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Synthesis of Molybdenum Pincer Complexes and Their Application in the Catalytic Hydrogenation of Nitriles

Thomas Leischner[a], Anke Spannenberg[a], Kathrin Junge[a], Matthias Beller[a]

Dedicated to Prof. Dr. Uwe Rosenthal on the occasion of his 70th birthday

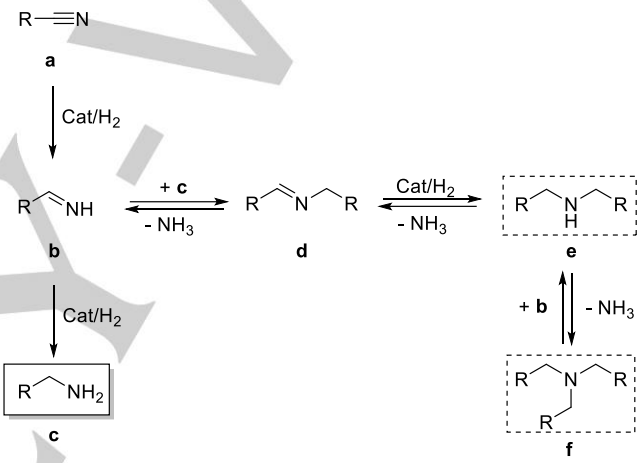
Abstract: A series of molybdenum(0), (I) and (II) complexes ligated by different PNP and NNN pincer ligands were synthesized and structurally characterized. Along with previously described Mo-PNP complexes **Mo-1** and **Mo-2**, all prepared compounds were tested in the catalytic hydrogenation of aromatic nitriles to primary amines. Among the applied catalysts, **Mo-1** is particularly well suited for the hydrogenation of electron-rich benzonitriles. Additionally, two aliphatic nitriles were transformed into the desired products in 80 and 86%, respectively. Moreover, catalytic intermediate **Mo-1a** was isolated and its role in the catalytic cycle subsequently demonstrated.

Introduction

Reduction of nitriles continues to attract significant attention of synthetic chemists for the preparation of diverse amines.[1] Traditionally, these reactions are carried out on laboratory scale using an excess of stoichiometric reducing agents, resulting in at least equimolar amounts of waste products.[2,3] On the contrary, catalytic homogenous hydrogenation using defined organometallic complexes provides an environmentally benign alternative, as it is more atom-economic with less waste generation.[3b,4] Nevertheless, the selective catalytic hydrogenation of nitriles to primary amines remains to be challenging for certain substrates, due to the underlying reaction mechanism (see Scheme 1).[5]

In general, primary amines are important intermediates for various applications in organic synthesis as well as in the production of bulk and fine chemicals.[6] Therefore, the development of novel (catalytic) protocols for their synthesis remains of particular interest. Until recently, noble metal-based catalyst systems prevailed for this purpose in both, industrial processes and academic research.[7] However, their comparably high price, limited availability and toxicity issues, set incentives for their replacement. Yet, in the past two decades significant progress in this direction has been achieved using for example Fe, Co and Mn complexes supported by pincer ligands.[8]

In this respect, also molybdenum constitutes an attractive substitute for precious metals, due to its low costs and environmentally benign nature.[9] Although the organometallic chemistry of molybdenum, particularly of its pincer complexes, has been studied in-depth in recent years[10], reports on its application in catalytic homogeneous nitrile hydrogenation are exceptionally scarce. In fact to date, only three examples have been reported for related reductions (Scheme 2). In 2012, Nikonov and co-workers described the application of imido-hydrido Mo(IV) complex **I** for the catalytic hydroboration of nitriles in the presence of HBCat (Cat = catechol). However, only aceto- and benzonitrile were tested as substrates.[11]



Scheme 1. General scheme for the hydrogenation of nitriles.

The group of Berke developed a molybdenum-catalyzed homogeneous nitrile hydrogenation, based on molybdenum(I)-amido pincer catalyst **II**. However, the developed protocol operated under relatively harsh conditions (5 mol% catalyst, 140 °C) to yield secondary imines in high selectivity.[5]

In 2020, Wang and co-workers published an efficient transfer hydrogenation of nitriles using molybdenum-thiolate complex **III** in combination with $NH_3{\cdot}BH_3$ as hydrogen donor. Notably, this methodology applies particularly mild conditions and is compatible with aliphatic and aromatic nitriles selectively forming primary amines. The versatility of the developed system is highlighted by the successful reduction of both cyano groups of industrially relevant adiponitrile to corresponding 1,6-diamino-hexane in 70% yield.[12]

In 2018, we described the synthesis of a series of molecular defined molybdenum PNP-pincer complexes and subsequently demonstrated their activity in the catalytic hydrogenation of acetophenones, styrenes and formamides (Figure 1).[13] Based on these works, herein we report the synthesis and structural characterization of a series of previously unknown molybdenum pincer complexes and their behavior in the hydrogenation of nitriles to primary amines.

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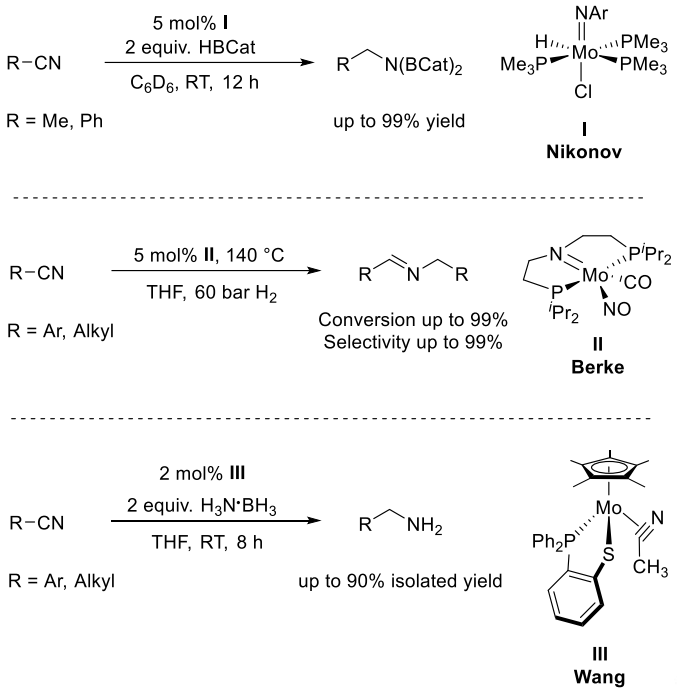


Scheme 2. Reported examples of molybdenum-catalyzed homogeneous nitrile reductions.

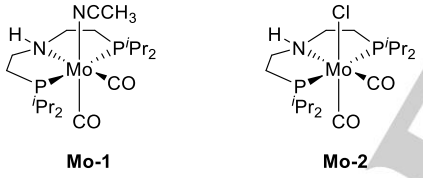
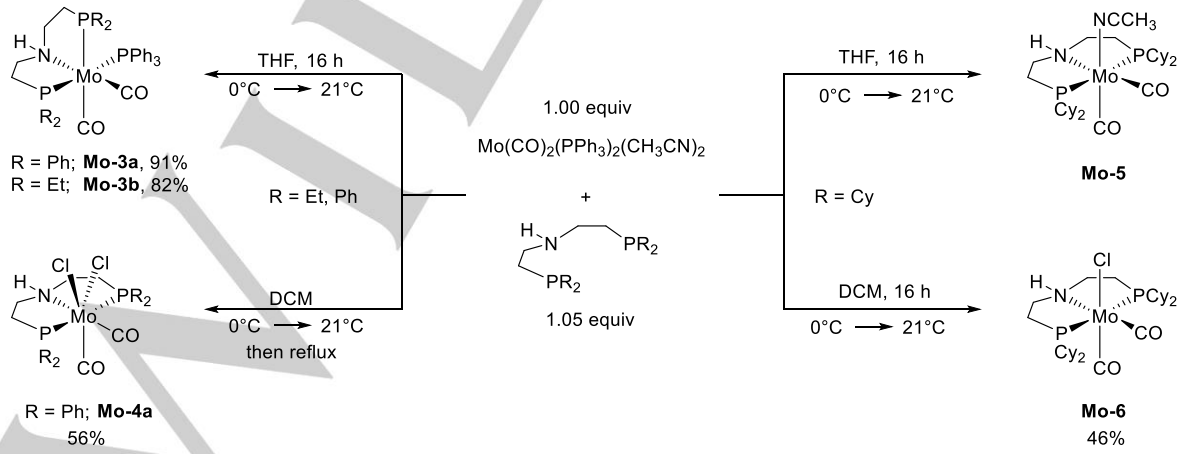


Figure 1. Catalytically active molybdenum pincer complexes recently synthesized by our group.

Results and Discussion

At the outset of our studies, we investigated whether our previously developed method for the synthesis of molybdenum complexes **Mo-1** and **Mo-2**, could be extended to other pincer ligands (Scheme 3).[13] Thus, PNP ligands $(Cy_2PCH_2CH_2)_2NH$, $(Ph_2PCH_2CH_2)_2NH$, $(Et_2PCH_2CH_2)_2NH$ as well as the NNN pincer ligand *bis*-(2-pyridylmethyl)amine were reacted with $Mo(PPh_3)_2(CH_3CN)_2(CO)_2$ in either dichloromethane (DCM) or tetrahydrofurane (THF). Applying $(Cy_2PCH_2CH_2)_2NH$ as ligand in DCM, resulted in the intended formation of Mo(I) complex **Mo-6** in 46% yield. However, when the reaction was carried out in THF as reaction solvent, the formation of a light green, ill-soluble powder was observed. Due to the extremely low solubility of this powder in all common organic solvents, we were not able to unequivocally confirm its identity by either NMR experiments or X-ray analysis of suitable single crystals. Nevertheless, EA, IR and HR/ESI-MS experiments strongly suggest the formation of the corresponding Mo(0) complex **Mo-5**.

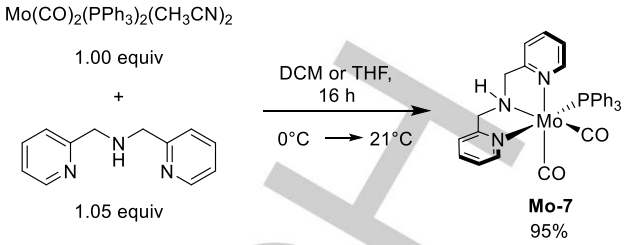
Next, we subjected $(Ph_2PCH_2CH_2)_2NH$ to the reaction with $Mo(PPh_3)_2(CH_3CN)_2(CO)_2$ in THF. Interestingly, we obtained Mo(0)-complex **Mo-3a**, featuring a PPh_3 ligand coordinated to the metal center, as the sole reaction product, in 91% yield. Attempts to transform **Mo-3a** into the corresponding CH_3CN derivative remained unsuccessful. Surprisingly, when the reaction was carried out in DCM under otherwise identical conditions, selective formation of **Mo-3a** was observed again. Even after stirring for several days at room temperature, $^{31}P\{^1H\}$ NMR analysis revealed **Mo-3a** as the main species. However, slow formation of a new resonance at 63 ppm occurred. Assuming, that **Mo-3a** is relatively stable towards chlorination, the reaction mixture was heated to 40 °C for three hours. $^{31}P\{^1H\}$ NMR analysis showed complete conversion of **Mo-3a** into the new species at 63 ppm. Subsequent isolation and characterization provided diamagnetic Mo(II) pincer complex **Mo-4a** in 56% yield.



Scheme 3. Synthesis of new molybdenum PNP pincer complexes.

When exploring the reactivity of $(Et_2PCH_2CH_2)_2NH$, we observed a similar reaction behavior as compared to $(Ph_2PCH_2CH_2)_2NH$. Performing the reaction in THF, we were able to isolate the corresponding Mo(0) **Mo-3b** in 82% yield. Nevertheless, carrying out the reaction in DCM resulted in the formation of complex product mixtures, even at –20 °C.

Finally, the NNN pincer ligand b*is*-(2-pyridylmethyl)amine was applied. The ligand reacted readily with $Mo(PPh_3)_2(CH_3CN)_2(CO)_2$ in DCM and THF, respectively, resulting in the formation of **Mo-7** in both cases (Scheme 4).



Scheme 4. Synthesis of previously unknown molybdenum NNN pincer complex **Mo-7**.

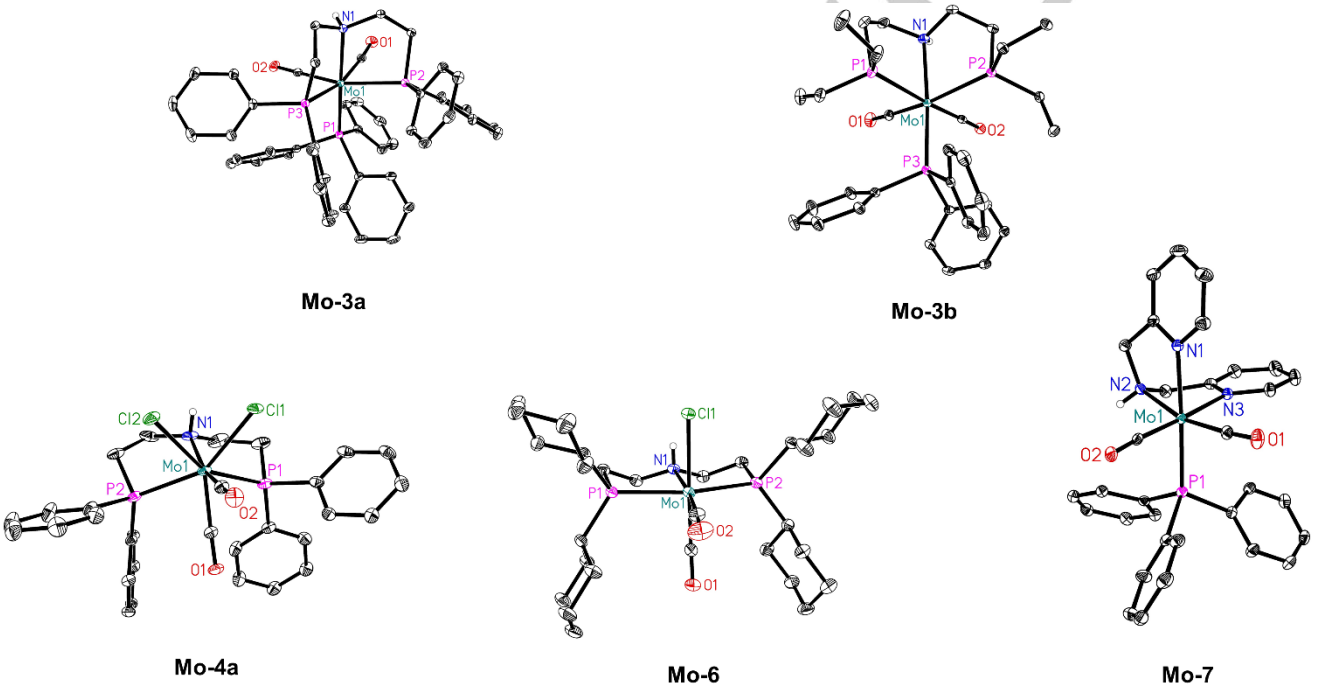


Figure 2. Molecular structures of **Mo-3a**, **Mo-3b**, **Mo-4a**, **Mo-6** and **Mo-7** in the solid state. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms, except the N-bound are omitted for clarity. For **Mo-6**, only one molecule of the asymmetric unit is shown.

Complex **Mo-7** proved to be remarkably stable towards chlorination and remained molecularly unchanged even after refluxing for 24h in DCM and DCE, respectively. All prepared coordination compounds have been characterized by standard techniques including ^{1}H, ^{13}C and $^{31}P\{^{1}H\}$ NMR (except **Mo-6** and **Mo-7**, see *vide infra*) and IR spectroscopy as well as elemental analysis (for NMR and IR spectra, see supporting information). Additionally, we were able to determine solid-state structures of complexes **Mo-3a**, **Mo-3b**, **Mo-4a**, **Mo-6** as well as **Mo-7** by X-ray analysis of suitable single crystals. Their structural views are depicted in Figure 2. However, due to the insolubility of **Mo-7** in all common NMR solvents, including benzene, toluene, THF, acetonitrile, DMSO and methanol, as well as the paramagnetic nature of **Mo-6**, we were unable to obtain meaningful NMR data of these complexes.

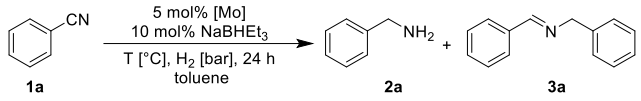
Complexes **Mo-3a**, **Mo-3b** and **Mo-7** adopt a distorted octahedral coordination geometry at the molybdenum center, with the CO ligands being in a *cis* orientation. The coordinated pincer ligands all exhibit a *fac* arrangement around the central metal atom. However, in complex **Mo-6** the *mer* coordination mode of the pincer ligand is observed with the CO ligands being in a *cis* arrangement. The described characteristics for **Mo-6** are in agreement with our previously published solid state structure of **Mo-2**.[13] The coordination geometry at the Mo atom of the hepta-coordinated Mo(II)-complex **Mo-4a** can be best described as distorted capped octahedral.

The recorded IR spectra of the reported complexes all show medium to strong carbonyl absorption bands between 1921 cm^{-1} and 1679 cm^{-1}.

Next, we tested the catalytic activity of the newly described molybdenum pincer complexes **Mo-3a**, **Mo-3b**, **Mo-4a**, **Mo-6**

and **Mo-7**, as well as of the previously reported compounds **Mo-1** and **Mo-2**, in the catalytic hydrogenation of benzonitrile **1a**. It has to be noted, that in our initial work some activity was reported in this transformation, using **Mo-2** as the catalyst, without further optimization. However, under the reported conditions, only modest conversion (42%) and poor product selectivity (13%) for the desired primary amine were observed.[13] In order to minimize potential decomposition of the homogeneous molybdenum catalysts, the initial catalyst screening was carried out at 100 °C in the presence of 10 mol% $NaBHEt_3$. Under these conditions full conversion was observed for **Mo-1** and **Mo-2**, yielding approximately 1:1 mixtures of **2a** and **3a** (Table 1, entries 1-2). All other Mo-complexes, however, provided inferior results (Table 1, entries 3-7). Interestingly, **Mo-4a** as well as **Mo-7** failed to give any conversion at all.

Table 1. Initial screening of Mo-catalysts and reaction parameters[a]



Entry	Catalyst	Conversion [%][b]	Yield **2** [%][b]	Yield **3** [%][b]
1	**Mo-1**	>99	58	40
2	**Mo-2**	>99	52	42
3	**Mo-3a**	62	38	20
4	**Mo-3b**	70	41	24
5	**Mo-4a**	<1	<1	<1
6	**Mo-6**	78	41	35
7	**Mo-7**	<1	<1	<1
8[c]	**Mo-1**	90	50	38
9[c]	**Mo-2**	81	42	35
10[d]	**Mo-1**	>99	55	41
11[e]	**Mo-1**	>99	96	<1
12[f]	**-**	4	<1	<1
13[g]	**Mo-1**	7	<1	<1

[a] Reaction conditions: 0.5 mmol substrate, 2 mL toluene, 5 mol% catalyst, 10 mol% $NaBHEt_3$ (1M in THF), 50 bar H_2, 100 °C, 24h. [b] Determined by GC using hexadecane as internal standard. [c] 80 °C. [d] 5 mol% $NaBHEt_3$ (0.5M in THF). [e] 5 mL toluene, 0.5 mmol substrate. [f] No catalyst was used. [g] No $NaBHEt_3$ added.

The activity of **Mo-1** and **Mo-2** was subsequently compared at a reduced temperature of 80 °C (Table 1, entries 8 and 9). Here, **Mo-1** provided a superior conversion of 90%. Based on this result and its more convenient synthesis, we focused on **Mo-1** in the due course of the optimization process. Selecting 80 °C reaction temperature and 5 mol% of **Mo-1** (Table 1, entry 8) as the optimal setting, we explored several different solvents. In contrast to previous reports on base metal catalyzed hydrogenation of nitriles, **Mo-1** was found to be completely inactive in *i*-PrOH, while toluene as solvent provided the best results. Applying THF, 1,4-dioxane and Bu_2O resulted in significantly lower activities and predominantly yielded **3a** as the reaction product. Other aliphatic solvents such as *n*-heptane and cyclohexane, were not suitable for the attempted transformation (Fig. 3).

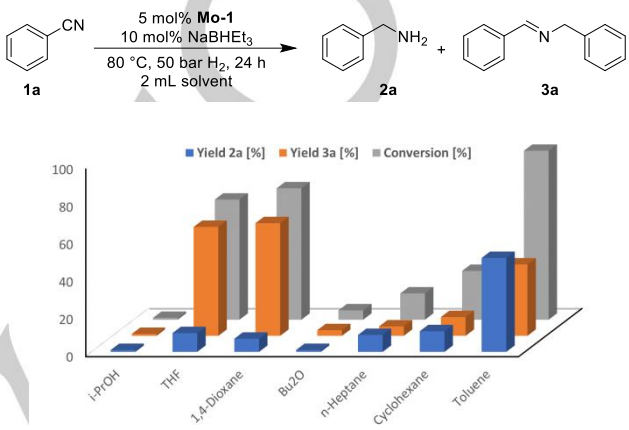


Figure 3. Study of the solvent effect in the hydrogenation of benzonitrile **1a** to benzylamine **2a** and *N*-benzylidenebenzylamine **3a** catalyzed by **Mo-1**.

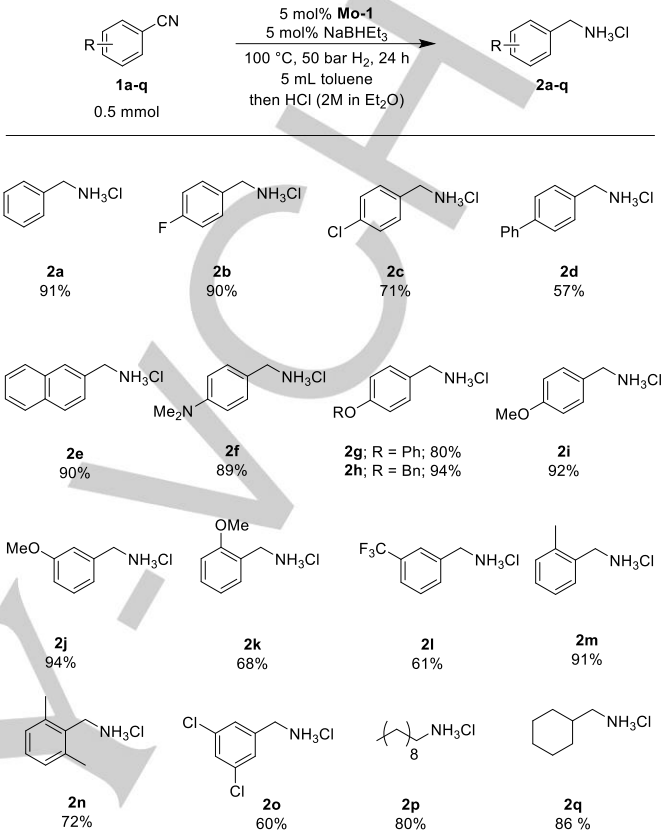
Subsequently, we investigated the influence of dihydrogen pressure, catalyst loading, the amount of additive used (Table S1, see supporting information), as well as the substrate concentration (Table S2, see supporting information) on the reaction outcome. Reducing the catalyst loading to 2.5 mol% resulted in a significantly less active system. However, lowering the amount of additive to 5 mol% led to no loss in reactivity.
Increasing the H_2 pressure to 80 bar showed no observable effect. Albeit, carrying out the reaction at 30 bar of dihydrogen caused a sharp drop in catalyst activity. A rise of the reaction temperature to 100 °C eventually resulted in full conversion of **1a** in the presence of 5 mol% $NaBHEt_3$ and **Mo-1**, respectively (Table 1, entry 10). Next, we evaluated several substrate concentrations based on 0.5 mmol of **1a**, ranging from 0.08M to 0.5M. Notably, using 5 mL of toluene proved to be the optimal concentration, providing the desired product benzylamine **2a** in 96% yield (Table 1, entry 11). Finally, a series of control experiments were carried out. In the absence of **Mo-1**, no catalytic reaction took place (Table 1, entry 12). Similarly, no product formation could be detected, when the reaction was performed in the absence of $NaBHEt_3$ (Table 1, entry 13). In order to confirm, that no heterogeneous catalysis takes place, a mercury poisoning experiment was conducted, revealing no loss of activity (Table S2, see supporting information).

Having optimized conditions in hand, we proceeded to the application of **Mo-1** in the hydrogenation of a variety of different

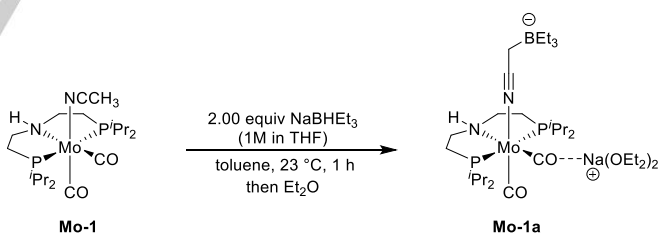
benzonitriles to the corresponding benzylamines. As shown in Scheme 5 our developed methodology appeared to be particularly well suited for electron-rich benzonitriles and the intended primary amines were consistently obtained in high yields. Substituents in *para*-, *meta*- and *ortho*-position of the phenyl ring were well tolerated and even sterically hindered nitriles **1k** and **1m** were successfully converted, furnishing **2k** and **2m** in isolated yields of 68% and 91%, respectively. Notably, when the steric bulk was further increased, using 2,6-dimethylbenzonitrile **1n**, we were still able to isolate the desired primary amine **2n** in a good yield of 72%. The system proved to be insensitive towards halides such as fluoride and chloride (**2b** and **2c**) and no dehalogenation products were observed during the catalysis. This was additionally the case when 3,5-dichloro benzonitrile (**1o**) was employed, providing 3,5-dichlorobenzylamine **2o** in 60% isolated yield. Moreover, also a benzylether moiety, often cleaved under hydrogenation conditions, remained unaffected and no deprotection could be detected in product (**2h**). However, some (hetero)benzonitriles with substituents in either *ortho*- or *para*-position, such as H_2N-, CF_3-, CO_2Me-, carbonyl-, cyano- and nitro groups, either gave only poor conversions or did not yield the desired primary amines in sufficient quantities (see Table S3, supporting information). Clearly, in these cases the observed reactivity of the catalyst is not an easy function of the electron-donating or electron-withdrawing character of the respective substituents. Apparently, there are several factors influencing the observed reactivity. In Table S3 some of the observed side products are mentioned.

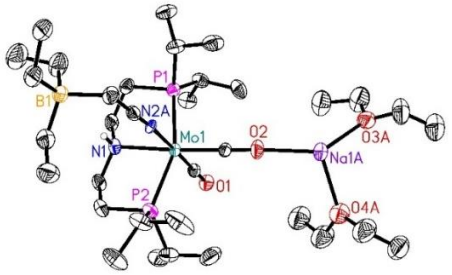
Interestingly, for 2- and 4-trifluoromethyl-substituted benzonitrile low conversion and negligible product yields were observed, while in the case of *meta*-CF_3-substituted nitrile **1l** the corresponding primary amine **2l** could be isolated in 61% yield. Furthermore, we successfully applied two aliphatic nitriles **1p** and **1q** to our reported protocol. In both cases, **Mo-1** proved to be a suitable catalyst and we were able to isolate the intended reaction products **2p** and **2q** in 80% and 86% yield, respectively.

Finally, with respect to the mechanism we became interested in the molecular structure of the organometallic species formed from the reaction of **Mo-1** and $NaBHEt_3$. Hence, we conducted a control experiment, treating 0.5 mmol of **Mo-1** with an excess of $NaBHEt_3$ in toluene at room temperature (for experimental details, see Supporting Information). The reaction proceeded rapidly, resulting in the formation of a clear red solution within less than one minute. The $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixture revealed the formation of a strong singlet resonance at 74 ppm as the main product alongside some free ligand. Attempts to characterize the corresponding species by X-ray analysis of suitable single crystals were successful and provided the solid-state structure of **Mo-1a** (Scheme 6). As expected, the applied additive acts as base and abstracts a proton from **Mo-1**. Interestingly, the deprotonation does not involve the NH moiety of the pincer ligand but takes place at the CH_3-group of the coordinated acetonitrile ligand, resulting in the formation of a covalent C–B bond. This observed reactivity is in sharp contrast to classical reaction patterns observed for pincer supported (base) metal catalysts, where basic additives typically activate the catalyst by deprotonation of the ligand backbone.[14]



Scheme 5. Substrate scope for nitrile reduction with molybdenum pincer complex **Mo-1**.

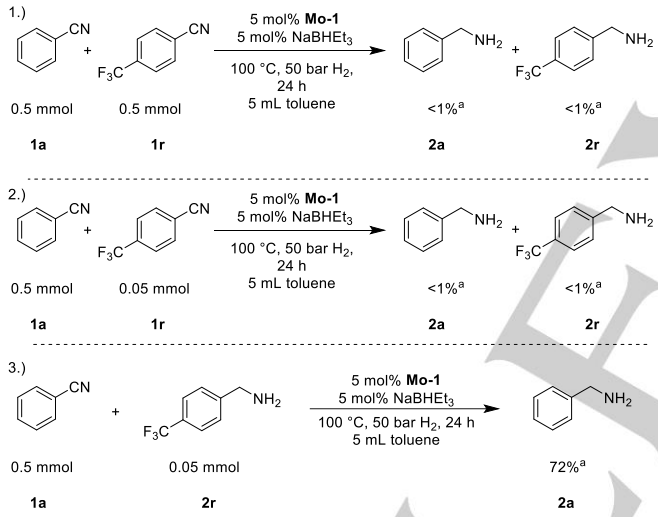




Scheme 6. Synthesis of **Mo-1a** (top). Molecular structure of **Mo-1a** in the solid state (bottom). Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms, except the N-bound are omitted for clarity. Disordered parts of the molecule are only shown in one orientation.

In order to confirm that **Mo-1a** indeed plays an active role in the catalysis, the benchmark reaction was carried out using 5 mol% **Mo-1a** in the absence of $NaBHEt_3$ under otherwise identical conditions. Benzylamine **2a** was observed in 92% yield, proofing the involvement of **Mo-1a** in in the catalytic hydrogenation of benzonitrile **1a**. Next, we were interested in the reactivity of **Mo-1a** towards dihydrogen. Therefore, **Mo-1** was activated with two equivalents of $NaBHEt_3$ in d_8-toluene and subsequently stirred for 3h at 100°C in the presence of 50 bar H_2 (for experimental details see Supporting Information). Analysis of the reaction mixture by ^{31}P NMR spectroscopy revealed two new main resonances at 89.1 and 75.9 ppm, thus proving that **Mo-1a** had undergone a reaction with H_2. However, no hydride signals could be detected according to the obtained ^1H NMR spectrum. The resonance at 75.9 ppm corresponds to the Mo(0) complex *fac*-$[(^iPr_2PCH_2CH_2)_2NH]Mo(CO)_3$[13a], revealing a potential catalyst deactivation pathway.

Furthermore, to understand the poor catalytic performance of **Mo-1** when electron deficient nitriles are applied, a series of control experiments were conducted, too (Scheme 7).



Scheme 7. Control experiments carried out. [a] Yields determined by GC using hexadecane as internal standard. 1.) Poisoning experiment using 1 equiv. of **1r**. 2.) Poisoning experiment using 10 mol% of **1r**. 3.) Poisoning experiment using 10 mol% of **2r**.

Adding 0.5 mmol of 4-(trifluoromethyl)benzonitrile **1r** to the benchmark reaction resulted in a complete shut-down of catalyst activity and no benzylamine **2a** could be detected. Interestingly, also in the presence of only 10 mol% of **1r**, no formation of **2a** occurred. We therefore conclude, that **1r** acts as a strong catalyst poison and thus inhibits the catalysis (for experimental details on the described reactions, see Supporting Information). Subsequently, we investigated whether the corresponding primary amine, 4-(trifluomethyl)benzylamine **2r**, could act as catalyst poison too. Interestingly, adding 10 mol% of **2r** resulted in full conversion of **1a** and benzylamine was observed in 72% yield.

Conclusions

In summary, we reported the synthesis and structural characterization of a series of previously unknown molybdenum pincer complexes. Depending on the used pincer ligand and the reaction solvent, different complex structures are obtained. Furthermore, the first molybdenum-catalyzed reduction of nitrile to primary amines using molecular hydrogen is described. In fact, Mo-pincer complex, **Mo-1**, can be used as efficient catalyst for the selective catalytic hydrogenation of selected aromatic and aliphatic nitriles to give the corresponding primary amines. Additionally, we isolated and identified catalytic intermediate **Mo-1a** and subsequently proved its role in the catalytic process.

Experimental Section

General Procedure for Catalysis Experiments: All hydrogenation reactions were set up under Ar in a 300 mL autoclave (PARR Instrument Company). In order to avoid unspecific reductions, all catalytic experiments were carried out in 8 mL glass vials, which were set up in an alloy plate and placed inside the autoclave.

In a glove box, an 8 mL glass vial containing a stirring bar was charged with complex **Mo-1** (12.5 mg; 5 mol%). Toluene (5 mL) was added and the corresponding greenish suspension was treated with $NaBHEt_3$ (0.5 M in THF; 50 µL; 5 mol%). The reaction mixture was stirred for 20 minutes and the corresponding substrate was subsequently added. Afterwards, the vial was capped and transferred into an autoclave. Once sealed, the autoclave was purged three times with 10 bar of hydrogen, then pressurized to the desired hydrogen pressure (50 bar) and placed into an aluminum block that was preheated to the desired temperature (100 °C). After 24 h, the autoclave was cooled in an ice bath and the remaining gas was released carefully. The solution was subsequently diluted with 50 mL Et_2O and filtered through a small pad of silica. The silica was washed with DCM (10 mL) and the combined filtrates were treated with 2 mL of HCl (2M in Et_2O). The obtained precipitate was filtered off, washed two times with 20 mL ethyl acetate and two times with 20 mL Et_2O and subsequently dried *in vacuo*. For the characterization of the products of the catalysis, see Supporting Information.

Acknowledgements

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Keywords: molybdenum • pincer complexes • hydrogenation • nitrile • primary amine

References:

[1] a) D. M. Bagal, B. M. Bhanage, *Adv. Synth. Catal.* **2015**, *357*, 883-900.

[2] For a general book about organic reductions, see: a) J. Seyden-Penne in *Reductions by the Alumino- and Borohydrides in Organic Synthesis*, *2nd edition*, Wiley-VCH, New Yorck, United States of America, **1997**; for selected examples see: b) S. Zhou, K. Junge, D. Addis, S. Das, M. Beller, *Angew. Chem. Int. Ed*. **2009**, *48*, 9507-9510; c) S. Das, D. Addis, S. L. Zhou, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 1770-1771; d) G. Pelletier, W. S. Bechara, A. B. Charette, *J. Am. Chem. Soc.* **2010**, *132*, 12817-12819; e) S. Das, D. Addis, K. Junge, M. Beller, *Chem. Eur. J.* **2011**, *17*, 12186-12192; f) C. Cheng, M. Brookhart, *J. Am. Chem. Soc.* **2012**, *134*, 11304-11307; g) S. Das, B. Wendt, K. Moller, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2012**, *51*, 1662-1666; h) S. Park, M. Brookhart, *J. Am. Chem. Soc.* **2012**, *134*, 640-653; i) T. Dombay, C. Helleu, C. Darcel, J. B. Sortais, *Adv. Synth. Catal*. **2013**, *355*, 3358-3362; j) J. T. Reeves, Z. L. Tan, M. A. Marsini, Z. X. S. Han, Y. B. Xu, D. C. Reeves, H. Lee, B. Z. Lu, C. H. Senanayakea, *Adv. Synth. Catal*. **2013**, *355*, 47-52; k) E. Blondiaux, T. Cantat, *Chem. Commun.* **2014**, *50*, 9349-9352; l) N. L. Lampland, M. Hovey, D. Mukherjee, A. D. Sadow, *ACS Catal.* **2015**, *5*, 4219-4226; m) D. Mukherjee, S. Shirase, K. Mashima, J. Okuda, *Angew. Chem. Int. Ed.* **2016**, *55*, 13326-13329.

[3] a) H. C. Brown, S. Narasimhan, Y. M. Choi, *Synthesis* **1981**, 441-442; b) S. Werkmeister, K. Junge, M. Beller, *Org. Process. Res. Dev.* **2014**, *18*, 289-302.

[4] a) P. A. Dub, T. Ikariya, *ACS Catal.* **2012**, *2*, 1718-1741; b) A. M. Smith, R. Whyman, *Chem. Rev.* **2014**, *114*, 5477-5510; c) A. M. Smith, R. Whyman, *Chem. Rev*. **2014**, *114*, 5477-5510.

[5] a) S. Chakraborty, H. Berke, *ACS Catal.* **2014**, *4*, 2191-2194.

[6] K. Levay, L. Hegedüs, *Curr. Org. Chem.* **2019**, *23*, 1881-1900.

[7] For selected examples see on Rh, Ru, Ir and Re-catalyzed nitrile hydrogenations see: a) T. Yoshida, T. Okano, S. Otsuka, J. Chem., *Chem. Commun*. **1979**, 870-871; b) R. A. Grey, G. P. Pez, A. Wall, J. Corsi, *J. Chem. Soc., Chem. Commun.* **1980**, 783-784; c) R. A. Grey, G. P. Pez, A. Wallo, *J. Am. Chem. Soc.* **1981**, *103*, 7536-7542; d) C. Chin, B. Lee, *Catal. Lett.* **1992**, *14*, 135-140; e) T. Li, I. Bergner, F. N. Haque, M. Zimmer-De Iuliis, D. Song, R. Morris, *Organometallics* **2007**, *26*, 5940-5949; f) S. Enthaler, D. Addis, K. Junge, G. Erre, M. Beller, *Chem. Eur. J.* **2008**, *14*, 9491-9494; g) S. Enthaler, K. Junge. D. Addis, G. Erre, M. Beller, *ChemSusChem* **2008**, *1*, 1006-1010; h) D. Addis, S. Enthaler, K. Junge, B. Wendt, M. Beller, *Tetrahedron Lett.* **2009**, *50*, 3654-3656; i) R. Reguillo, M. Grellier, N. Vautravers, L. Vendier, S. Sabo-Etienne, *J. Am. Chem. Soc.* **2010**, *132*, 7854-7855; j) C. Gunanathan, M. Hölscher, W. Leitner, *Eur. J. Inorg. Chem.* **2011**, 3381-3386; k) K. Rajesh, B. Dudle, O. Blacque, H. Berke, *Adv. Synth. Catal.* **2011**, *353*, 1479-1484; l) S. Werkmeister, K. Junge, B. Wendt, A. Spannenberg, H. Jiao, C. Bornschein, M. Beller, *Chem. Eur. J.* **2014**, *20*, 427-431; m) J. Neumann, C. Bornschein, H. Jiao, K. Junge, M. Beller, *Eur. J. Org. Chem.* **2015**, 5944-5948; n) J.-H. Choi, M. H. G. Prechtl, *ChemCatChem* **2015**, *7*, 1023-1028; o) R. Adam, C. B. Bheeter, R. Jackstell, M. Beller, *ChemCatChem* **2015**, *8*, 1329-1334; p) R. Adam, E. Alberico, W. Baumann, H.-J. Drexler, R. Jackstell, H. Junge, M. Beller, *Chem. Eur. J.* **2016**, *22*, 4991-5002; q) Y. Sato, Y. Kayaki, T. Ikariya, *Organometallics* **2016**, *35*, 1257-1264.

[8] For a general review regarding Co, Fe and Mn catalyzed homogeneous nitrile hydrogenations see: a) D. M. Sharma, B. Punji, *Chem. Asian. J.* **2020**, 15, 690-708; For selected examples see: b) C. Bornschein, S. Werkmeister, B. Wendt, H. Jiao, E. Alberico, W. Baumann, H. Junge, K. Junge, M. Beller, *Nat. Commun.* **2014**, *5*, 4111; c) A. Mukherjee, D. Srimani, S. Chakraborty, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2015**, *137*, 8888-8891; d) S. Lange, S. Elangovan, C. Cordes, A. Spannenberg, H. Jiao, S. Bachmann, M. Scalone, C. Topf, K. Junge, M. Beller, *Catal. Sci. Technol.* **2016,** *6*, 4768-4772; e) S. Charkraborty, D. Milstein, *Chem. Commun.* **2016**, *52*, 1812-1815; f) S. Elangovan, C. Topf, S. Fischer, H. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge, M. Bellller, *J. Am. Chem. Soc.* **2016**, *138*, 8809-8814; g) S. Chakraborty, D. Milstein, *ACS Catal.* **2017**, *7*, 3968-3972; h) K. Tokmic, B. J. Jackson, A. Salazar, T. J. Woods, A. R. Fout, *J. Am. Chem. Soc*. **2017**, *139*, 13554-13561; i) R. Adam, C. B. Bheeter, J. R. Cabrero-Antonino, K. Junge, R. Jackstell, M. Beller, *ChemSusChem* **2017**, *10*, 842-846; j) H. Li, A. Al-Dakhil, D. Lupp, S. S. Gholap, Z. Lai, L.-C. Liang. K. W. Huang, *Org. Lett.* **2018**, *20*, 6430-6435; k) H. Dai, H. Guan, *ACS Catal,* **2018**, *8*, 9125-9130; l) J. Schneekönig, J. Tannert, H. Hornke, M. Beller, K. Junge, *Catal. Sci. Technol.* **2019**, *9*, 1779-1783.

[9] S. Chakraborty, O. Blacque, T. Fox, H. Berke, *Chem. Asian J.* **2014**, *9*, 328-337.

[10] a) W. Schirmer, U. Flörke, H. Haupt, *Z. anorg. Allg. Chem.* **1987**, *545*, 83-97; b) J. Ellermann, M. Moll, N. Will, *J. Organomet. Chem.* **1989**, 378, 73-79; c) H. F. Lang, P. E. Fanwick, R. A. Dalton, *Inorg. Chim. Acta* **2002**, *329*, 1-8; d) B. Benito-Garagorri, E. Becker, J. Wiedermann, W. Lackner, M. Pollak, K. Meireiter, J. Kisala, K. Kirchner, *Organometallics* **2006**, *25*, 1900-1913; e) K. Arashiba, Y. Miyake, Y. Nishibayashi, *Nature Chem.* **2011**, *3*, 120-125; f) K. Arashiba, K. Sasaki, S. Kuriyama, Y. Miyake, Y. Nakanishi, Y. Nishibayashi, *Organometallics* **2012**, *31*, 2035-2041; g) E. Kinoshita, K. Arashiba, S. Kuriyama, Y. Miyake, Y. Shimazaki, H. Nakanishi, Y. Nishibayashi, *Organometallics*, **2012**, *31*, 8437.8443; h) O. Öztopcu, C. Holzhacker, M. Puchberger, M. Weil, K. Meireiter, L. F. Veiros, K. Kirchner, *Organometallics*, **2013**, *32*, 3042-3052; i) S. R. M. M. de Aguiar, B. Stöger, B. Pittenauer, M. Puchberger, G. Allmair, L. F. Veiros, K. Kirchner, *J. Organomet. Chem.* **2014**, *760*, 74-83; j) S. R. M. M. de Aguiar, O. Öztopcu, B. Stöger, K. Meireiter, L. F. Veiros, B. Pittenauer, G. Allmair, K. Kirchner, *Dalton Trans.* **2014**, *43*, 14669-14679; k) S. Chakraborty, O. Blacque, H. Berke, *Dalton Trans.* **2015**; *44*, 6560-6570; l) R. Castro-Rodrigo, S. Chakraborty, L. Munjanja, W. Brennessel, W. D. Jones, *Organometallics* **2016**, *35*, 3124-3131; m) Y. Zhang, P. G. Williard, W. H. Bernskoetter, *Organometallics* **2016**, *35*, 860-865; n) S. R. M. M. de Aguiar, B. Stöger, B. Pittenauer, G. Allmaier, L. F. Veiros, K. Kirchner, *Dalton Trans.* **2016**, *45*, 13834-13845; o) G. A. Silantyev, M. Förster, S. Schluschlaß, J. Abbensetz, C. Würtele, C. Volkmann, M. C. Holthausen, S. Schneider, *Angew. Chem. Int. Ed.* **2017**, *56*, 5872-5876; p) S. M. M. de Aguiar, O. Öztopcu, A. Troiani, G. de Petris, M. Weil, B. Stöger, L. F. Veiros, B. Pittenauer, G. Allmair, K. Kirchner, *Eur. J. Inorg. Chem.* **2018**, *7*, 876-884; q) M. V. Joannou, M. J. Bezdek, P. J. Chirik, *ACS Catal.* **2018**, *8*, 5276-5285; r) M. J. Bezdek, P. J. Chirik, *Angew. Chem. Int. Ed.* **2018**, *8*, 2224-2228; s) M. J. Bezdek, P. J. Chirik, *Organometallics* **2019**, *38*, 1682-1687; t) Y. Ashida, S. Kondo, K. Arashiba, T. Kikuchi, K. Nakajima, S. Kakimoto, Y. Nishibayashi, *Synthesis* **2019**, *51*, 3792-3795; u) M. Alvarez, A. Galindo, P. J. Perez, E. Carmona, *Chem. Sci.* **2019,** *10*, 8541-8546; v) R. Tran, S. M. Kilyanek, *Dalton Trans.* **2019**, *48*, 16304-16311; w) M. Pfeil, T. A. Engesser, A. Koch, J. Junge, J. Krahmer, C. Näther, F. Tuczek, *Eur. J. Inorg. Chem.* **2020**, 1437-1448.

[11] A. Y. Khalimon, P. Farha, L. G. Kuzmina, G. I. Nikonov, *Chem. Commun.* **2012***, 48*, 455-457.

[12] S. F. Hou, J. Y. Chen, M. Xue, M. Jia, X. Zhai, R.-Z. Liao, C.-H. Tung, W. Wang, *ACS Catal.* **2020***, 10*, 380-390.

[13] a) T. Leischner, A. Spannenberg, K. Junge, M. Beller, *Organometallics* **2018**, *37*, 4402-4408; b) T. Leischner, L. A. Suarez, A. Spannenberg, K. Junge, A. Nova, M. Beller, *Chem. Sci.* **2019**, *10*, 10566-10576.

[14] (a) E. Ben-Ari, G. Leitus, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2006***, 128*, 15390-15391, (b) J. R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed*. **2015**, *54*, 12236-12273.

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