

Reduction of carbonyl groups by high-valent rhenium oxides

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Abstract

The oxo-rhenium complexes $[\text{Re}_2\text{O}_7]$ (**1**), $[\text{ReMeO}_3]$ (**2**), $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)\text{O}_3]$ (**3**), $[\text{ReO}_2\text{Cl}(\text{DMSO})_2]$ (**4**), $[\text{ReO}_2\text{Me}(\text{PhC}\equiv\text{CPh})]$ (**5**), and $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (**6**) catalyze the hydrosilylation of aliphatic and aromatic aldehydes with dimethylphenylsilane in C_6D_6 solutions. Compound **1** catalyzes the hydrosilylation of aldehydes at room temperature, affording the corresponding silyl ethers in good yield, but is ineffective as ketone hydrosilylation catalyst. The reactions of aldehydes and ketones with dimethylphenylsilane using compounds **2–6** as catalysts, require heating at 80°C . The scope of rhenium oxides-mediated hydrosilylation with a variety of aldehydes and ketones has been studied. Methyltrioxorhenium(VII) (**2**) and oxotrichlorobis(triphenylphosphine)rhenium(V) (**6**) shown to be the most active and versatile catalysts for the hydrosilylation of aliphatic and aromatic aldehydes and also ketones. The dioxo-rhenium derivatives $[\text{ReO}_2\text{Me}(\text{PhC}\equiv\text{CPh})]$ and $[\text{ReO}_2\text{Cl}(\text{DMSO})_2]$ also catalyze the reaction of dimethylphenylsilane and aldehydes, although longer reaction times were required. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The chemistry of oxo-rhenium complexes has been greatly expanded during the last few years [1]. The exploratory research of Herrmann and Kühn has led to the discovery of one of the most versatile oxidation catalysts known to date, methyltrioxorhenium(VII) (MeReO_3 , abbreviated as MTO) [2]. Among the numerous applications found, were aldehyde olefination [3,4], metathesis of functionalized olefins [5,6], olefin epoxidation [7,8], and a wide variety of other oxidation and oxygen transfer reactions [9]. Besides these reactions, applications of rhenium oxides to other organic transformations are very rare. In 2003, Toste and co-workers reported the use of the dioxo-rhenium(V) derivative $[\text{ReO}_2\text{I}(\text{PPh}_3)_2]$ as catalysts for the hydrosilylation of aldehydes and ketones [10]. This novel reactivity represents a complete reversal from the traditional role of these complexes as oxidation catalysts [11]. Our interest in the study of high valent

transition metals as catalysts led us to explore this new pathway of catalytic activity and we recently reported that $[\text{MoO}_2\text{Cl}_2]$ is also a highly effective catalyst for the hydrosilylation of carbonyl groups [12]. In the present study, we extend this screening to other complexes with terminal oxygen ligands in order to establish a pattern of reactivity for this reaction. With this criterion in mind, we chose a series of simple, well-characterized oxo-rhenium complexes of the types Re(VII)O_3 , Re(V)O_2 and Re(V)O , and studied their behavior as hydrosilylation catalysts for aldehydes and ketones.

2. Experimental

2.1. General methods

All manipulations were carried out using standard Schlenk-line techniques under a nitrogen atmosphere. Solvents were purified by conventional methods and distilled under nitrogen, prior to use. NMR spectra were measured on a Bruker CXP 300 spectrometer, and IR spectra were measured

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on a Unicam Mattson model 7000 FTIR spectrometer. Gas chromatography study was performed with a Thermo Finnigan Trace GC (TCD) gas chromatograph. Silanes were purchased from Aldrich and used without further purifications. Compounds [ReMeO₃] [13], [Re(η^5 -C₅H₅)O₃] [14], [ReO₂Me(PhC≡CPh)] [15], [ReOCl₃(PPh₃)₂] [16], and [ReO₂Cl(DMSO)₂] [17] were prepared, as published.

A combination of ¹H NMR, ¹³C NMR, and IR spectrometry was used to identify the reaction products. These data are presented in the [Supporting Information](#).

2.2. General procedure for the hydrosilylation of aldehydes and ketones with dimethylphenylsilane

A dried J. Young NMR tube equipped with a Teflon screw cap, was flushed with nitrogen and charged with a catalytic amount of catalyst (0.050 mmol). *d*₆-Benzene (0.4 mL), followed by the corresponding aldehyde or ketone (1.01 mmol) and neat dimethylphenylsilane (1.24 mmol) were added, and the NMR tube was then placed in a pre-heated oil bath (80 °C) and monitored periodically by ¹H NMR. Upon completion (the reaction times are indicated in [Tables 1–3](#)), the reaction mixture was diluted with hexanes (ca. 2 mL), loaded directly on to a silica gel column and chromatographed with the appropriate mixture of hexanes and diethyl ether to give the corresponding silyl ethers.

Table 2
Hydrosilylation of aldehydes (0.66 mmol) with Me₂PhSiH (0.79 mmol) in C₆D₆

Entry	Catalyst (5 mol%)	Substrate	Time/temperature (°C)	Yield (isolated) (%)
1	[Re ₂ O ₇]	Hexanal (a)	30 min/25	96
2	[Re ₂ O ₇]	2,2-Dimethyl-4-pentenal (b)	30 min/25	95
3	[Re ₂ O ₇]	4-Bromobenzaldehyde (d)	30 min/25	93
4	[Re ₂ O ₇]	Methyl 4-formylbenzoate (e)	30 min/25	74
5	[Re ₂ O ₇]	4-Cyanobenzaldehyde (f)	30 min/25	No reaction
6	[ReMeO ₃]	Hexanal (a)	20 h/80	87
7	[ReMeO ₃]	2,2-Dimethyl-4-pentenal (b)	20 h/80	96
8	[ReMeO ₃]	4-Bromobenzaldehyde (d)	6 h/80	90
9	[ReMeO ₃]	Methyl 4-formylbenzoate (e)	24 h/80	41
10	[ReMeO ₃]	4-Cyanobenzaldehyde (f)	24 h/80	78
11	[ReOCl ₃ (PPh ₃) ₂]	Hexanal (a)	2 h/80	96
12	[ReOCl ₃ (PPh ₃) ₂]	2,2-Dimethyl-4-pentenal (b)	2 h/80	95
13	[ReOCl ₃ (PPh ₃) ₂]	4-Bromobenzaldehyde (d)	2 h/80	87
14	[ReOCl ₃ (PPh ₃) ₂]	Methyl 4-formylbenzoate (e)	2 h/80	97
15	[ReOCl ₃ (PPh ₃) ₂]	4-Cyanobenzaldehyde (f)	2 h/80	86

Table 3
Hydrosilylation of ketones with Me₂PhSiH^a

Entry	Catalyst (5 mol%)	Substrate	Time (h)	Yield ^b (%)
1	[ReMeO ₃]	4-Phenyl-2-butanone (g)	24	98
2	[ReMeO ₃]	Cyclopropylmethylketone (h)	24	98
3	[ReMeO ₃]	4- <i>tert</i> -butylcyclohexanone (i)	15	97
4	[ReMeO ₃]	5-Methoxy-1-tetralone (j)	15	96
5	[ReOCl ₃ (PPh ₃) ₂]	4-Phenyl-2-butanone (g)	4	96
6	[ReOCl ₃ (PPh ₃) ₂]	Cyclopropylmethylketone (h)	15	85
7	[ReOCl ₃ (PPh ₃) ₂]	4- <i>tert</i> -butylcyclohexanone (i)	4	93
8	[ReOCl ₃ (PPh ₃) ₂]	5-Methoxy-1-tetralone (j)	15	80

^a Reaction conditions: catalyst (5 mol%), aldehyde (0.66 mmol) and Me₂PhSiH (0.79 mmol) in C₆D₆ at 80 °C; reaction was monitored by ¹H NMR.

^b Isolated yields.

Table 1

Catalyst screening for hydrosilylation of 4-trifluoromethylbenzaldehyde with Me₂PhSiH^a

Entry	Catalyst	Temperature (°C)/time	Extent of reaction ^b (%)
1	[Re ₂ O ₇] (1)	25/30 min	>95
2	[ReMeO ₃] (2)	80/5 h	>95
3	[ReCpO ₃] (3)	80/20 h	40
4	[ReO ₂ Cl(DMSO) ₂] (4)	80/10 h	>95
5	[ReO ₂ Me(PhC≡CPh)] (5)	80/10 h	>95
6	[ReOCl ₃ (PPh ₃) ₂] (6)	80/2 h	>95

^a Reaction conditions: catalyst (5 mol%), 4-trifluoromethylbenzaldehyde (0.66 mmol) and Me₂PhSiH (0.79 mmol) in 0.4 mL of C₆D₆.

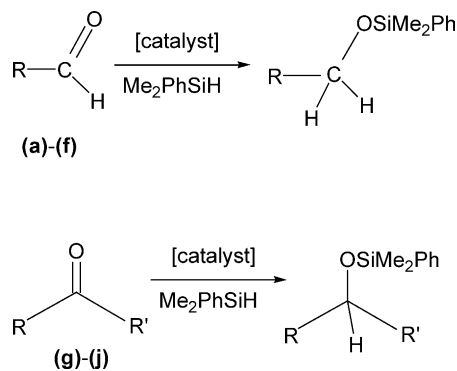
^b Reaction was monitored by ¹H NMR spectroscopy; only starting materials and dimethyl-phenyl-(4-trifluoromethyl-benzyloxy)-silane were detected in the brown solutions.

3. Results

The hydrosilylation of aldehydes and ketones with catalytic amounts of the oxo-rhenium catalysts **1–6** (5 mol%) in the presence of dimethylphenylsilane in benzene is represented in [Scheme 1](#).

3.1. Hydrosilylation of aldehydes

The complexes, in [Plate 1](#), were preliminarily screened as catalysts in hydrosilylation of 4-(trifluoromethyl)



Scheme 1.

benzaldehyde. The hydrosilylation reaction was carried out with dimethylphenylsilane by using the oxo-rhenium complexes **1–6**, as catalysts in d_6 -benzene. The identification of the products, as well as the determination of reaction yields was easily performed by means of ^1H NMR analysis (see [Supplementary material](#)). Results are summarized in [Table 1](#). As shown, under the conditions noted, 4-(trifluoromethyl)benzaldehyde is transformed to dimethylphenyl-(4-trifluoromethyl-benzyloxy)-silane, in essentially quantitative yields with catalysts **1**, **2**, and **4–6**. The cyclopentadienyltrioxorhenium [ReCpO_3] (**3**; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) yielded the corresponding silyl ether in 40% yield.

The hydrosilylation of 4-(trifluoromethyl)benzaldehyde catalyzed by [Re_2O_7] (**1**) reveals that this catalyst is both the most active, as well as the only one that shows reactivity at room temperature (entry 1, [Table 1](#)). It should be noted that an exothermic reaction takes place within 1 min when a mixture of catalyst **1** and 4-(trifluoromethyl)benzaldehyde in d_6 -benzene is mixed with dimethylphenylsilane. When the reaction was carried out in THF, instead of deuterated benzene, an intractable black precipitate was immediately formed. The Re(VI) and (IV) oxides, ReO_3 and ReO_2 , do not catalyze the hydrosilylation reaction. When a benzene suspension of ReO_3 and ReO_2 is treated with

Me_2PhSiH and 4-(trifluoromethyl)benzaldehyde no reaction occurs.

Methyltrioxorhenium (MTO) (**2**) and [$\text{ReOCl}_3(\text{PPh}_3)_2$] (**6**) are effective catalysts reaching total conversion of the aldehyde to the silylated ether after 5 and 2 h, respectively, at 80°C (entries 2 and 6, [Table 1](#)). Their catalytic activity is comparable to that of [$\text{ReO}_2\text{I}(\text{PPh}_3)_2$], already reported by Toste and co-workers [10]. In contrast, the “ $\text{ReO}_2(\text{V})$ ” catalysts **4** and **5** required longer reaction times to reach similar conversion values (Entries 4 and 5, [Table 1](#)). Cyclopentadienyltrioxorhenium is the least active catalyst among the complexes examined (Entry 3, [Table 1](#)). Exploratory experiments, carried out with other silanes, such as Ph_3SiH or Et_3SiH showed virtually no activity. Reaction of 4-(trifluoromethyl)benzaldehyde with dimethylphenylsilane in the presence of catalysts **2–6**, using dichloromethane, chloroform or THF as solvent, instead of benzene, did not proceed. Additionally, no reaction was observed when the catalytic experiments were performed in toluene at room temperature.

A selection of these complexes was further tested in the hydrosilylation of a variety of aldehydes, as summarized in [Table 2](#). Compounds **1**, **2** and **6** were tested as hydrosilylation catalysts for hexanal, 2,2-dimethyl-4-pentenal, 4-bromobenzaldehyde, 4-cyanobenzaldehyde and methyl-4-formylbenzoate, using the following reaction ratios: aldehyde/ Me_2PhSiH /catalyst:1.0/1.2/.05 in deuterated benzene solutions at room temperature for catalyst **1** and at 80°C for catalysts **2** and **6**. Both aliphatic and aromatic aldehydes were converted to the corresponding silyl ethers. Under the conditions used, several functional groups (e.g., bromide, trifluoromethyl, cyano, esters groups) are well tolerated, even though the yield isolated for the ester functionality was 41% when MTO was used as catalyst (Entry 9, [Table 2](#)) and 4-cyanobenzaldehyde was not converted to the corresponding 4-[(dimethyl-phenyl-silyloxy)-methyl]-benzonitrile when [Re_2O_7] was used as catalyst, even after heating the benzene solution at 80°C for 10 h (entry 5, [Table 2](#)).

In order to confirm, if a hydride species is formed in the catalytic hydrosilylation reaction, methyltrioxorhenium was reacted with excess of dimethylphenylsilane and the reaction was monitored by ^1H NMR spectroscopy. No reaction was observed when the mixture was kept at room temperature during 24 h. After 2 h at 80°C , the resonance corresponding to the methyl protons of MTO (δ 2.55 in C_6D_6) vanished and a black precipitate was formed in the NMR tube. The formation of methane was detected by gas chromatography. The black powder formed in the reaction does not contain carbon and hydrogen, as has been revealed by its elemental analysis. These results suggest that an intermediate hydride specie of the type “[$\text{Re}(\text{H})\text{O}_2\text{Me}(\text{OSiMe}_2\text{Ph})$]” was initially formed. In the absence of a suitable substrate, methane is liberated and subsequent decomposition leads to uncharacterized rhenium oxides. However, the formation of a hydride specie was not detected by ^1H NMR spectroscopy, probably due to a rapid

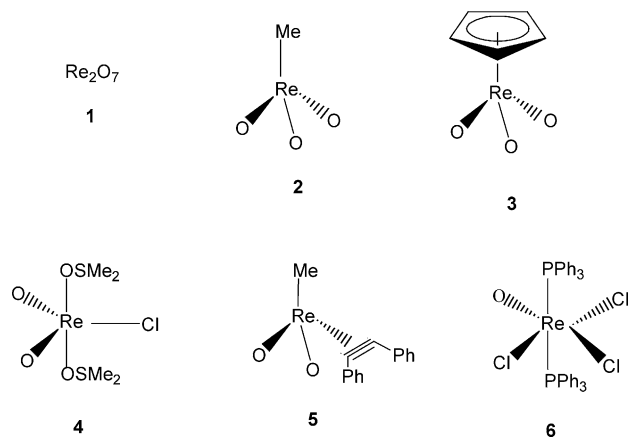


Chart 1. Oxo-rhenium catalysts for hydrosilylation of aldehydes and ketones.

methane liberation in “[Re(H)O₂Me(OSiMe₂Ph)]” when the substrate is not present.

In an attempt to make [ReHO₃], [Re₂O₇] was treated with Bu₃SnH at –100 °C in THF-*d*₆ in the hope of taking advantage of the formation of the very stable polymeric Bu₃SnOREO₃. At –85 °C the whole reaction mixture was already totally black. A series of rapid scans around this temperature revealed broad resonances in the region $\delta > 10$ ppm that disappeared rapidly. A similar experiment with Me₂PhSiH only showed reaction above –25 °C, but no hydride resonance could be observed during the scans performed between –25 °C and rt, where total decomposition was observed. Similar results were achieved when [Re₂O₇] was treated with Me₂PhSiH in toluene and dichloromethane.

3.2. Hydrosilylation of ketones

Table 3 summarizes the results of using the complexes **2** and **6** as catalysts for the hydrosilylation of 4-phenyl-2-butanone, cyclopropylmethylketone, 4-*tert*-butylcyclohexanone and 5-methoxy-1-tetralone with dimethylphenylsilane. The catalysis conditions match those reported in the survey reactions of Table 3 (5 mol% catalyst, 1:1.2 ketone:dimethylphenylsilane in deuterated benzene), and the reaction times designate essentially quantitative conversion of ketones to products. With Me₂PhSiH, catalysts **2** and **6** transformed the ketones **g–j** (Plate 2) to the corresponding alkoxysilanes in high yields. Surprisingly, [Re₂O₇] (**1**) which had shown high catalytic activity in the hydrosilylation of aldehydes, did not catalyze the hydrosilylation of ketones. Reaction of dimethylphenylsilane and ketones **g–j** in the presence of a catalytic amount of **1** in deuterated benzene at room temperature or heating at 80 °C did not yield the corresponding alkoxysilane products.

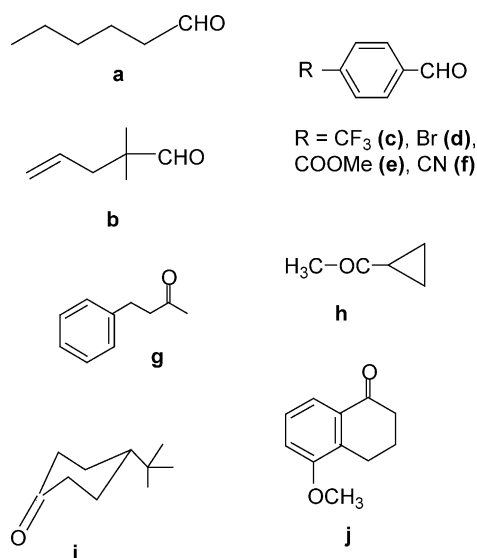
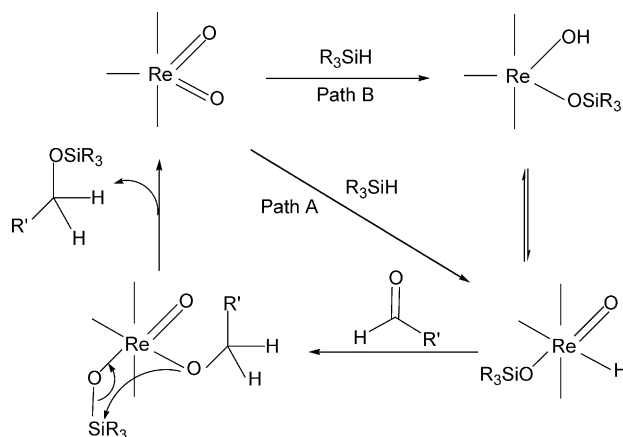


Chart 2. Aldehydes and ketones used as substrates for the hydrosilylation reaction.

4. Discussion

The results described above, taken together with the results of Toste and co-workers [10] and those obtained with [MoO₂Cl₂] [12], make it clear that oxo-complexes are a novel class of effective catalysts for the hydrosilylation of aldehydes and ketones. The precursor Re oxo-complexes span oxidation states VII–V, comprise inorganic (Cl, I, ReO₄) and organic (Me, Cp) ancillary ligands and bear one, two or three terminal oxo-ligands. Of course, some differences in reactivity are observed that depend on the complex, the substrate, the solvent, and even on the silane used. From a general point of view, little differences are observed in the reactivity of the several aldehydes, irrespective of being aromatic or aliphatic, since all are hydrosilylated with similar efficiency for a given catalyst. However, some exceptions are evident that result in much slower conversions under otherwise identical conditions. The poor activity of the catalyst precursor **3** (ReCpO₃) and the modest performance of both **4** and **5** are one important remark (Table 1). They may be attributed to either electronic saturation or steric congestion around the Re atom. In contrast, all other precursors are either strongly unsaturated at Re, e.g., MTO, [Re₂O₇], or possess labile ligands, e.g., [ReOCl₃(PPh₃)₂]. The importance of having accessible coordination positions around the Re center can also be hinted by the lack of reactivity of all the compounds tested in THF solution. Besides, the absence of reaction between 4-cyanobenzaldehyde and Me₂PhSiH in the presence of [Re₂O₇] can be due to the inactivation of the reaction centre, since nitriles are very good coordinating agents of [Re₂O₇] and are present in a large excess [1]. Likewise, the lack of a catalytic hydrosilylation of ketones with [Re₂O₇] is most certainly due to the same type of effect.

In the seminal publication by Toste and, in a critical highlight comment by Thiel [11], the mechanism has been discussed in its most important features, based upon [ReIO₂(PPh₃)₂] as catalyst. These features are summarized in Scheme 2.

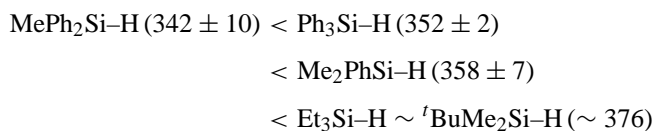


Scheme 2.

In the light of our results, it becomes clear that the [2+3] addition in path B is not a necessary condition to produce a catalytically active species. Indeed, the complex [ReOCl₃(PPh₃)₂], that has only one oxo-ligand, is actually rather effective. Nevertheless, path B may still be operative in dioxo and trioxo catalysts.

The intermediacy of a hydride, common to both mechanisms, was shown by Toste based on NMR data and agrees with Mayers's finding that the Re(V) oxo-hydride in [Tp*ReO(H)(OTf)] has hydridic character, since it is not deprotonated by pyridine and reacts with acetaldehyde to form [Tp*ReO(OCH₂CH₃)(OTf)] even in a rather sterically congested environment [18]. We have attempted to observe hydride (or hydroxo) intermediates by ¹H NMR but failed to identify them, either due to low stability or too rapid reaction with substrate. Both pathways are very difficult to distinguish from each other and less reactive models or more adequate reaction conditions may have to be searched for.

A last observation concerns an apparent limitation of the catalysts used for this reaction: they work well with Me₂PhSiH but were incapable of silylating even the more reactive aldehydes with both Ph₃SiH and Et₃SiH. These differences in reactivity can reflect both the differences in Si–H and Si–O bond strengths as well as steric factors. Addition of the R₃Si–H bond across a given Re=O bond should become easier with the weakening of the Si–H bond. The ascending order of the bond dissociation energies (kJ/mol) of the Si–H bond is [19]:



Accordingly, Et₃SiH is expected to be the least reactive of the three reagents, but the small difference between the other two does not seem to justify why PhMe₂SiH is so much more reactive than Ph₃SiH. We believe that this effect comes from the steric hindrance that takes place in the addition step of the Si–H to the Re=O bond. In this step, the coordination number increases in both the centers: from 4 to 5 around Si and from 4 to 5 or from 5 to 6 around Re. This will increase the repulsive forces within both coordination spheres and bring steric constraints to the transition state for the addition. Such constraints should be smaller in the case of pathway B in Scheme 2.

In this context, it is interesting to note that most of these constraints are loosened for the [ReIO₂(PPh₃)₂] catalyst, described by Toste and co-workers; although benzene is the best solvent other donors like THF or NCMc can be used in some cases; all silanes listed above can be used; the order of reactivity is Me₂PhSiH > Et₃SiH > MePh₂SiH » ^tBuMe₂SiH. This decreased sensitivity to sterics and solvent (donor) constraints suggests that, this particular catalyst might be initi-

ated via pathway B which then crosses over to the hydride common to both pathways A and B.

5. Conclusions

The oxo-rhenium complexes 1–6 proved to be effective catalysts in the hydrosilylation of aliphatic and aromatic aldehydes, revealing a general behaviour of high valent oxo-rhenium derivatives as catalysts in a reduction reaction. The hydrosilylation of aldehydes was compatible with a wide range of functional groups, such as cyano, ester, aryl, halo and alkene. The more active and versatile catalysts resulted to be methyltrioxorhenium(VII) and oxotrichlorobis(triphenylphosphine)rhenium(V). Work aimed at investigating further applications of this kind of complexes in other reduction reactions is currently under way in our laboratories.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2005.04.030.

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