on the first catalytic C–N cleavage of amides. Applying ruthenium catalysts and molecular hydrogen as the reductant, excellent selectivities were achieved.[5,6] Although the reductive cleavage of C–N bonds in amides applying molecular hydrogen is currently the preferred route, the application of hydrosilanes is a desirable choice, because of the mild reaction conditions and practical simplicity.[7] However, to date, no protocol has been realized for C–N bond cleavage in the presence of catalysts and hydrosilanes, and only cleavage of the C–O bond has been reported.[3]

Recently, some of us investigated the ability of low-valent, bimetallic dimolybdenum hexaalkoxides (Scheme 1) as catalyst precursors in reduction chemistry applying hydrosilanes as reductants. Excellent performance was observed for the deoxygenation of sulfoxides[8] and the reduction of tertiary amides.[9] Interestingly, in the case of the amide reduction, cleavage of the C–O bond was mainly observed and the corresponding amines were obtained in excellent yields. With regard to these results we wondered if it would be possible to realize the C–N bond cleavage with hydrosilanes as reductants by modifying the ligand sphere of the dimolybdenum alkoxides. Based on this idea, we present herein our initial results in the molybdenum-catalyzed C–N cleavage of tertiary amides.



1: R^1 = Ph
2: R^1 = CH_3

4: R = *t*Bu, R^1 = Ph
5: R = *t*Bu, R^1 = CH_3

Scheme 1. Synthesis of dimolybdenum complexes **4** and **5**.

Initially, pyrazoline ligands **1** and **2** were chosen as interesting motifs for the modification of dimolybdenum hexaalkoxide **3** in order to introduce greater steric bulk and to add Lewis basic sites to stabilize the complex (Scheme 1).[10] In accordance with a previously established protocol, we were able to synthesize disubstituted complexes [{Mo(**1**-H)-($OtBu)_2$}$_2$] (**4**) and [{Mo(**2**-H)($OtBu)_2$}$_2$] (**5**) in 48–75% yield by direct protolysis of **3** (Scheme 1).[8,11] ^{1}H, ^{19}F, and ^{13}C NMR investigations of these diamagnetic complexes confirmed the desired double substitution and successful coordination to the triple bond (see Supporting Information).

[a] Dr. S. Krackl, C. I. Someya, Dr. S. Enthaler
Technische Universität Berlin
Department of Chemistry
Cluster of Excellence, "Unifying Concepts in Catalysis"
Str. des 17. Juni 115/C2, 10623 Berlin (Germany)
Fax: (+49) 3031429732
E-mail: stephan.enthaler@tu-berlin.de

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Moreover, the obtained complexes were investigated with single-crystal X-ray diffraction analysis revealing isomorphous molecular structures of triply-bonded complexes with a staggered-ligand arrangement and typical Mo–Mo bond lengths of 2.260 and 2.254 Å for **4** and **5,** respectively (Figure 2). Interestingly, the oxygen O2 of the acetyl or benzoyl function of the ligand coordinates to the same molybdenum atom as the O1 atom and does not bridge the triple bond as observed for other bidentate ligands.[11a] Further details on bond lengths, bond angles and other crystallographic data are described in the Supporting Information. Advantageously, the synthesized complexes are, to some extent, more stable to oxygen and moisture compared with the parent compound **3**, which potentially makes them resistant to unwanted catalyst deactivation.

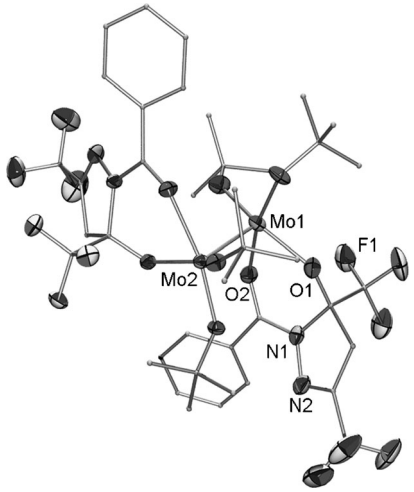
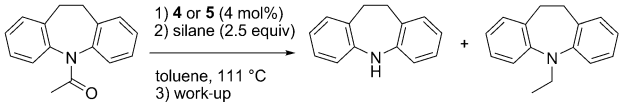


Figure 2. ORTEP presentation of complex **4**. Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules (toluene), hydrogen atoms, and ellipsoids of carbon atoms are omitted for clarity.

Table 1. Reduction of amide **6** with complexes **4** and **5** as precatalysts and different silanes as reducing reagents.[a]



6 **7** **8**

	Pre-catalyst	Silane	Solvent	Select. **7** [%][b]	Conv. [%] (Yield [%]) 6 h[c]	24 h[c]
1	**3**	$PhSiH_3$	toluene	<1	97	–
2	**4**	$PhSiH_3$	toluene	62	>99 (62)	>99 (62)
3	**5**	$PhSiH_3$	toluene	60	>99 (60)	>99 (60)
4	**4**	Ph_2SiH_2	toluene	78	73 (59)	>99 (78)
5	**4**	Ph_3SiH	toluene	>99	<1 (<1)	5 (5)
6	**4**	Et_3SiH	toluene	>99	9 (9)	16 (15)
7	**4**	Me_2PhSiH	toluene	>99	15 (15)	32 (30)
8	**4**	$(EtO)_3SiH$	toluene	>99	63 (54)	>99 (81)
9	**4**	Me_2ClSiH	toluene	<1	27 (<1)	>99 (<1)
10	**4**	Ph_2SiH_2	diglyme	78	77 (60)	>99 (78)
11[d]	**4**	Ph_2SiH_2	diglyme	48	51 (32)	>99 (68)[e]
12[d]	**4**	Ph_2SiH_2	decaline	24	73 (22)	>99 (32)[e]

[a] Reaction conditions: A solution of silane (828 μmol, 2.5 equiv) in the stated solvent (2.0 mL) was added dropwise over a period of 1 h with a syringe pump to a stirred solution containing the precatalyst (13 μmol, 4.0 mol%), substrate **6** (331 μmol) in the stated solvent (2.0 mL), 111 °C. [b] Selectivity refers to **7**. [c] The yields of **7** and the deoxygenated side product as well as the conversion were determined by GC (internal standard *n*-dodecane). Ethanol was detected qualitatively. The yield is given in brackets. [d] $T = 130$ °C. [e] Reduced yield due to unknown side product.

Having suitable complexes in hand, we were interested in their catalytic abilities for the reduction of organic amides. As a model substrate, we chose the acetyl-protected dihydro dibenzoazepine derivative **6**. It is worth noting that **6** was chosen, because the azepine core is a key structural motif in synthetic and medicinal chemistry as well as natural products and the deprotection of such compounds often requires harsh conditions.[12] Initially, the precatalyst **4** (4 mol%) and substrate **6** were dissolved in toluene followed by slow addition of phenylsilane (2.5 equiv), as the reducing agent, through a syringe pump (over 1 h) under reflux (Table 1, entry 2). After 6 h an excellent conversion of >99% was observed. The desired C–N bond cleaved compound **7** was formed as the major product (62%) accompanied by the C–O bond cleaved product **8** (36%). Cleary, modification of **3** with ligand **1** showed potential for the reductive cleavage of the C–N bond, whereas the parent complex $Mo_2(OtBu)_6$ (**3**) produced mainly the deoxygenation product **8** and only small amounts of **7** were detected (Table 1, entry 1). It is worth noting that keeping the silane concentration at a low level throughout the reaction seemed to be essential, since the reaction with one-time addition of 2.5 equivalents of the phenylsilane afforded a reduced amount of **7** (37%). Moreover, the analogous reaction with complex **5** generates **7** in a similar yield (60%) (Table 1, entry 3). The obtained results prompted us to focus ongoing studies on complex **4**. We next examined the influence of the substitution level of the silane by testing different reducing reagents (Table 1, entries 4–9). By increasing the number of phenyl substituents on the silicon, an increased selectivity for the C–N cleavage was noticed. For example, with diphenylsilane (Table 1, entry 4) the selectivity is increased to 78% after 24 h. Following this trend, the reaction of triphenylsilane under the same conditions gave the C–N cleavage product exclusively, but with a dramatically reduced conversion of 5% (Table 1, entry 5).

Other tertiary hydrosilanes, namely Et_3SiH and Me_2PhSiH, gave higher, but still unsatisfying yields of 15 and 30%, respectively, after 24 h, although the high selectivity was retained (Table 1, entries 6 and 7). The most active tertiary silane was $(EtO)_3SiH$ with an excellent selectivity of >99% and a yield of 81% of **7** (Table 1, entry 8). Moreover, the influence of the reaction solvent and temperature were studied. Applying diglyme under the same reaction conditions resulted in an increased yield of **7** after 24 h over entries 5–9 and comparable results to entry 4 (Table 1, entry 10). Higher temperatures resulted in a decrease in reactivity and selectivity (Table 1, entries 11 and 12). Furthermore, the generation of **7** was studied over time. A presen-

tation of the time-dependent yield for the reaction of **6** with Ph_2SiH_2 in toluene is given in Figure 3, showing significantly faster generation of **7** compared with **8**.

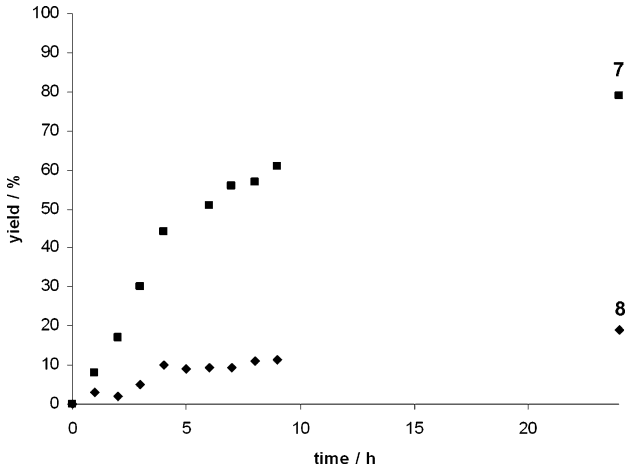


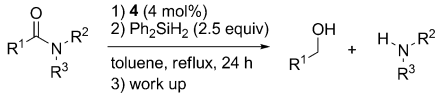
Figure 3. Time-dependent yield for the reaction of **6** with Ph_2SiH_2 in toluene catalyzed by **4** (Table 1, entry 3). Yields were determined by GC-MS with an internal standard (*n*-dodecane).

To evaluate the scope and applicability of the observed reaction, we investigated various organic amides with diphenylsilane as the reductant and **4** (4 mol%) as the precatalyst in toluene (Table 2, entries 1–10). First, the reduction of a series of tertiary heterocyclic carboxamides was examined (Table 2, entries 1–5). High yields of the corresponding C–N cleavage products were obtained. On the other hand, non-heterocyclic amides were converted in only moderate yields with deoxygenation representing the main reaction pathway (Table 2, entries 6–10). Less sterically demanding substituents on the nitrogen resulted in decreased amounts of the desired product. Secondary amides were also investigated, however, only poor yields were observed.

The mechanism for such C–N bond cleavage reactions is currently unknown (Scheme 2). Nevertheless, based on previously reported mechanistic assumptions[13] and our experimental observations,[8] we assume that **4** serves as a precatalyst for Si–H bond activation, while no reactivity was monitored for complex **4** in the presence of amides. An earlier low-temperature NMR study with complex **3** revealed the formation of a Mo–H species by oxidative addition of $PhSiH_3$ to dinuclear molybdenum complexes.[8] Interestingly, the obtained results suggest unsymmetrical addition, meaning the silyl residue and the hydride are connected to one molybdenum, while two alkoxides bridge the molybdenum–molybdenum double bond. Unfortunately, attempts to isolate the species failed so far because of instability; hence the structure of the bimetallic complex is currently unknown.[9]

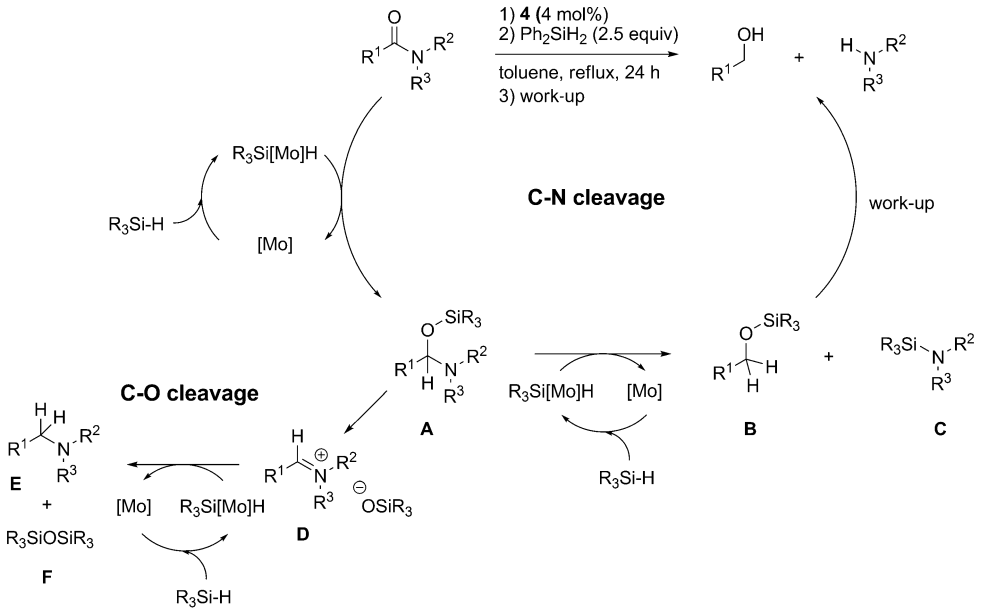
Due to the hemilability of the acetyl or benzoyl function of the ligands, a free coordination site can be generated and allow coordination of the carboxamide. By coordination through the amide oxygen, activation of the amide carbon can occur. The Mo–H intermediate transfers the hydride to the electrophilic carbon and the silyl residue to the oxygen to form O-silylated *N,O*-acetal **A**.[3t,p] In the next step, a

Table 2. Reduction of different amides applying **4** as precatalyst and Ph_2SiH_2 (2.5 equiv) as reducing reagent.[a]



	Substrate	Product		Conv. [%][b]	Yield [%][b]
1		**6**	**7**	>99	78
2		**9**	**7**	>99	75
3		**10**	**11**	>99	64[c]
4		**12**	**13**	86	72
5		**14**	**15**	98	63
6		**16**	**17**	>99	34
7		**18**	**19**	89	29
8		**20**	**19**	>99	31
9		**21**	**22**	>99	25[d]
10		**23**	**24**	>99	5[d]

[a] Reaction conditions: A solution of diphenylsilane (828 μmol, 2.5 equiv) in toluene (2.0 mL) was added dropwise over a period of 1 h with a syringe pump to a stirred solution containing the precatalyst **4** (13 μmol, 4 mol%) and the respective substrate (331 μmol) in toluene (2.0 mL). [b] The yields of the C–N cleavage products (sec. amine) and deoxygenated side product as well as the conversion were determined by GC (internal standard *n*-dodecane). The corresponding alcohols were detected qualitatively. [c] Isolated yield. [d] Yield was determined by ^1H NMR spectroscopy.



Scheme 2. Mechanistic proposal for molybdenum-catalyzed reduction of amides.

second equivalent of the Mo–H intermediate transfers a hydride to the carbon of **A** and the silyl residue to the nitrogen function.

As a consequence, the C–N bond is cleaved to produce silyl ether **B** and silyl amine **C,** which afford the corresponding alcohol and amine under workup conditions. In order to study the transfer of the hydrides, labeling experiments were performed with different substrates. For instance, the reductive cleavage of *N,N*-dibenzyl-4-iodobenzamide **18** (Table 2, entry 7) with Ph_2SiD_2 as the reducing reagent showed the incorporation of two deuterium atoms in the corresponding benzyl alcohol **25**. It is worth noting that no exchange reactions with the aromatic systems of the substrates or products were detected.

As was proposed for the reduction of amides to amines, O-silylated *N,O*-acetal **A** can also be transformed into the iminium species **D** to avoid the deoxygenation pathway. A second equivalent of the activated hydrosilane is transferred to **D** to produce the corresponding amine **E** and siloxane **F**.[3t]

In summary, we have demonstrated that triply-bonded dimolybdenum complexes modified by ligands **1** and **2** could serve as precatalysts for the C–N bond cleavage of amides by applying a hydrosilane as the reductant. The corresponding alcohols and amines were accessible under mild reaction conditions. It is worth noting that the observed C–N bond cleavage of amides is in contrast to reported protocols based on other transition metals and hydrosilanes, in which the C–O bond of the amide is cleaved. In general, the described methodology may be of interest for protection/deprotection chemistry or peptide chemistry. Future studies will be directed to the improvement of the C–N cleavage selectivity and gaining a deeper understanding of the underlying reaction mechanism.

Experimental Section

General experimental data, synthetic details, and analytical data (NMR spectra, single crystal XRD) are given in the Supporting Information.

General procedure for the reduction of amides: A solution of silane (828 μmol, 2.5 equiv) in toluene (2.0 mL) was added dropwise over a period of 1 h with a syringe pump to a stirred solution containing the precatalyst **4** (13 μmol, 4 mol%) and **6** (331 μmol) in toluene (2.0 mL). At the end of the reaction, the catalyst was removed by passing the reaction mixture through a short path of alumina followed by elution with ethyl acetate (2.0 mL). Furthermore, *n*-dodecane was added as an internal standard. The reaction mixture was treated with aqueous HCl and the organic layer was dried over $MgSO_4$. The mixture was analyzed by GC-MS and the C–N cleavage products, deoxygenated products, and residual starting material were either quantified by GC by comparison with a calibration curve made with the pure compound or by NMR spectroscopy.

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Keywords: amides · homogeneous catalysis · molybdenum · reductive cleavage

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