Molybdenum Cluster Catalysis

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Chemoselective Transfer Hydrogenation to Nitroarenes Mediated by Cubane-Type Mo_3S_4 Cluster Catalysts**

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Functionalized anilines are valuable intermediates for the manufacture of dyes, pigments, agrochemicals, and pharmaceuticals.[1] Furthermore, they represent key precursors for the synthesis of important chemicals, such as imines[2] and aromatic azo compounds.[3] Among the well-established synthetic methods for the preparation of aromatic amines, the chemoselective reduction of nitro groups is preferred on both industrial and laboratory scales. In general, the most frequently used catalysts for this benign nitro group hydrogenation make use of noble metals such as Pt and Pd supported on active carbon or alumina, although Ni-based systems are applied as well.[4]

A crucial issue for the general application of catalysts for nitro reduction is selectivity. In this respect, adding surface modifiers, tailoring the metal particle size, or modifying the support, can all improve the chemoselectivity of heterogeneous catalysts. Recently, Corma and co-workers demonstrated that Au-based catalysts show high selectivity for the reduction of the nitro arenes.[5] Nevertheless, the limited availability of precious metals makes it desirable to search for alternatives that are more economical. For example, significant attention is being focused on iron-based catalysts as a promising solution.[6] Compared to heterogeneous catalysis, homogeneous catalysis often offers a more rational tuning of the catalysts to obtain a broad functional group tolerance and high activity under mild conditions.

Transfer hydrogenation using formic acid provides an attractive alternative to catalytic hydrogenation, where autoclaves and the handling of hydrogen are required for the reduction of nitroarenes.[7,8] Hence, a wide variety of organometallic catalysts based on Pd,[7] Ru,[7–9] Rh,[7] Co,[10] Cu,[10] and even Fe[11] have been described. However, to the best of our knowledge, molybdenum complexes have never been used as catalysts following this protocol. Furthermore, few examples of molybdenum-mediated reductions have been reported and all employ hydrogen,[12] expensive silanes,[13] or stoichiometric amounts of molybdenum compounds.[14]

Based on our experience with the transfer hydrogenation mechanism for the reaction between trinuclear Mo_3S_4 cluster hydrides and acids,[15,16] we became interested in pursuing their potential applications as catalysts in the reduction of organic substrates. Molecular complexes of the general formula $[M_3S_4X_3(\text{diphosphane})_3]^+$, shown in Figure 1, are air-stable and easily accessible, which makes them excellent candidates for further mechanistic and catalytic investigations. The M_3S_4 cluster unit in these complexes is a robust entity in solution and as such it does not coexist in equilibrium with lower nuclearity species. In general, the reaction of $[M_3S_4H_3(\text{dmpe})_3]^+$ (dmpe = 1,2-(bis)dimethylphosphinoethane) with acids occurs with the formation of dihydrogen-bonded species, either as transition states or reaction intermediates.

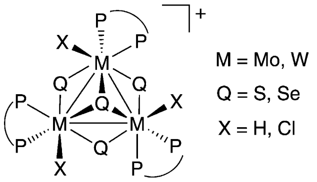

Figure 1. Cubane-type M_3Q_4 clusters.

Transition metal clusters may lead to multiple metal–metal reactivity, providing new families of catalysts that exhibit novel or unique properties.[17] Well-defined cluster complexes have also been postulated as reasonable models for heterogeneous catalysis. Therefore, a better understanding, in which mechanistic arguments prevail over heuristic experiments, of the reaction steps governing these homogeneous processes is crucial for the improved design of more efficient catalysts.

Herein, we present the first study on the molybdenum-catalyzed transfer hydrogenation of nitroarenes. Our work shows that trinuclear Mo_3S_4 hydrides functionalized with outer diphosphane ligands are excellent catalysts for the highly selective reduction of nitroarenes to the corresponding anilines.

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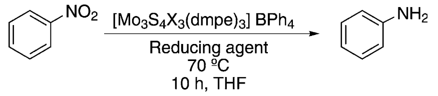
At the start of our work, the reduction of nitrobenzene was investigated as a benchmark system. Optimization of the reaction conditions (temperatures, hydrogen sources, catalyst loading, and solvents; see also the Supporting Information, Table SI1) showed that the best results were obtained in tetrahydrofuran at 70 °C, where full conversion and up to 99% yield of aniline were observed. Among the different hydrogen sources (Table 1, entries 1–5) an azeotropic 5:2 mixture of HCOOH and NEt_3 gave the best result as a reducing agent. Longer reaction times are required when formic acid or formates were used for the reduction. The reaction selectivity decreased (75% yield) when expensive silanes such as phenylsilane are employed. Relevant mechanistic information is obtained from the lack of reactivity observed when the reaction is carried out under H_2, as only traces of aniline (5%) are detected. This result clearly indicates that Mo_3S_4-mediated nitro reduction catalysis occurs by transfer hydrogenation, discarding the possibility of direct hydrogenation by hydrogen generated from formic acid decomposition.

Table 1: Reductant testing for the reduction of nitrobenzene catalyzed by molybdenum clusters.[a]



Entry	X	Reducing agent	Conversion [%][b]	Yield [%][b]
1	H	$HCOOH/Et_3N$ (5:2)	> 99	> 99
2	H	$HCOO(NH_4)$	32	29
3	H	HCOOH	23	22
4[c]	H	$PhSiH_3$	> 99	75
5[d]	H	H_2	9	5
6[e]	H	$HCOOH/Et_3N$ (5:2)	73	73
7[f]	H	–	41	35
8[f]	Cl	–	–	–
9	Cl	$HCOOH/Et_3N$ (5:2)	65	63
10[g]	Cl	$HCOOH/Et_3N$ (5:2)	> 99	> 99

[a] Reaction conditions: nitrobenzene (0.1 mmol), reducing agent (3.5 equiv), catalyst (3 mol%), THF (2 mL), 10 h, 70 °C. [b] Determined by GC analysis using *n*-hexadecane as an internal standard. [c] Catalyst (8 mol%), 18 h. [d] 5 or 30 bar H_2, 15 h, 80 °C. [e] Catalyst (2 mol%). [f] Catalyst (55 mol%), 18 h. [g] 19 h.

Furthermore, optimal quantities of reducing agent were found by gradually increasing the concentration of formic acid using the azeotropic $HCOOH/NEt_3$ 5:2 mixture. In the presence of stoichiometric amounts (3 equiv) of HCOOH, a 97% yield of aniline is obtained; thus indicating that there is basically no unproductive decomposition of formic acid to hydrogen (Table SI2).

Because of safety concerns, the formation of hydroxylamine as a reaction intermediate constitutes a drawback in some catalytic reductions of nitroarenes. Fortunately, in our case the conversion of nitrobenzene occurred almost quantitatively with > 99% yield of aniline. No traces of hydroxylamine were observed during catalysis (< 1%; Figure SI1).

From a mechanistic point of view, the (transfer) hydrogenation of nitroarenes can occur through two routes: 1) direct reduction and 2) an indirect pathway involving condensation of the initially formed nitrosoarene and the hydroxylamine to produce azo derivatives.[18] The feasibility of this second route was investigated by using azoxybenzene or azobenzene as reactants. These experiments were carried out using a higher cluster loading (20 mol%), because the transient nature of these intermediates during the reaction from nitrobenzene makes the relative amount of catalyst much higher than the normal catalytic amount. The reduction of azobenzene needed up to 18 h to reach a conversion of 90%, with only a 25% yield of aniline. When azoxybenzene was used as a reactant, azobenzene appeared as the primary product (20% yield) and aniline was only formed in 16% yield. Therefore, we conclude that the formation of aniline in the presence of the active molybdenum hydride cluster preferentially takes place through the direct reduction route.

Obviously, cluster catalysis requires that the polynuclear metal fragment remains intact during the catalytic cycle or at least that mononuclear species, which are produced from cluster decomposition, are not responsible for the catalytic activity. To prove cluster catalysis, several experiments were carried out using various lower nuclearity molybdenum complexes (Table SI3) in the presence and absence of the dmpe ligand under the optimized catalytic conditions. In all cases, little or no reactivity was observed, which shows the unique behavior of the Mo_3S_4 hydride. Further evidence of cluster integrity during the catalytic reaction comes from reaction monitoring by electrospray ionization mass spectrometry (ESI-MS) techniques, which in turn can be used to extract valuable mechanistic information.[19] For ESI-MS reaction monitoring, the recently reported pressurized sample infusion (PSI) method was used.[20] Under catalytic conditions, the base peak corresponds to Et_3NH^+, which inhibits ionization of the rest of the cluster species under ESI conditions. Consequently, higher cluster loading (50 mol%) is needed when ESI-MS is used to unravel the nature of the species present during the reaction. For this purpose, the reaction mixture was heated to 70 °C and re-examined over time for 90 min, whereupon a 25% yield of aniline was formed (Figure 2).

At room temperature ($t = 0$ min), a prominent peak centered at $m/z = 870.9$ is initially observed, which is assigned to $[Mo_3S_4H_3(dmpe)_3]^+$ ($\mathbf{1}^+$) hydride on the basis of the m/z value as well as its characteristic isotopic pattern. Additional signals of the monosubstituted $[Mo_3S_4H_2(OOCH)(dmpe)_3]^+$ ($\mathbf{2}^+$) and disubstituted $[Mo_3S_4H(OOCH)_2(dmpe)_3]^+$ ($\mathbf{3}^+$) formate complexes at $m/z = 914.8$ and $m/z = 959.8$, respectively, are also observed. After 15 min, the trisubstituted $[Mo_3S_4(OOCH)_3(dmpe)_3]^+$ ($\mathbf{4}^+$) formate complex is also identified at $m/z = 1000.8$. After 30 min (up to 90 min), only $\mathbf{1}^+$ and $\mathbf{4}^+$ are observed and their relative intensities remain largely unchanged, indicating that a stationary state has been achieved. Apparently, $\mathbf{1}^+$ is the active species, which is subsequently regenerated from the $\mathbf{4}^+$ formate cluster. Additional support for this hypothesis is provided by investigation of the characteristic gas-phase dissociation of $\mathbf{4}^+$ by collision induced dissociation (CID) experiments, which are commonly used to unravel elementary steps in catalytic cycles.[21] In general, these experiments demonstrate that Mo–formate

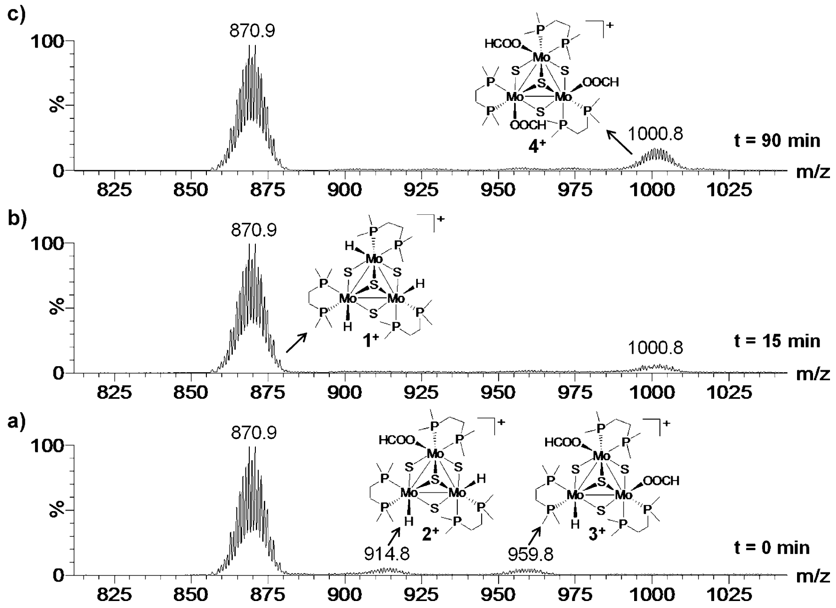
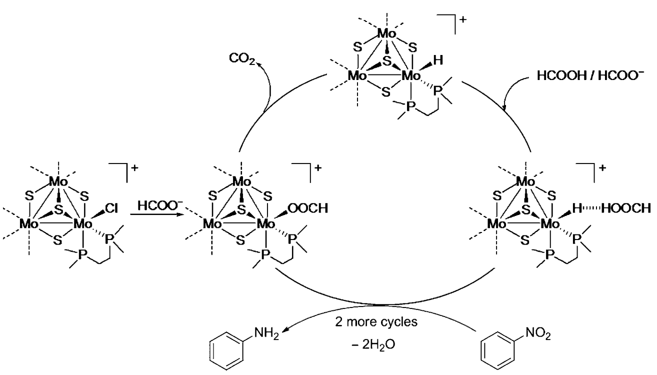


Figure 2. ESI mass spectra from monitoring of the nitrobenzene reduction at a) $t=0$ min , b) $t=15$ min, and c) $t=90$ min.

functional groups in the trinuclear **4**$^+$ cluster are prone to be transformed into Mo–hydride groups through the liberation of CO_2, very likely by a β-hydride elimination process (Figure SI2).[11,22] Once it was shown that degradation of the hydride cluster does not take place during the catalytic process, some additional experiments were done to confirm **1**$^+$ as the active species in the catalytic cycle (Table 1, entries 7–8). Following our typical protocol, the reaction of **1**$^+$ (55 mol%) in the absence of any additional reducing agent affords aniline in 35% yield, but no reaction is observed when the hydride cluster is replaced by its chloride analogue. On the other hand, when the chloride cluster is reacted in combination with HCOOH and NEt_3, an excellent yield of aniline (> 99%) is obtained, although longer reaction times are needed (19 h). In consequence, all of this experimental evidence allows us to conclude that the Mo_3S_4 hydride cluster is in fact the active species and that this complex can also be generated from its halide analogue upon reaction with formic acid (Table 1, entries 9–10).



Scheme 1. Proposed catalytic cycle for the molybdenum cluster species involved in the reduction of nitrobenzene.

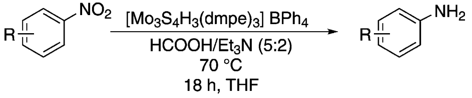
As shown in Scheme 1, we tentatively propose the following catalytic cycle for the molybdenum cluster species involved in the reduction of nitrobenzene: Initially, HCOOH reacts with the cluster hydride site to generate an unstable dihydrogen bonded species. This hypothesis is supported by our previous studies on the mechanism of proton transfer to molybdenum and tungsten diphosphino M_3S_4 cluster hydrides.[15,16] Next, hydrogen is transferred to nitrobenzene to afford the formate-substituted cluster complex. This last step is favored in the presence of formate in solution. Subsequent β-hydride elimination accompanied by CO_2 release regenerates the cluster hydride. In the specific case where the Mo_3S_4 cluster chloride is used as a catalyst precursor, the chlorine atom is replaced by formate to afford the corresponding hydride active cluster.

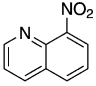
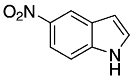
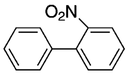
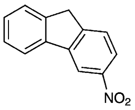
Next, we were interested in the functional group tolerance of this novel catalyst system. Hence, more than 30 different nitro-substituted arenes and heteroarenes were tested under the optimized conditions. As shown in Table 2, various alkyl-substituted nitroarenes are reduced to afford the corresponding anilines in up to 99% yield (Table 2, entries 1–4). When the nitro group is sterically hindered, an increased catalyst loading is needed (Table 2, entries 3 and 4). Interestingly, no dehalogenation processes are observed during the reduction of halogenated nitroarenes, which give the halogen-substituted aniline products in 97–99% yield (Table 2, entries 5–12), independently of the number of halogens and their ring position. Notably, 4-nitrobenzotrifluoride and 5-bromo-2-nitrobenzotrifluoride are also completely reduced to the corresponding anilines in excellent yield (Table 2, entries 13–14). This cluster catalyst is also able to reduce nitroanilines to diaminoanilines in 90–99% yields (Table 2, entries 15–18), which can also be obtained from the reduction of 2,4-dinitrotoluene in quantitative yields (Table 2, entry 19).

From a synthetic point of view, the selective transfer hydrogenation of nitroarenes functionalized with other reducible groups is more challenging. In this respect, we tested nitroarenes with different functional groups, such as nitrile, olefin, ketone, ester, amides, and even aldehydes. To our delight, the corresponding anilines are obtained in good to excellent yields (Table 2, entries 20–31). Finally, we applied different heterocyclic and biphenyl nitroarenes, which also gave the respective anilines in 95–99% yield (Table 2, entries 32–35).

In conclusion, cubane-type $[Mo_3S_4X_3(dmpe)_3]^+$ clusters have been established for the first time as excellent catalysts (X = H) or precatalysts (X = Cl) for the reduction of functionalized nitroarenes using formates as a reducing agent. Notably, the procedure is highly chemoselective in the presence of other reducible functional groups. Hence, the corresponding functionalized anilines are obtained in 89–99% yield. Furthermore, through the use of a pressurized

Table 2: Reduction of nitroarenes catalyzed by molybdenum clusters in the presence of several functional groups.[a]



Entry	Substrate	Catalyst (mol %)	Conversion[b] [%]	Yield[b] [%]
1	R = 4-Me	3	> 99	> 99 (96)[c]
2	R = 4-*t*Bu	3	> 99	> 99
3	R = 2-*i*Pr	6	> 99	> 99
4	R = 2,5-Me	10	98	97
5	R = 2-Cl	3	> 99	> 99
6	R = 4-Cl	3	> 99	98 (93)[c]
7	R = 3-Cl	3	> 99	> 99
8	R = 2-I	3	> 99	> 99
9	R = 4-Br	3	> 99	97 (95)[c]
10	R = 4-F	3	> 99	97
11	R = 3,4,5-Cl	3	> 99	98 (92)[c]
12	R = 3-Cl;4-F	3	> 99	99
13	R = 4-CF$_3$	3	> 99	93
14	R = 2-CF$_3$;4-Br	3	> 99	> 99
15	R = 3-NH$_2$;4-Me	3	> 99	> 99
16[d]	R = 2-Me;5-NH$_2$	6	> 99	> 99
17	R = 4-NH$_2$	3	> 99	90
18	R = 2-NHMe	3	> 99	94
19[e]	R = 2-Me;5-NO$_2$	6	> 99	> 99
20	R = 4-OMe	3	> 99	93
21	R = 4-SMe	3	> 99	96
22	R = 4-CN	3	> 99	90
23	R = 3-CHCH$_2$	3	> 99	> 99 (95)[c]
24	R = 4-CHCHPh	3	> 99	> 99
25	R = 4-COMe	3	> 99	> 99
26	R = 4-CO$_2$Me	3	> 99	> 99 (96)[c]
27	R = 4-CHCHCO$_2$Et	3	> 99	99
28	R = 2-CHO	3	> 99	90
29	R = 4-CONH$_2$	3	> 99	> 99
30	R = 2-SO$_2$NH$_2$	3	> 99	89
31[f]	R = 3-CH$_2$OH	3	> 99	> 99
32[g]	 NO$_2$ N	6	> 99	> 99
33	 O$_2$N N H	3	> 99	95
34	 O$_2$N	5	> 99	> 99
35	 NO$_2$	3	> 99	> 99

[a] Reaction conditions: nitrobenzene (0.1 mmol), formic acid (3.5 equiv) as a HCOOH/Et$_3$N (5:2) mixture, THF (2 mL), 18 h. [b] Determined by GC analysis using *n*-hexadecane as an internal standard. [c] Yield of isolated products given in parentheses. [d] Dodecane used as an internal standard. [e] Reaction product is 2,4-diaminotoluene. [f] Anisole used as an internal standard. [g] 24 h reaction time.

sample infusion (PSI) ESI-MS technique, we demonstrated that cluster catalysis is actually taking place without fragmentation of the catalytically active molybdenum hydride cluster.

Experimental Section

General procedure for the reduction of nitrobenzene: Under an argon atmosphere, dry nitrobenzene (10 μL, 0,097 mmol), dry *n*-hexadecane (20 μL; added as an internal standard) and HCOOH (3.5 equiv), as a 5:2 mixture of HCOOH/Et$_3$N (29.4 mg), were added to a red solution of [Mo$_3$S$_4$(dmpe)$_3$H$_3$]BPh$_4$ (3.47 mg, 0.0029 mmol) in dry THF (2 mL). The reaction mixture was heated to 70 °C for 10 h. Then the mixture was cooled down and a sample was taken from the resulting green solution. All catalytic reactions were performed at least twice to ensure reproducibility. To determine the yield of isolated products for different functionalized anilines, the general procedure was scaled up by the factor of five and no internal standard was added. After full conversion was achieved, diethyl ether (70 mL) was added to the reaction mixture to precipitate the cluster catalyst. The resultant suspension was filtered through celite and the solvent of the filtrate was removed under vacuum. In a general protocol, triethylamine was separated from the anilines by column chromatography (silica gel; *n*-hexane/ethyl acetate, 9:1→6:4). Alternatively, for solid anilines, triethylamine can be removed by washing the solid residue that remains after solvent evaporation with *n*-hexane.

Trinuclear [Mo$_3$S$_4$X$_3$(dmpe)$_3$](BPh$_4$) (X = H, Cl) clusters were prepared according to literature methods.[16,23]

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