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A Manganese N-Heterocyclic Carbene Catalyst for Reduction of Sulfoxides with Silanes

Sara C. A. Sousa,[a]† Carlos J. Carrasco,[a]† Mara F. Pinto,[a] and Beatriz Royo*[a]

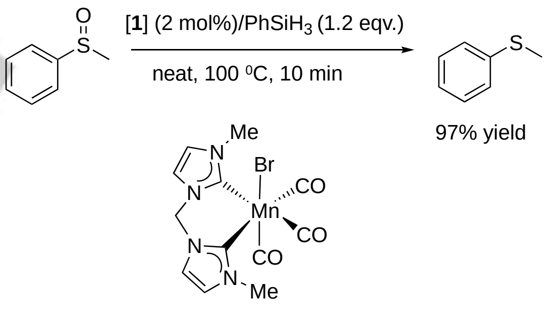
Abstract: The first reduction of sulfoxides catalysed by a well-defined manganese complex is described. A variety of sulfoxides are reduced to the corresponding sulfides in high yields using phenylsilane, diphenylsilane, and the economically feasible 1,1,3,3-tetramethyldisiloxane (TMDS) as reducing agents in the presence of a Mn-NHC complex. The reaction is performed under air and without the need of any additive. The involvement of radicals in the catalytic reaction is probed by spin-trap experiments.

Introduction

Economic and environmental pressure for more sustainable catalysis has provided a driving force for the incorporation of new catalysts based on cheap and abundant metals.[1] Among them, manganese represents an attractive candidate for catalysis due to its nontoxic nature and natural abundance, since it is the third most abundant transition metal in Earth´s crust. In fact, the development of manganese catalysis has experienced a spectacular growth in the last few years.[2] In particular, manganese-mediated hydrosilylation reactions[3] have proved to be a convenient method for the reduction of carbonyl groups, including aldehydes and ketones,[4] esters,[5] amides,[6a] carboxylic acids,[6b] CO_2,[6c] and C=C/C≡C unsaturated bonds.[7] Last year, we disclosed the excellent reactivity of Mn(I) complexes supported by bidentate NHC ligands (NHC = N-heterocyclic carbene) in the catalytic reduction of carbonyl groups.[8,9] Motivated by these findings, we became interested in further exploring the potential of $[Mn(bis\text{-}NHC)(CO)_3Br]$ complexes in reductions with silanes. Surprisingly, despite the enormous success of metal NHC complexes in catalysis,[10] very few catalytic applications of Mn-NHC complexes can be found in the literature.[4f,4g,8,9,11,12] We report in this work the deoxygenation of sulfoxides to sulfides with silanes mediated by the manganese complex $[Mn(bis\text{-}NHC)(CO)_3Br]$ bearing a bis-N-heterocyclic carbene ligand. The deoxygenation of sulfur-containing compounds is a fundamental reaction in organic synthesis and biochemistry.[13] Moreover, organic sulfides are valuable intermediates in the synthesis of pharmaceutical, biological, and natural active molecules. While they may be prepared by a variety of means,[14] transition metal-based reductions using silanes represent an interesting approach.[15] To date, the majority of the metal/silane catalytic systems relay on expensive metals.[15,16] Recent efforts have directed to replace those metals for more sustainable catalysts based on 3d transition metals such as Fe,[17] Cu,[18] and Zn.[19] Unexpectedly, manganese-catalysed reduction of sulfoxides has been so far unexplored.

Results and Discussion

Initially, the catalytic activity of the manganese complex $[Mn(bis\text{-}NHC)(CO)_3Br]$ (**1**)[9] was studied using methyl phenyl sulfoxide as a model substrate and phenylsilane as a reductant under solvent-free conditions, at 100 °C with a catalyst loading of 2 mol% (Scheme 1). Under these conditions methyl phenyl sulfoxide was fully converted into the corresponding sulfide in 10 min. Control experiments confirmed that no reaction took place in the absence of catalyst.



1

Scheme 1. Reduction of methyl phenyl sulfoxide with $PhSiH_3$ catalysed by Mn complex **1**.

The course of the catalytic reaction was monitored following both the formation of methyl phenyl sulfide and the consumption of methyl phenyl sulfoxide by ^1H NMR spectroscopy using diphenylmethane as internal standard. The kinetic profile of the reaction showed that the reduction reaction is very fast—no induction period was observed—indicating that the active species are formed rapidly upon addition of the silane (Figure 1). A turnover frequency, TOF_{50} of 788 h^{-1} was obtained (measured at 2 min of reaction), which represents the highest TOF value reported so far for a metal-based catalyst, surpassing the activity of its third row counterpart, rhenium, in reduction of sulfoxides with silanes.[16a] When the catalyst loading was lowered to 1 mol%, a significant decrease in its activity was observed (Table 1, entry 2, Figure S1). In addition, the reaction temperature plays an

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important role in the catalytic reaction. The activity of **1** is substantially reduced when the reaction was performed under 100 °C; at 90 °C, the conversion yield drops to 75% in 16 h (Table 1, entry 3, Figure S6). No reaction occurred at ambient temperature. Thus, the optimal reaction conditions were proposed to be 2 mol% of catalyst **1** in neat conditions at 100 °C.

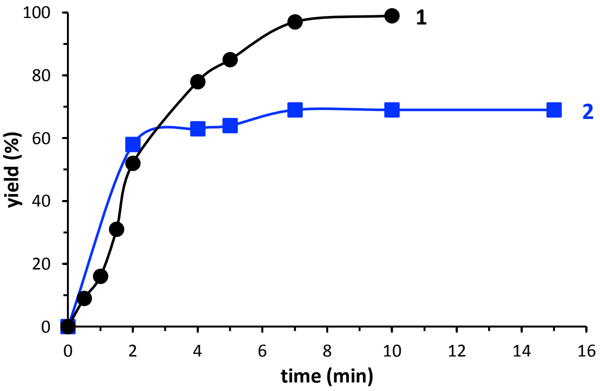


Figure 1. Kinetic profile of the deoxygenation of methyl phenyl sulfoxide (1 mmol) with $PhSiH_3$ (1.2 mmol) catalysed by [Mn(bis-NHC)$(CO)_3$Br] (**1**) and [Mn$(CO)_5$Br] (**2**) (2 mol%) in neat conditions at 100 °C.

Table 1. Reduction of methyl phenyl sulfoxide with $PhSiH_3$ catalysed by **1**.[a]

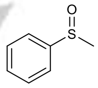
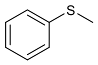
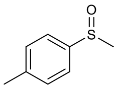
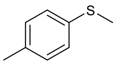
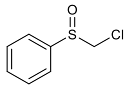
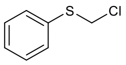
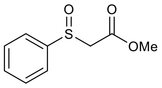
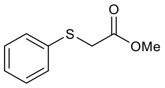
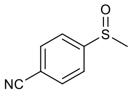
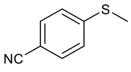
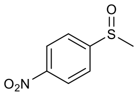
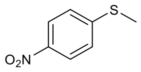
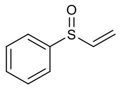
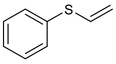
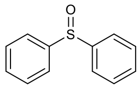
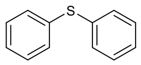
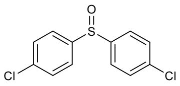
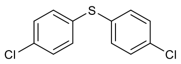
Entry	Catal. loading (mol%)	T (°C)	Time	Yield (%)[b]	TOF$_{50}$ (h^{-1})[c]
1	2	100	10 min	97	788
2	1	100	30 min	95	466
3	2	90	16 h	75	141
4	2	25	24 h	0	0
5	-----	100	1 h	0	0

[a] Reaction conditions: methyl phenyl sulfoxide (1 mmol), catalyst **1**, $PhSiH_3$ (1.2 mmol), neat conditions. [b] Yields determined by ^{1}H NMR using Ph_2CH_2 as internal standard. [c] TOF$_{50}$ calculated at 50% of conversion.

To evaluate the impact of the N-heterocyclic carbene ligand, we compared the catalytic activity of **1** to that of [Mn$(CO)_5$Br] (**2**) under the same reaction conditions. As shown in Figure 1, the reaction catalysed by **2** was very fast in the first 2 minutes, reaching 58% yield of the corresponding sulfide. Then, the reaction slowed down and stopped at 69% conversion, indicating the rapid deactivation (7 min) of the active species. These findings showed that the presence of the NHC ligand in the coordination sphere of Mn stabilises the intermediate active species. To confirm the robustness of **1**, we explored the reuse of the catalyst by adding new charges of methyl phenyl sulfoxide and phenylsilane in the same amount used in the first catalytic run. Interestingly, the catalyst could be reused up to 9 cycles, although longer reaction times (up to 6 h) were needed after the second cycle to reach quantitative conversion of the sulfoxide. The total turnover attained was 450 (after 24 h, Figure S3).

The scope and limitations of the catalytic reaction was studied for a variety of sulfoxides, including aryl-alkyl, aryl-aryl, and alkyl-alkyl sulfoxides under the optimal reaction conditions (2 mol% of **1**, 1.2 eqv. of $PhSiH_3$, 100 °C in neat conditions or in toluene, depending on the substrate). When the reaction was performed in THF, chloroform, or acetonitrile lower conversions were obtained (Table S1). As shown in Table 2, symmetric and asymmetric diaryl and dialkyl, both acyclic and cyclic sulfoxides were readily reduced affording excellent yields of the corresponding sulfides (84-98% isolated yields, entries 1, 8-13 and 16) in short times (5 min-4 h). Notably, asymmetric aliphatic sulfoxides, including the most sterically hindered *tert*-butyl methyl sulfoxide were also reduced in high-good yields (entries 14 and 15). In addition, the reduction of sulfoxides containing functional groups such as halogens, alkyl, ester, cyano, and nitro were reduced with excellent selectivities and good to moderate yields (entries 2-6 and 9), whereas olefinic groups were not tolerated. Reduction of the alkenyl group occurred in large extent (entry 7). In addition, methionine sulfoxide could not be reduced by the Mn(**1**)/$PhSiH_3$ catalytic system, probably due to the poor solubility of the substrate in organic solvents, and methionine sulfoxide was recovered intact at the end of the reaction (entry 17).

Table 2. Reduction of sulfoxides to sulfides with $PhSiH_3$ catalysed by **1**.[a]

Entry	Substrate	Product	Time	Yield (%)[b]
1			10 min	97
2			7 min	92
3[c]			4 h	71
4			16 h	70
5			16 h	50
6			16 h	73
7			16 h	12[d]
8[c]			1 h	98
9[c]			3 h	84

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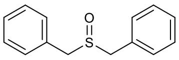
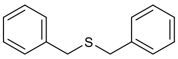
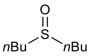
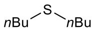
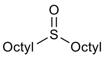
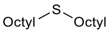
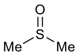
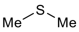
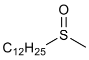
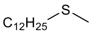
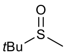
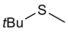
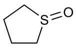
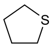
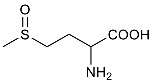
10[c]			4 h	86
11			4 h	85
12[c]			4 h	84
13			<5 min	96
14[c]			4 h	89
15[c]			16 h	74
16			15 min	86
17		------	24 h	0[e]

[a] Reaction conditions: substrate (1 mmol), **1** (2 mol%), $PhSiH_3$ (1.2 mmol), 100ºC, neat conditions. [b] Isolated yields. [c] Substrate (0.5 mmol), **1** (2 mol%), $PhSiH_3$ (0.6 mmol), toluene (0.4 mL) at 100 ºC. [d] along with phenyl vinyl sulfide, products with reduction of the alkenyl group were detected by GC. [e] no reaction occurred, starting material was recovered after 24 h.

The major drawbacks of the use of phenylsilane as reducing agent is its high price and toxicity, which prevents its use in large scale applications. Thus, replacement of phenylsilane by cheaper and safer silanes is highly desirable. Among commercially available silanes, diphenylsilane (Ph_2SiH_2) and triethylsilane (Et_3SiH) represent a good choice for a small and medium scale processes, while tetramethyldisiloxane (TMDS) and polymethylhydrosiloxane (PMHS) are the best options for large scale synthesis.[20] Other cheap silanes, such as triethoxysilane present safety problems since can disproportionate partially to SiH_4, which is a pyrophoric and explosive gas.[20] As shown in Table 3, triethylsilane, triethoxysilane, and PMHS resulted inactive in the catalytic reaction mediated by **1** (residual activity, 20% and 10% conversion, was obtained with PMHS and triethoxysilane, respectively, entries 4 and 9). Gratifyingly, diphenylsilane and TMDS displayed excellent reactivity in the reduction of methyl phenyl sulfoxide, affording 90 and 91% of the corresponding sulfide, respectively (entries 2 and 7), although higher catalyst loading was required (3 and 5 mol%, respectively). In the case of TMDS, toluene was added to increase the solubility of the substrate. A further advantage of the use of TMDS is the benign silicon-based byproducts that are formed (mainly octamethylcyclotetrasiloxane), which are essentially non-toxic and can be readily removed under reduced pressure or chromatographically.[20]

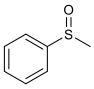
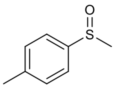
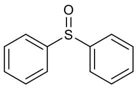
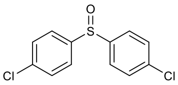
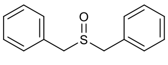
Table 3. Reduction of methyl phenyl sulfoxide with silanes catalysed by **1**.[a]

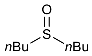
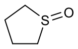
Entry	Silane (eqv.)	Catal. loading (mol%)	Solvent	Time	Yield (%) [b]
1	$PhSiH_3$ (1.2)	2	neat	10 min	97
2	Ph_2SiH_2 (1.2)	3	neat	3 h	90
3	PMHS (1.2)	5	toluene	24 h	0
4	PMHS (5)	5	NCMe	24 h	20
5	PMHS (5)	5	MeOH	24 h	0
6	PMHS (5)	5	THF	24 h	17
7	TMDS (1.2)	5	toluene	16 h	91
8	Et_3SiH (1.2)	3	neat	24 h	0
9	$(EtO)_3SiH$ (1.2)	3	neat	24 h	10

[a] Reaction conditions: methyl phenyl sulfoxide (1 mmol), catalyst, silane, solvent (0.4 mL) at 100 ºC. [b] Isolated yields.

Interestingly, a variety of sulfoxides were reduced using diphenylsilane and TMDS; results are summarised in Table 4. When diphenylsilane was used as reducing agent, the reactions were performed under neat conditions or toluene (to solubilise the solid substrates) using 3 mol% of catalyst and 1.2 eqv. of silane at 100 °C. Under these conditions, excellent yields (88-93%) were obtained for a variety of sulfoxides (Table 4, entries 2, 4, 6, 8, 10, 12, and 14). Notably, TMDS displayed remarkable activity in the reduction of aryl-alkyl, aryl-aryl, and alkyl-alkyl sulfoxides mediated by **1**, considering the common lower reactivity of TMDS compared to other silanes such as $PhSiH_3$ and Ph_2SiH_2. As shown in Table 4 (entries 1, 3, 5, 7, 9, 11, and 13), sulfides were obtained in high yields (72-93%) using 1.2 eqv of TMDS in the presence of **1** (5 mol%) at 100°C. The choice of the reaction solvent (THF, toluene or acetonitrile) was done depending on the solubility of the substrates. This work represents the first application of TMDS as a reducing agent in Mn-mediated reactions.[2,20] Noteworthy, PMHS and TMDS have been successfully applied in reduction reactions with several Earth abundant metals *eg*. Fe, Ni, Co, and Zn.[17a,20,21]

Table 4. Reduction of sulfoxides to sulfides with TMDS and Ph_2SiH_2 catalysed by **1**.[a]

Entry	Substrate	Silane	Solvent	Time	Yield (%)[b]
1		TMDS	toluene	16 h	91
2		Ph_2SiH_2	neat	3 h	90
3		TMDS	toluene	16 h	74
4		Ph_2SiH_2	neat	8 h	88
5		TMDS	NCMe	22 h	72
6		Ph_2SiH_2	toluene	8 h	90
7		TMDS	THF	16 h	75
8		Ph_2SiH_2	toluene	9 h	87
9		TMDS	THF	22 h	93
10		Ph_2SiH_2	toluene	7 h	93

11		TMDS	toluene	22 h	77
12		Ph_2SiH_2	neat	8 h	82
13[c]		TMDS	neat	24 h	82
14[c]		Ph_2SiH_2	neat	3 h	93

[a] Reaction conditions: substrate (1 mmol), **1** (2 mol%), silane (1.2 mmol) and 100 ºC. [b] Isolated yields. [c] Yields determined by ^1H NMR using Ph_2CH_2 as internal standard.

In order to get an insight into the mechanistic details of the catalytic reduction, the stochiometric reaction of **1** with phenylsilane was investigated. Complex **1** was treated with one equivalent of $PhSiH_3$ in a J Young valve NMR tube in deuterated benzene, and the reaction was monitored by ^1H NMR. At room temperature, no reaction occurred. The temperature was then gradually increased to reach 80 °C. After 15 min at 80 °C, partial conversion of **1** to a new Mn complex featuring a hydride signal at -6.9 ppm was observed in the ^1H NMR spectrum.[8] The identification of Mn-H species as catalytically relevant intermediates has also been described by Trovitch in the hydrosilylation of carbonyl groups mediated by a bis(imino)pyridine manganese complex.[4c] In addition, we explored the reaction of **1** with the substrate. Complex **1** was treated with a toluene solution of methyl phenyl sulfoxide (in a 1:1 ratio) and heated to 100 °C for 1 h. The recorded NMR and IR spectra of the reaction mixture indicated that no reaction occurred. Based on these experimental observations, initial coordination of the sulfoxide to Mn is excluded. It is proposed that the reaction initiates by reaction of complex **1** with silane, which readily generates a catalytically relevant Mn-H species. Spin-trap experiments indicated the involvement of radical intermediates in the reduction of sulfoxides. When the catalytic reaction is performed in the presence of stoichiometric amounts of the persistent radical TEMPO, a significant decrease in the activity of **1** was observed. Other radical scavengers such as Ph_2NH and $CBrCl_3$ also slowed down the reaction to a great extent (see kinetic profiles in Figure S4). Similar results have been described by us in the reduction of ketones with silanes catalysed by **1**.[8]

Conclusions

In conclusion, the first Mn-catalysed reduction of sulfoxides to sulfides has been developed using a Mn-NHC complex as catalyst and silanes as reducing agents. Noteworthy, the catalytic reaction is performed under non-inert conditions and without the need of any additive. The utility of the method is outlined by the application of a readily accessible manganese NHC complex as catalyst, and the cost-efficient and easy to handle TMDS as a hydride source. Further effort directed toward the extension of the catalytic system to the reduction of other functional groups is in progress in our laboratory.

Experimental Section

General methods

All compounds were used as received without further purification. The [Mn(bis-NHC)$(CO)_3$Br] complex was synthesised following the procedure already published by us.[9] Solvents were dried according to standard procedures. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance III 400 MHz. Infrared spectra were obtained in a Mattson 7000 FTIR spectrometer.

General procedure for the reduction of sulfoxides with silanes catalysed by complex 1

An open-air flask was charged with complex **1** and the corresponding substrate. Then, silane was added and the reaction mixture was stirred and heated at 100 ºC. With solid substrates, the addition of the appropriate solvent was needed to facilitate the solubilisation of the reagents. The progress of the reaction was monitored by TLC and by ^1H NMR in chloroform-*d*. Upon completion, the product was purified by silica gel column chromatography to afford the corresponding pure sulfides, which are all known compounds. For some samples, conversion was determined by ^1H NMR spectroscopy using diphenylmethane as internal standard. Yields were calculated by integration ratios of the methyl resonance of the product and the CH_2 resonance of the standard Ph_2CH_2.

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Keywords: manganese • reduction • sulfoxides • silanes • TMDS

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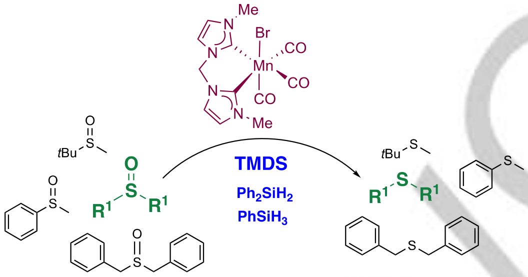

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