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Oxo/imido heterometathesis between *N*-sulfinylamines and ketones catalyzed by a silica-supported molybdenum imido complex

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Grafting the molecular complex $(MesN)_2Mo(CH_2CMe_2Ph)_2$ onto the surface of silica dramatically enhances its catalytic activity in the oxo/imido heterometathesis reaction of *N*-sulfinylamines with carbonyl compounds.

The transition metal-mediated metathesis of nitrogen–carbon and nitrogen–heteroatom multiple bonds (heterometathesis) is a quite novel type of nonoxidative nitrogen transfer reactions with exciting prospects for organic synthesis. The reports on such type of reactions are still sparse and include the metathesis of imines,^{1,2} carbodiimides³ and nitriles;⁴ the condensation of isocyanates and *N*-sulfinylamines to carbodiimides⁵ and sulfurdiimines,⁶ respectively; and the imido-deoxygenation of aldehydes with isocyanates,² *N*-sulfinylamines⁷ and iminophosphoranes.⁸

We found previously that vanadium and molybdenum oxo chlorides, as well as bis(imido)molybdenum diaroxides, exhibit catalytic properties in the heterometathetical imidation of aldehydes with N-sulfinylamines.⁷ The immobilization of VOCl₃ onto silica dramatically enhances its catalytic activity, which allowed us not only to successfully develop a water-free express method for the preparation of imines of a wide range of aldehydes but also for the first time to introduce some ketones into the reaction.⁹ However, aside from N-sulfinyl-2-trifluoromethylaniline, the scope of N-sulfinylanilines reactive towards ketones turned out to be limited to those lacking o-substituents as a consequence of a steric factor. So far as molybdenum oxo chlorides were earlier noted to be superior to VOCl₃ as homogeneous catalysts for the oxo/imido heterometathesis of sterically hindered substrates, silica-supported oxo or imido molybdenum complexes can be expected to be more efficient catalysts than their vanadium analogue with an expanded range of applicability in the imido-transfer reactions.

Here we report preliminary results on the preparation of a silica-supported molybdenum imido complex that acts as a heterogeneous catalyst for the 0x0/imido heterometathesis between a wide range of *N*-sulfinylamines and simple ketones.

Since molybdenum oxochlorides are inappropriate precursors for immobilization because of their low solubility that prevents uniform dispersion of catalytic sites on the surface, we chose the toluene-soluble molybdenum bis(imido) dialkyl complex (MesN)₂Mo(CH₂CMe₂Ph)₂ (Mes = 2,4,6-Me₃C₆H₂) for this purpose being guided by the methodology of grafting transition metal alkyl complexes onto inorganic supports.¹⁰

The immobilized complex Mo/SiO₂-300 **1** was prepared by grafting (MesN)₂Mo(CH₂CMe₂Ph)₂ onto the surface of silica (partially dehydroxylated at 300 °C) from a toluene solution at ambient temperature.[†] The elemental analysis of **1** revealed 0.32 mmol Mo per gram of the solid (3.1 wt%), whereas the value of 0.40 mmol Mo g⁻¹ was expected at the total chemisorption of the complex added. The Mo:N:C ratio was approximately 1:2:32, which is close to 1:2:28 corresponding to the monografted surface species with two imido and one alkyl ligands (Scheme 1).



Scheme 1

To estimate the catalytic activity of surface complex 1, it was tested in the oxo/imido heterometathesis of *N*-sulfinyl-*p*-toluidine with acetophenone (Table 1) and compared with its molecular precursor and other homogeneous and heterogeneous catalysts. It was found that grafting the complex (MesN)₂Mo(CH₂CMe₂Ph)₂ onto silica dramatically enhanced its catalytic activity (Table 1, entries 1 and 3), likewise it had been earlier noted for VOCl₃.⁹ At

 Table 1 Comparison of the catalytic activities of 1 and some homogeneous and heterogeneous catalysts.

Tol	IN=S=O	+ $O = \langle Ph \rangle$	$\frac{\text{cat. (5 mol\%)}}{\text{heptane, }\Delta}$	TolN=	$\stackrel{\text{Me}}{\prec}_{\text{Ph}} + \text{SO}_2$	
ntry	Catalyst		Time	e/h	Conversion (%)	a

Entry	Catalyst	Time/h	Conversion $(\%)^a$
1	Mo/SiO ₂ -300 (1)	1	≥95
2	2V/SiO ₂ -500 (2) ^b	5	90
3	(MesN) ₂ Mo(CH ₂ CMe ₂ Ph) ₂	5	37
4	$MOCl_3$ (M = V, Mo)	5	No reaction

^{*a*}Spectroscopically estimated conversion. ^{*b*}Obtained by grafting 2 mol% VOCl₃ onto SiO₂-500 according to the procedure described earlier.⁹

[†] All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. The NMR spectra were recorded using Bruker AMX 400 and Avance 300 spectrometers in CDCl₃. Chemical shifts were measured relative to residual solvent ¹H (7.24 ppm) and ¹³C (77 ppm) resonances. The ¹⁹F NMR spectra were referenced externally to TFA. The IR spectra were measured with a Specord M82 spectrophotometer in CHCl₃. Elemental analyses were performed in the Laboratory of Microanalysis of INEOS RAS.

Preparation of Mo/SiO_2 -300 **1**. (MesN)₂Mo(CH₂CMe₂Ph)₂⁶ (1.36 g, 2.16 mmol) was dissolved in 15 ml of toluene and added slowly to a stirred suspension of silica (4.30 g, 71.60 mmol) in 20 ml of toluene. The mixture was stirred overnight at room temperature and then filtered. The residue was washed with toluene (3×10 ml) until the filtrate became colourless and then dried *in vacuo* to give 5.30 g of an orange-red solid. Found (%): C, 12.40; N, 0.89; Mo, 3.1.

the same time, a comparison of both silica-supported complexes convincingly shows that molybdenum catalyst 1 is superior to vanadium one 2 (Table 1, entries 1 and 2) in the heterometathetical imidation of ketones. Note that no reaction was observed in the presence of vanadium and molybdenum oxochlorides (Table 1, entry 4) or in the absence of any catalyst.

To reveal the peculiarities and a scope of application of the heterometathetical imidation of ketones with N-sulfinylamines catalyzed by surface complex 1, we studied the interaction of various reactants using 5 mol% of the catalyst (Table 2).[‡] The reactions were carried out in *n*-heptane as a solvent under reflux and monitored by IR spectroscopy. Final conversion was estimated by ¹H NMR spectroscopy. The reaction of acetophenone and 2-acetylfurane with sterically unhindered o-unsubstituted N-sulfinylanilines or o-monosubstituted ones with small electron-withdrawing groups like the fluorine atom proceeds smoothly reaching a nearly quantitative conversion within 1-2 h (Table 2, entries 1-3, 6 and 7), whereas an introduction of electron-donating groups in both ketone and N-sulfinylaniline slows down the reaction (cf. entries 1, 3, 4 and 8). However, the reaction is more sensitive to steric factor rather than to electronic effects (cf. entries 3 and 4; 2 and 9; 1, 4 and 5; 5 and 10). Thus, acetophenone and its derivatives give quantitative conversions in several hours, whereas the reactions of benzophenone with the same N-sulfinylanilines are much slower. For example, the reaction of the former with 2-trifluoromethyl-N-sulfinylaniline (entry 10) did not reach quantitative conversion even within 10 h. o-Disubstituted derivatives, e.g., N-sulfinyl-2,4,6-trichloroaniline (entry 11), do not afford the ketimine in a reasonable yield even after prolonged heating. Interestingly, in this case, apart from N-(1-phenylethylidene)-2,4,6-trichloroaniline, up to 10% di(2,4,6-trichlorophenyl)sulfurdiimine as a by-product was spectroscopically detected. This fact points out that the alternative oxo/imido heterometathesis occurs, in which N-sulfinylaniline is both imidating and oxo component as it was earlier found in a similar reaction of the imidation of dimethylformamide (DMF) with N-sulfinylamines homogeneously catalyzed by (MesN)₂Mo(CH₂CMe₂Ph)₂.⁶ Indeed, as it was exemplified by N-sulfinyl-2-fluoroaniline, in the absence of ketone, the condensation of N-sulfinylamine results in di(2-fluorophenyl)sulfurdiimine in 57% yield within 5 h.

The proposed scheme of the imido-transfer reaction of *N*-sulfinylamines with ketones[§] (Scheme 2) is analogous to that for the related reactions of *N*-sulfinylamines with DMF and aldehydes catalyzed by $(MesN)_2Mo(CH_2CMe_2Ph)_2^6$ and $MOCl_3$ (M = V, Mo),⁷ respectively. It includes the initial step of transimidation of starting

Table 2 Reactions of N-sulfinylanilines with ketones.

	RN=S=O + O $\stackrel{R'}{\longrightarrow} $ $\frac{1(5 \text{ mol}\%)}{\text{heptane, }\Delta}$			$RN = \begin{pmatrix} R' \\ R'' \end{pmatrix} + SO_2$		
Entry	R	R′	R"	Time/h	Yield of RN=CR'R"(%)	
1	4-MeC ₆ H ₄	Me	Ph	1	$\geq 95^a (99^b)$	
2	$2-FC_6H_4$	Me	Ph	1.5	≥95 (99)	
3	4-MeOC ₆ H ₄	Me	Ph	2	≥95 (77)	
4	$2-MeOC_6H_4$	Me	Ph	6	93	
5	2-F ₃ CC ₆ H ₄	Me	Ph	3	92	
6	$2-FC_6H_4$	Me	2-furyl	1.5	≥95 (91)	
7	$2-FC_6H_4$	Me	$2-FC_6H_4$	2	≥95 (92)	
8	$4-MeC_6H_4$	Me	4-MeOC ₆ H ₄	4	≥95 (88)	
9	$2-FC_6H_4$	Ph	Ph	10	≥95 (86)	
10	2-F ₃ CC ₆ H ₄	Ph	Ph	10	49	
11	$2,4,6-Cl_3C_6H_2$	Me	Ph	24	25	

^a Spectroscopically estimated conversion. ^b The yield of isolated spectroscopically pure product.



Scheme 2

silica-supported complex **1** with *N*-sulfinylamine (step *a*) affording respective arylimide **I** and *N*-sulfinylmesitylamine.[¶] The further oxo-deimidation of complex **I** proceeds under the action of ketone (route *b*) to lead to surface oxide **II** and ketimine. For poorly reactive substrates, the competitive route to **II** can be observed (route *c*) involving the second molecule of *N*-sulfinylamine instead of ketone to produce sulfurdiimine. The final imido-deoxygenation of **II** with *N*-sulfinylamine (step *d*) regenerates surface complex **I**. Both oxo-deimidation¹¹ and imido-deoxygenation¹² processes are well-documented for molecular oxo and imido molybdenum complexes.

In summary, grafting the molecular complex $(MesN)_2Mo-(CH_2CMe_2Ph)_2$ onto the surface of silica dramatically enhances its catalytic activity in the oxo/imido heterometathesis reaction of *N*-sulfinylamines with carbonyl compounds. As compared with silica-supported vanadium oxochloride, the application of silicasupported molybdenum imide allows expanding the scope of reactive *N*-sulfinylamines for the imidation of ketones.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.03.003.

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[‡] For experimental details, see Online Supplementary Materials.

[§] The mechanism of the reaction is now under investigation and will be published elsewhere.

[¶] Detected spectroscopically. Spectral data correspond to that of the authentic substance. ¹H NMR, δ : 6.91 (s, 2H, H_{Ar}), 2.27 (s, 3H, *p*-Me), 2.23 (s, 3H, *o*-Me).

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