Host−Guest Chemistry in a Urea Matrix: Catalytic and Selective Oxidation of Triorganosilanes to the Corresponding Silanols by Methyltrioxorhenium and the Urea/Hydrogen Peroxide Adduct

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Abstract: The oxidation of silanes to silanols, catalyzed by methyltrioxorhenium (MTO), proceeds in high conversions and excellent selectivities in favor of the silanol (no disiloxane product) when the urea/hydrogen peroxide adduct (UHP) is used as oxygen source instead of 85% aqueous H_2O_2. It is proposed that this novel Si−H oxidation takes place in the helical urea channels, in which the urea matrix serves as host for the silane substrate, the H_2O_2 oxygen source, and the MTO metal catalyst as guests. In this confined environment, the metal catalyst is stabilized against decomposition, and this enhances higher conversions while condensation of the silanol to its disiloxane is avoided for steric reasons. The oxidation of the optically active silane (*S*)-(α-Np)PhMeSiH proceeds with retention of configuration in excellent yield. To date, no catalytic Si−H oxygen insertion has been reported for the preparation of optically active silanols. In analogy with the stereoselectivity in the dioxirane oxidation of (+)-(α-Np)PhMeSiH to (+)-(α-Np)PhMeSiOH, a concerted spiro-type transition-state structure is proposed for this novel Si−H oxidation. Herewith, a valuable synthetic method for the preparation of silanols has been made available through catalytic and selective oxidation of silanes to silanols by the MTO/UHP system.

Introduction

The catalytic activation of H_2O_2 and ROOH (usually *t*-BuOOH) for the selective oxidation of organic and organometallic compounds continues to be one of the challenging problems in synthetic chemistry.[1] Through intensive efforts, a number of efficient and useful catalysts for oxidation have emerged over recent years.[2] Among these is the versatile and highly active methyltrioxorhenium (MTO) catalyst, which has gained increasing importance for the activation of H_2O_2 in oxidation reactions such as epoxidation, sulfoxidation, and arene oxidation.[3] Under more drastic reaction conditions, C−H insertions may also be performed with this rhenium catalyst.[4] To date, however, the insertion of an oxygen atom into the Si−H bond of silanes to give silanols has not been reported.

Industrially, silanols are used for the production of silicon-based polymeric materials; the sol−gel process is among the prominent applications.[5] In addition, there has been much interest in recent years in silicon compounds with biological activity,[6] and among these also are silanols.[7] Although numerous synthetic methods are known for the preparation of silanols,[5] most of these use either acid or alkali as reagents. In many cases, the silanol forms the corresponding siloxane, an undesirable side-product. Such a condensation is particularly serious for sterically exposed substrates;[8] therefore, silanols that are prone to condensation have previously been made either by the hydrolysis of silyl halides under strictly buffered conditions[9] or by the Si−H oxidation of silanes. For the latter oxidation method, several reagents are known; however, these either are stoichiometric or form appreciable amounts of siloxane, especially for unhindered silanols.[10] The stoichiometric oxidants

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include silver salts,[11] perbenzoic acid,[12] ozone,[13] potassium permanganate,[14] dioxiranes,[15] and oxaziridines.[16] Some catalytic methods for the oxyfunctionalization of silanes to silanols have been reported for nickel, palladium, chromium, rhodium, or copper catalysts.[17,18] However, these catalysts have been used for only a limited range of substrates, or again, the undesirable siloxane is produced in significant quantity. In view of these shortcomings, a catalytic and selective method for the synthesis of silanols from silanes is needed.

The preparation of optically active silanols has also been a matter of long-standing interest. For the stereoselective oxidation of optically active silanes with *retention* of configuration, only stoichiometric oxidants, i.e., *m*-CPBA,[12b] dimethyldioxirane,[15] and oxaziridines,[16] have been used to date. Metal-catalyzed oxidations of the Si−H bonds of optically active silanes are not known.[7e,19] Two metal-assisted hydrolyses of optically active silanes are known;[17] however, these occur with *inversion* of configuration, in contrast to the previously mentioned stoichiometric oxidants.

We have for some time been interested in the catalytic potential of the combination of MTO and the urea/hydrogen peroxide adduct (UHP) as oxidant and were previously able to show its advantages for the epoxidation of olefins.[3d] Thus, with the MTO/UHP combination, such reactions may be conducted in nonaqueous media and the hydrolysis of the epoxides to the corresponding diols and subsequent cleavage and rearrangement reactions are suppressed. Herein, we present the full details of the MTO-catalyzed oxidation of silanes to silanols with UHP as oxygen source, according to the catalytic cycle in Scheme 1. Our results demonstrate that the MTO/UHP oxidizing system applies to a wide range of substrates and affords the silanols in high yields and selectivities. The presence of urea plays a pivotal role in that its helical channels serve as a host for this oxygen-transfer process.

(10) In the oxidation of dimethylethylsilane with dimethyldioxirane, a chemoselectivity (silanol versus disiloxane) of only ca. 23:77 is observed after workup. Peracids and oxaziridines have not been used for the oxidation of such substrates.

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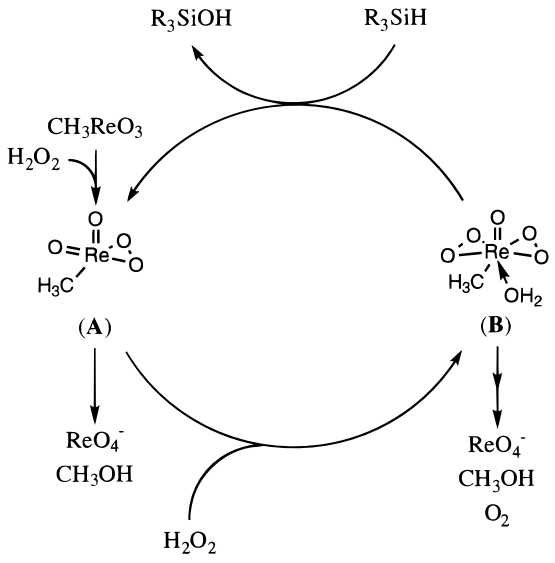
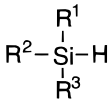
Scheme 1. Oxidation and Decomposition Reactions of the MTO/H_2O_2 System

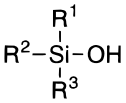


Results

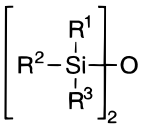
The syntheses of the catalyst MTO and of methyl(oxo)bis-(η^2-peroxo)rhenium(VIII) hydrate were conducted according to literature procedures.[20,21] The silanes **1a**,**b**,**f**,**h** and **(*S*)-1h** were prepared by reduction of the corresponding chloro-, methoxy-, or menthoxysilane with lithium aluminum hydride.[19a,22] Authentic samples of the silanols **2a−d**,**f−h** and **(*R*)-2h** were obtained by oxidation of the Si−H compounds **1a−d**,**h** and **(*S*)-1h** with dimethyldioxirane or hydrolysis of the corresponding chlorosilane.[5] Disiloxanes **3a−c**,**g** were synthesized from the chlorosilane with sodium iodide in aqueous acetonitrile, and the disiloxane **3h** was prepared from the silane **1h** by hydrolysis under phase-transfer conditions.[23]



1a-h



2a-h

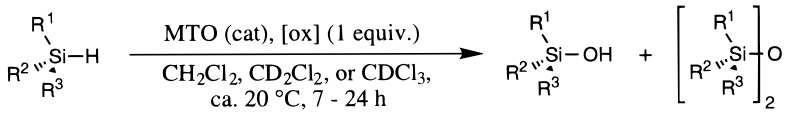


3a-e,g,h

1-3	R^1	R^2	R^3
a	Et	Me	Me
b	*n*-Pr	Me	Me
c	*t*-Bu	Me	Me
d	Ph	Me	Me
e	Et	Et	Et
f	*i*-Pr	*i*-Pr	*i*-Pr
g	Ph	Ph	Ph
h	α-Np	Ph	Me

The MTO-catalyzed oxidations were carried out at ambient temperature with UHP or 85% H_2O_2 (1.0−10.0 equiv), 1−20 mol % of the rhenium catalyst, and in some cases, with 0.1−

Table 1. MTO-Catalyzed Oxidation of Silanes **1** with Hydrogen Peroxide as Oxygen Source



1 **2** **3**

entry	silane	oxidant	MTO (mol %)	time (h)	m.b. (%)[a,b]	convn (%)[b]	products (%)[c,d] silanol (**2**)	products (%)[c,d] disiloxane (**3**)
1	$EtMe_2SiH$ (**1a**)	UHP	1.0	18	77	≥95	94	6
2		85% H_2O_2	1.0	18	74	55	<5	≥95
3	*n*-$PrMe_2SiH$ (**1b**)	UHP	1.0	18	≥95	77	82	18
4		85% H_2O_2	1.0	18	92	56	<5	≥95
5	*t*-$BuMe_2SiH$ (**1c**)	UHP	1.0	18	82	98	≥99	<1
6		85% H_2O_2	1.0	18	79	70	≥99	<1
7	$PhMe_2SiH$ (**1d**)	UHP	1.0	13	≥99	87	98	2
8		85% H_2O_2	1.0	13	≥99	26	20	80
9	Et_3SiH (**1e**)	UHP	1.0	24	76	78	≥99	<1
10		85% H_2O_2	1.0	24	89	54	54	46
11	*i*-Pr_3SiH (**1f**)	UHP	1.0	14	*e*	*e*	≥99	<1
12		85% H_2O_2	1.0	14	*e*	*e*	≥99	<1
13	Ph_3SiH (**1g**)	UHP	1.0	24	*e*	*e*	≥95	<5
14		85% H_2O_2	1.0	24	*e*	*e*	≥95	<5
15	(+)-(α-Np)PhMeSiH [(*S*)-**1h**]	UHP	1.0	14	93	12	96 (91)	4
16		UHP	10.0	7	64	14	97 (53)	3
17		UHP	20.0	12	70	15	97 (15)	3
18		85% H_2O_2	1.0	14	81	2	90 (1)	10

[a] M.b., mass balance. [b] Entries 1−6 determined by ^{1}H NMR spectroscopy (error limit ±5% of stated values); entries 7−10 determined by GC analysis (SE 54 capillary column, 30 m × 0.25 mm; error limit ±1% of stated values); entries 15−18 determined by HPLC analysis (LiChrosorb Diol, 9:1 *n*-hexane/MTB; error limit ±2% of stated values). [c] Entries 1−4 determined by ^{1}H NMR spectroscopy (error limit ±5% of stated values); entries 5−12 determined by GC analysis (SE 54 capillary column, 30 m × 0.25 mm; error limit ±1% of stated values); entries 13 and 14 determined by ^{1}H NMR spectroscopy (error limit ±5% of stated values); entries 15−18 determined by HPLC analysis (LiChrosorb Diol, 9:1 *n*-hexane/MTB; error limit ±2% of stated values). [d] The ee values are given in parentheses for the silanol (*R*)-**2h**, determined by HPLC analysis (Chiracel OD-H, 9:1 *n*-hexane/2-propanol; error limit ±2% of stated values). [e] Not determined.

10.0 equiv (urea) or 44−445 wt % (amylose) of an additive. No conversion of the silane was observed with UHP or 85% H_2O_2 in the absence of the MTO catalyst. The results for the MTO-catalyzed Si−H insertion of the silanes **1a**−**h** with UHP or 85% H_2O_2 are given in Table 1.

The conversion to the silanols was good to excellent (≥75%) for silanes **1a**−**e** when the MTO/UHP oxidant was used (Table 1, entries 1, 3, 5, 7, and 9), and significantly better than when MTO/85% H_2O_2 was used (entries 2, 4, 6, 8, and 10). For the sterically encumbered optically active silane **(*S*)-1h**, the conversion to silanol **(*R*)-2h** was low (entries 15−18) for both UHP and 85% H_2O_2.

The chemoselectivity of silanol versus disiloxane was good to excellent (≥80:20) with MTO/UHP (Table 1, entries 1, 3, 5, 7, 9, 11, 13, and 15) for all silanes studied; for MTO/85% H_2O_2, this was the case only for the sterically hindered substrates **1f**−**h** (entries 12, 14, and 18). The product selectivity dropped dramatically from ≥99:1 to 54:46 for silane **1e** (entries 9 and 10); for the silanes **1a** (entries 1 and 2), **1b** (entries 3 and 4), and **1d** (entries 7 and 8), the corresponding disiloxane even prevails. The selectivity was hardly changed for the sterically encumbered substrates **1f**−**h** (entries 11−15 and 18). Indeed, it is significant to note that the disiloxane **3f** is not known and attempts to prepare it analogously to the other disiloxanes led only to the silanol **2f**.

The presence of urea not only is beneficial for the efficiency and the product selectivity in the oxidation of the silanes but also makes this novel Si−H insertion highly stereoselective, as demonstrated in Table 1 (entries 15−18) for the enantiomerically pure silane (+)-(α-Np)PhMeSiH [**(*S*)-1h**; ee ≥ 98%]. Best results were obtained with the combination MTO/UHP (entry 15), which afforded (+)-(α-Np)PhMeSiOH [**(*R*)-2h**] in high enantiomeric excess (ee = 91%) and excellent silanol selectivity (96:4). When the urea is omitted (entry 18), only traces of the *racemic* silanol **2h** were obtained. Similarly, a high retention of configuration may be achieved by the use of in situ generated UHP (data not shown). Unfortunately, under the conditions employed in Table 1 (entry 15), the conversion is only modest. Attempts to remedy this deficiency by employing higher amounts of catalyst did not raise the extent of conversion but increased the degree of racemization (entries 15−17). However, the increase of the amount of both catalyst and UHP led to the desired high yield of silanol **2h** in excellent enantiomeric purity (Scheme 2). In control experiments, it was shown that MTO (10 mol %), the oxygen donors H_2O_2 (1.0 equiv) or UHP (1.0 equiv) individually, or small amounts of water (0.33 equiv) do not racemize the silane **(*S*)-1h** or the silanol **(*R*)-2h** to any significant extent even after 24 h. Furthermore, the disiloxane product **3h** was not hydrolyzed under the reaction conditions, and therefore, it is not the source of racemic silanol **2h**. Nonetheless, both the silane **(*S*)-1h** and the silanol **(*R*)-2h** gave completely racemized silanol **2h** within minutes with complex

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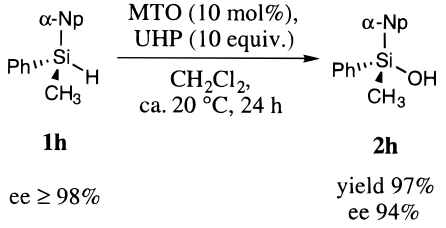
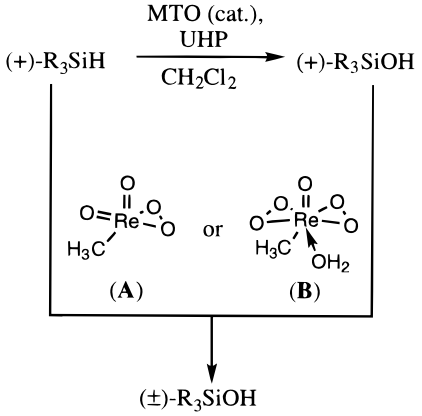
Scheme 2. Oxidation of (+)-(α-Np)PhMeSiH (**1h**) by MTO/UHP



Scheme 3. Racemization of (+)-(α-Np)PhMeSiOH (**2h**)



A, prepared in situ, or with authenic complex **B** (Scheme 3). Racemic **2h** was also obtained with MTO/85% H_2O_2 and MTO/UHP when methanol (in which the urea additive is completely dissolved) was used as reaction medium.

To elucidate the beneficial urea effect of the MTO/UHP versus the MTO/85% H_2O_2 oxidant, a detailed study was conducted with silane **1d** as model substrate. Longer reaction times did not enhance the conversion, because the catalyst decomposed. Thus, the oxidation kinetics of silane **1d** showed that although the MTO/85% H_2O_2 oxidant was initially more catalytically active than MTO/UHP, significant decomposition of the catalyst (Scheme 1; the decomposition product MeOH[24] was detected by ^{1}H NMR spectroscopy) and also of the oxygen source (monitored by peroxide test; KI/AcOH) had already occurred after ca. 1.5 h versus ca. 8 h for the MTO/UHP combination. Even a 10-fold excess of 85% H_2O_2 (Table 2, entry 2) resulted in only a slightly higher conversion, whereas an improvement from 26% to 69% was achieved by using a 10-fold higher amount of catalyst (entry 3). The use of more dilute aqueous solutions of H_2O_2 (30% and 3%) also did not give the silanol **2d** in good yield and selectivity (data not shown). In solvents such as acetone or acetonitrile, the MTO/85% H_2O_2 oxidant showed lower catalytic activity, although in methanol, the oxidation was more efficient.

Dichloromethane proved to be the best solvent for the heterogeneous liquid−solid system MTO/UHP. In contrast to MTO/85% H_2O_2, the conversion could not be improved for MTO/UHP by the use of more catalyst; rather, increasing amounts of the MTO catalyst (amount of UHP constant at 1.0 equiv.) led to decreased conversions (Table 2, entries 4−6). The MTO/UHP oxidant may also be generated in situ by the addition of 1.0 equiv urea to the MTO/85% H_2O_2 combination (entry 8). The selectivity is as high as with MTO/UHP (entry 4), albeit at somewhat diminished conversion. When the amount of urea additive was decreased or increased (entries 7 and 9), the conversion dropped substantially, whereas the silanol/disiloxane ratio remained high for an excess of urea but was lowered at reduced amounts. In contrast to these heterogeneous oxidations, when the CH_2Cl_2-soluble tetramethylurea (entry 10) was used as additive, the silane **1d** was converted in only 20%, although the silanol **2d**/disiloxane **3d** ratio was high at 96:4 (entry 10). A small red shift of the UV−vis absorption maximum indicates coordination of the tetramethylurea to the rhenium metal center. In the case of the insoluble urea, no such complexation could be detected by UV−vis or ^{1}H NMR spectroscopy.

When larger amounts of the MTO catalyst were used to drive the reaction with 85% H_2O_2 to completion, the silanol/disiloxane selectivity was shifted toward the disiloxane (Table 2, entries 1 and 3). For the MTO/UHP oxidant, higher amounts of the MTO catalyst also resulted in more disiloxane (entries 4−6). Control experiments revealed that the condensation of silanol **2d** to the corresponding disiloxane **3d** is catalyzed by MTO/85% H_2O_2 (but not by MTO or 85% H_2O_2 alone) or by MTO in the presence of several equivalents of water; the presence of silane is also not required. When a water-free 50% solution of H_2O_2 in ethyl ether was employed, the silanol (**2d**)/disiloxane (**3d**) ratio was 2:98. Thus, under these anhydrous conditions, more disiloxane was generated than for 85% H_2O_2 (cf. Table 1, entry 8).

In the heterogeneous MTO/UHP oxidant, the urea additive may be replaced by amylose (entries 11−13), which is made up of helical chains of glucose molecules and, like urea, is known to form channel inclusion complexes.[25] In the presence of amylose, the silanol/disiloxane selectivity also substantially improves. Thus, with increasing amounts of this additive, the product ratio was raised to as high as 98:2 in favor of silanol, but the extent of conversion was only 9% (entry 13). In contrast, silica gel (entry 14) and the insoluble 1,3-diphenylurea derivative (data not shown), which do not form inclusion complexes, afford a poor silanol/disiloxane selectivity under these heterogeneous conditions (silanol/disiloxane ratio 17:83 for SiO_2 and 8:92 for 1,3-diphenylurea), which is similar to the homogeneous reaction (20:80) without urea.

In view of the beneficial effect of the pyridine additive reported recently by Sharpless et al.,[26] a comparative study of the MTO/UHP and MTO/30% H_2O_2/pyridine systems in the oxidation of silanes **1d** and **(*S*)-1h** was made. For a 0.005:1.00:0.12 ratio of MTO/30% H_2O_2/pyridine (no excess of H_2O_2 was used because this was previously found to be detrimental to the silanol/disiloxane ratio), only 65% conversion of silane **1d** and a **2d**/**3d** product ratio of 36:64 were obtained, which are substantially worse than results for the MTO/UHP oxidant without pyridine as additive (Table 1, entry 7). More significantly, the oxidation of the enantiomerically pure silane **(*S*)-1h** by the MTO/30% H_2O_2/pyridine combination gave racemic silanol **2h** (data not shown), which must be contrasted with the stereoselective MTO/UHP system without pyridine (Table 1, entry 15).

The peroxo complexes **A** and **B** have both been proposed as being catalytically active species in the oxidation of organic compounds, with the complex **A** claimed to be the somewhat faster one.[24] In contrast, for the MTO-catalyzed oxidation of silanes, the diperoxo complex **B** is the more catalytically active

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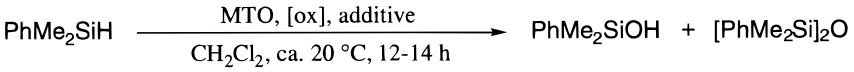
Table 2. MTO-Catalyzed Oxidation of $PhMe_2SiH$ (**1d**) with Hydrogen Peroxide as Oxygen Source in the Presence of Additives

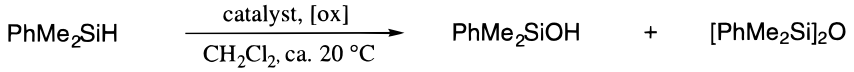


1d **2d** **3d**

entry	oxidant	(equiv)	additive (equiv)	MTO (mol %)	m.b. (%)[a,b]	convn (%)[b]	products (%)[b] silanol	products (%)[b] disiloxane
1	85% H_2O_2	(1.0)		1.0	≥99	26	20	80
2	85% H_2O_2	(10.0)		1.0	88	36	31	69
3	85% H_2O_2	(1.0)		10.0	≥99	69	2	98
4	UHP	(1.0)		1.0	≥99	87	98	2
5	UHP	(1.0)		10.0	≥99	70	70	30
6	UHP	(1.0)		20.0	≥99	50	61	39
7	85% H_2O_2	(1.0)	urea (0.1)	1.0	84	34	65	35
8	85% H_2O_2	(1.0)	urea (1.0)	1.0	91	72	≥99	<1
9	85% H_2O_2	(1.0)	urea (10.0)	1.0	97	34	99	1
10	85% H_2O_2	(1.0)	tetramethylurea (1.0)	1.0	93	20	96	4
11	85% H_2O_2	(1.0)	amylose (44 wt %)	1.0	75	49	44	56
12	85% H_2O_2	(1.0)	amylose (111 wt %)	1.0	87	28	93	7
13	85% H_2O_2	(1.0)	amylose (445 wt %)	1.0	93	9	98	2
14	85% H_2O_2	(1.0)	SiO_2 (135 wt %)[c]	1.0	82	28	17	83

[a] M.b., mass balance. [b] Determined by GC analysis (SE 54 or HP-5 capillary column, 30 m × 0.25 mm; error limit ±1% of the stated values). [c] Particle size 32−63 μm.

Table 3. Metal-Catalyzed Oxidation of Silane **1d** to Silanol **2d** and Disiloxane **3d**



1d **2d** **3d**

entry	catalyst (mol %)	oxidant	time (h)	m.b. (%)[a,b]	convn (%)[b]	products (%)[b] silanol	products (%)[b] disiloxane
1	$MeReO_3$ (1.0)	UHP	13	≥99	87	98	2
2	$MeReO_3$ (1.0)	85% H_2O_2	13	≥99	26	20	80
3	Re_2O_7 (1.0)	85% H_2O_2	24	98	20	17	83
4	Mn(salen)[c] (7.4)	PhIO[d]	0.6	≥99	≥99	80	20
5	Ti(O*i*-Pr)$_4$[e] (10.0)	*t*-BuOOH[f]	41	74	38	39	61
6	VO(acac)$_2$ (1.0)	*t*-BuOOH[f]	24	≥99	31	56	44
7	MoO_2(acac)$_2$ (1.0)	*t*-BuOOH[f]	24	90	69	5	95

[a] M.b., mass balance. [b] Determined by GC analysis (SE 54 or HP-5 capillary column, 30 m × 0.25 mm), error limit ±1% of stated values. [c] (*S*,*S*)-(−)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane-manganese(III) chloride [Mn(salen)]. [d] Conducted at 0 °C, necessary to suppress the direct oxidation of the silane by PhIO. [e] Diethyl L-tartrate used as auxiliary. [f] As a 3.64 M solution in CH_2Cl_2.

species (Scheme 1). Thus, in the oxidation of the test silane **1d** with the authentic **B** complex (0.50 equiv), the silane **1d** was converted in 43% to the disiloxane **3d** after 4 h and only traces of the silanol **2d** were formed. The monoperoxo complex **A** (1.00 equiv), which was generated in situ, gave only ca. 20% conversion of silane **1d** to the corresponding siloxane.[27]

The catalytic efficiency of the MTO/UHP oxidant was compared with other well-known oxidants (Table 3) for the test substrate dimethylphenylsilane (**1d**). Only Mn(salen)/PhIO (entry 4) compares favorably with MTO/UHP (entry 1). Although the reaction rate and conversion for Mn(salen) are substantially higher than for MTO, the product selectivity is lower and extensive racemization was observed in the oxidation of the optically active silane **(*S*)-1h**. Furthermore, more than seven times the amount of catalyst must be used. For the Mn(salen) catalyst, iodosobenzene (entry 4) is the more effective oxygen-atom donor than NaOCl or 30% H_2O_2 (data not shown). Moreover, PhIO oxidizes the silane directly, and the reaction must be conducted at a lower temperature (≤0 °C) to suppress this direct oxidation. For all the other catalytic systems, i.e., Re_2O_7/85% H_2O_2 (entry 3), (Ti(O*i*-Pr)$_4$/L-DET/*t*-BuOOH (entry 5), VO(acac)$_2$/*t*-BuOOH (entry 6), or MoO_2(acac)$_2$/*t*-BuOOH (entry 7), both the conversion and the silanol selectivity are drastically decreased.

Ti(O*i*Pr)$_4$/L-DET/*t*-BuOOH and VO(acac)$_2$/*t*-BuOOH were ineffective for the stereoselective oxidation of (+)-(α-Np)-PhMeSiH [**(*S*)-1h**] to the desired (+)-(α-Np)PhMeSiOH [**(*R*)-2h**]. Thus, the enantiomeric excess in the former case was 51% and in the latter only 8%; almost complete racemization was also observed for MoO_2(acac)$_2$/*t*-BuOOH and Mn(salen)/PhIO (data not shown in Table 3).

Discussion

The results above demonstrate unequivocally that the MTO/UHP combination constitutes a convenient oxidation system to catalytically convert silanes to the corresponding silanols in good to excellent yields (Table 1). The catalytic nature, the high chemoselectivity for the silanols versus the disiloxane, and the excellent enantioselectivity in the case of the optically active silane **(*S*)-1h** render this novel oxidation especially advantageous. These favorable features of MTO/UHP are in stark contrast to those of MTO/85% H_2O_2. For the latter, lower conversions are obtained, the chemoselectivity is shifted toward the undesired disiloxane, and no enantiomeric excess is obtained

(27) The condensation of silanol **2d** to disiloxane **3d** is catalyzed by complexes **A** and **B** and by one of the decomposition products of the MTO catalyst, e.g., perrhenate.

with the optically active **(*S*)-1h**. The striking differences between the two oxidation systems, MTO/85% H_2O_2 and MTO/UHP, point to the essential role played by the urea additive in the catalytic Si−H insertion.

The question arises what the possible causes are for the higher reactivity and improved selectivity in the presence of urea, although urea is insoluble in the reaction mixture. What influence do the oxygen source, the catalyst, and the urea additive have in this heterogeneous process? The water in the 85% H_2O_2 cannot be the culprit, because the conversion remained low when a water-free solution of H_2O_2 in ethyl ether was used. Additionally, the silanol/disiloxane selectivity was shifted even further toward the disiloxane product under these anhydrous reaction conditions.

Whereas the amount of H_2O_2 has no significant effect on the conversion of **1d** and the product distribution **2d**/**3d** (Table 2, entries 1 and 2), the concentration of the rhenium catalyst shows a marked influence. Thus, with MTO/85% H_2O_2, for the test substrate **1d**, more catalyst led as expected to higher conversion (Table 2, entries 1 and 3). In contrast, for MTO/UHP, the use of more catalyst resulted in decreasing conversions of silane **1d** and a deterioration of the silanol selectivity (entries 4−6). This decrease in both conversion and product distribution (**2d**/**3d**) indicates that an optimal catalyst/urea additive ratio is necessary to obtain the silanol **2d** selectively in high yield, a conclusion which may also be reached when the amount of the urea additive is varied (entries 7−9). The fact that both conversion and product selectivity depend on the amount of urea employed is all the more astonishing if one considers that the urea additive is insoluble in dichloromethane as reaction medium. Because the urea is not in solution but nevertheless favorably assists the catalytic Si−H insertion, this heterogeneous process presumably takes place at the urea−solvent interface, possibly within the urea interior.

It is known that urea can form channel-like structures, which are made up of helical chains of hydrogen-bonded urea molecules.[25a] These hexagonal channels are generated spontaneously when urea forms inclusion complexes. Even when the urea is not dissolved, its crystal lattice changes from tetragonal to hexagonal without passing through the dissolved state.[25b] Indeed, a broad range of guest compounds, e.g., alkanes, olefins, alcohols, ethers, ketones, acids, esters, amines, nitriles, halogenated compounds, and even silanes,[25d] form inclusion complexes with urea. Moreover, suspensions of urea inclusion complexes were recently shown to exchange guest molecules with the liquid phase.[28] Nothing appears to be known in the literature about metal-catalyzed reactions inside urea channels.

In view of these facts, we suggest that the MTO-catalyzed Si−H insertions take place within the urea channels. The effective channel diameter in urea inclusion complexes is reported to be ca. 5.5-5.8 Å;[25c] however, in analogy to amylose,[29] it is suggested that the lattice possesses a degree of flexibility. Thus, the channels are large enough to absorb the oxygen source H_2O_2, the catalyst MTO, and the rhenium peroxo complexes **A** and **B**, and the absorption should be especially advantageous for polar guest molecules as a result of hydrogen bonding with the urea.[30] Not too sterically encumbered silanes[31] also fit inside the urea channels, whereas larger silanes are oxidized at the entrance of the urea channels by the rhenium oxidant inside the channels. However, because of spatial constraints in the urea channels, the condensation of the silanols is prevented and excellent selectivities of silanol versus disiloxane are observed for all silane oxidations with the heterogeneous MTO/UHP but not with the homogeneous MTO/H_2O_2 oxidant. That the ordered structure of the undissolved urea inclusion compound is responsible is evident from the additional fact that the insoluble 1,3-diphenylurea, for which no inclusion complexes have been reported, leads to both low conversion (21%) and poor selectivity (8:92). Furthermore, the CH_2Cl_2-soluble tetramethylurea (Table 2, entry 10) also results in low conversion (only 20%) like the MTO/H_2O_2 combination, albeit with high selectivity (96:4) like the MTO/UHP one. The reason for the selectivity with tetramethylurea differs from that of the MTO/UHP case. Because the tetramethylurea complexes with the rhenium metal center,[32] the reactivity is reduced (low conversion), but the Lewis acidity is buffered, and thus, a high selectivity results. In the case of the insoluble urea, no such coordination takes place. Additional support that the Si−H insertion takes place inside the urea channels and not on the outer surface was provided by using silica gel as additive, which is commonly used by zeolite chemists for similar control experiments.[33] In this heterogeneous system, no effect on either the conversion of silane **1d** or the product ratio **2d**/**3d** was observed with MTO/85% H_2O_2 as oxidant (Table 2, entries 1 and 14). Silica gel does not form inclusion complexes, and thus, the oxidation takes place at the surface and/or in solution.

Alternatively, amylose, which is made up of glycopyranose channels with 6−7 glucose units per turn of the helix,[34] is known to make inclusion complexes and should serve as a matrix like urea. The inner diameter of these helical structures is 4.5−7.0 Å and, thus, in the same range as that of the urea channels. Indeed, amylose has previously been used as a 'reaction vessel' for photochemical reactions.[29b,35] This hunch proved to be correct in that amylose served as a host for the MTO-catalyzed silane oxidation;[36] unfortunately, the silane conversions were lower than those with urea (Table 2, entries 11−13). Presumably, this is due to the more polar environment and the conformationally fixed structure of the amylose compared to the urea channels. The higher polarity of the amylose may be counterproductive for the absorption of the relatively nonpolar silanes. Nevertheless, in analogy to urea, the silanol (**2d**)/disiloxane (**3d**) ratio was improved with increasing amounts of the amylose additive.

The dependence of the reactivity and selectivity for the MTO/UHP oxidant on the catalyst/urea ratio is also indicative of host−guest chemistry. Thus, with higher amounts of the catalyst (Table 2, entries 4−6) or less urea (Table 2, entries 7−9), the Si−H oxidation takes place only partially inside the urea matrix and a significant portion occurs in solution, as displayed by the lower conversions and worse silanol/disiloxane (**2d**/**3d**) selec-

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(30) Hollingsworth, M. D.; Santarsiero, B. D.; Harris, K. D. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 649−652.

(31) Force-field calculations reveal that the silane **1d** fits inside the urea channels.

(32) The analogous complexation of hexamethylphosphoramide (HMPA) to the yellow diperoxo complex $CH_3Re(O)(O_2)_2 \cdot H_2O$ (by ligand exchange with the coordinated water) leads to the orange-reddish complex $CH_3Re(O)(O_2)_2 \cdot$HMPA: Herrmann, W. A.; Correia, J. D. G.; Artus, G. R. J.; Fischer, R. W.; Romão, C. C. *J. Organomet. Chem.* **1996**, *520*, 139−142.

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(36) In some cases, the amylose additive turned yellow in the reaction mixture, which is due to the presence of the rhenium diperoxo complex **B**.

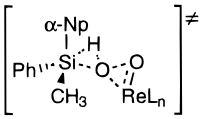

Figure 1. Possible transition state in the oxidation of (+)-(α-Np)-PhMeSiH (**1h**) with MTO/UHP.

tivities. Nevertheless, when larger amounts of urea were employed (entry 9), only the extent of conversion of silane **1d** was reduced, while the selectivity of silanol **2d** remained high. The excellent product ratio indicates that the oxidation takes place inside the urea channels. However, the concentrations of both the catalyst and the oxygen donor H_2O_2 inside the tubes is significantly lower (dilution effect), and consequently, the reaction rate is reduced.

For the sterically encumbered silane **(*S*)-1h**, which is oxidized relatively slowly, we propose that the Si−H insertion occurs at the entrance of the urea channels, presumably with the Si−H bond pointing inside. This sluggish silane is completely converted when larger amounts of UHP (10 equiv) and MTO (10 mol %) are employed (Scheme 2). When only the amount of catalyst is increased, the conversion is not improved, but the enantiomeric purity of the silanol **2h** is decreased (Table 1, entries 16 and 17). This implies that appreciable amounts of the catalyst are present in solution, because the oxidation of **(*S*)-1h** in the absence of urea leads to *racemic* **2h** (entry 18), whereas in the presence of urea, the **(*R*)-2h** is obtained in high enantiomeric excess (entry 15).

The high degree of retention of configuration in the oxidation of (+)-(α-Np)PhMeSiH **(*S*)-1h** by MTO/UHP (Table 1, entry 15) gives important insight into the mechanism of this metal-catalyzed Si−H insertion. In analogy to the stoichiometric oxidants dimethyldioxirane (98% ee),[15] *m*-CPBA (86% ee),[12b] or oxaziridines (98.5% ee),[16] which all oxidize the silane **(*S*)-1h** to the silanol **(*R*)-2h** in high optical purity, a 'butterfly' transition state is suggested for the oxygen transfer (Figure 1). Radical intermediates are unlikely, because the chiral information is almost completely conserved and because previously investigated MTO-catalyzed oxidations have been shown not to involve radical species.[24] Moreover, a dioxirane-type structure has generally been proposed as the transition state in MTO-catalyzed oxidations, as expected for the catalytically active rhenium diperoxo complex **B**, which has been isolated and structurally characterized.[21]

The MTO/UHP oxidant compares very favorably with other catalytic oxidizing systems such as Re_2O_7/85% H_2O_2, Mn(salen)/PhIO, Ti(O*i*-Pr)$_4$/L-DET/*t*-BuOOH, VO(acac)$_2$/*t*-BuOOH, or MoO_2(acac)$_2$/*t*-BuOOH for Si−H insertions (Table 3). Larger amounts of these metal catalysts were needed for comparable conversion, the selectivity for silanol **2d** was poorer, and none of these metal catalysts gave acceptable results with the environmentally friendly oxidant H_2O_2 in any form. The Re_2O_7/H_2O_2 system (Table 3, entry 3), which has previously been used for the oxidation of olefins, arenes, and certain organometallic compounds,[37] gives a result similar to that for MTO/85% H_2O_2. The former catalyst is known to hydrolyze to $HReO_4$,[38] which does not react with H_2O_2 but which assists the condensation of silanols to disiloxanes. Thus, deactivation of the catalyst is a prominent feature in the catalytic oxidation system Re_2O_7/H_2O_2, and this explains the low conversion and poor silanol/disiloxane ratio.

A comparison with the stoichiometric oxidants *m*-CPBA[12] and DMD (cf. Supplementary Information, pp S-6 to S-9, and ref 15) reveals that the selectivities and yields of silanol are similar to those of the MTO/UHP system. However, *m*-CPBA has not been used for the oxidation of critical substrates such as dimethyl-*n*-propylsilane (**1b**), whose silanol readily forms the disiloxane. It must be stressed that the advantage of MTO/UHP is its catalytic nature.

In summary, we have developed a novel, catalytic, and highly efficient route to silanols by the oxidation of silanes with the MTO/UHP combination. Thus, high conversions of the silane and excellent selectivities of the silanol versus disiloxane products are obtained, and the optically active silane (+)-(α-Np)PhMeSiH [**(*S*)-1h**] may be transformed with a high degree of retention to the corresponding silanol **(*R*)-2h**. This is the first catalytic oxidation of optically active silanes to their silanols with *retention* of configuration. It is proposed that the urea acts as host in these MTO-catalyzed Si−H insertions and that the reactions take place inside the urea channels. Under these heterogeneous conditions, the condensation of silanols is prevented for steric reasons and the catalyst is stabilized. This novel feature of urea as a reaction matrix opens up new and challenging prospects to control the selectivity in a wide range of organic reactions, which should be a worthwhile pursuit.

Acknowledgment. The generous financial support of the *Deutsche Forschungsgemeinschaft* (SFB 347 "Selektive Reaktionen Metall-aktivierter Moleküle"), the *Bayerische Forschungsstiftung* (Bayerischer Forschungsverbund Katalyse − FORKAT), and the *Fonds der Chemischen Industrie* is gratefully appreciated. This paper is dedicated to Prof. Dr. Helmut Werner, University of Würzburg, on the occasion of his 65th birthday.

Supporting Information Available: Synthetic details and characteristic spectral data of the silanes **1a**−**c**,**f**,**h**, silanols **2a**−**d**,**f**−**h**, and disiloxanes **3a**−**c**,**g**,**h**, the general catalytic oxidation procedures, analytical protocols for determining the product ratios of silanols **2a**−**h** to disiloxanes **3a**−**h**, and also the enantiomeric excess of silanol **2h** are given (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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