at pH 6.5 initiated the fragmentation of the linker and released the DMTr-protected thymidine **16** from the solid support under gentle conditions (Scheme 4).

The results demonstrate that the 4-acetyloxybenzyloxy linker allows for the detachment of amines (like leucine *tert*-butyl ester), carboxylic acids (like the tetrahydro-β-carbolines **14**), and alcohols (like the protected nucleoside **16**) from the polymeric support under very mild conditions (pH 5–7, room temperature) and with complete selectivity. The results are not only relevant to combinatorial chemistry, they also indicate that enzymes in general may be valuable reagents for transformations on solid supports.[12]

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Novel Distorted Pentagonal-Pyramidal Coordination of Anionic Oxodiperoxo Molybdenum and Tungsten Complexes**

Jean-Yves Piquemal, Sabine Halut, and
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There is currently much interest in the preparation of new polyoxo(peroxo)metalates for homogeneous catalysis[1] and heterogeneous systems[2] in order to understand the chemistry of surface species and the nature of the catalytically active sites of transition metal containing molecular sieves or other materials. While studying oxidation reactions with mesoporous materials,[1m] which are potentially interesting catalysts and/or catalyst supports,[3] we became interested in comparing anionic or neutral oxoperoxo complexes with those that can be formed on silica and/or alumina. From studies on systems of aqueous $[MoO_4]^{2-}$ and $[Mo_7O_{24}]^{6-}$ solutions and silica, it is known that Mo^{VI} uptake by SiO_2 is relatively low over the entire pH range, except for a small increase at pH 2 or lower owing to the formation of $[SiMo_{12}O_{40}]^{4-}$ ions, which can partially desorb into solution.[4] Furthermore, silica (BET specific surface area 263 $m^2\,g^{-1}$) and molybdenum– (or tungsten–) oxoperoxo species interact in aqueous acidic medium to form surface peroxo species with characteristic IR bands $\tilde{\nu}_{O-O}$ near 870 cm^{-1} ($\tilde{\nu}_{O-O}$ is expected to be in the range of 845–885 cm^{-1}).[1] These observations suggest that it might be possible to synthesize oxoperoxoheterosiloxanes involving the various functionalities on the silica surface (i.e., lone

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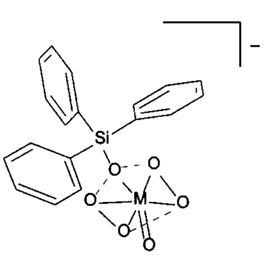
(free) geminal silanols and vicinal silanols from siloxane bridges).

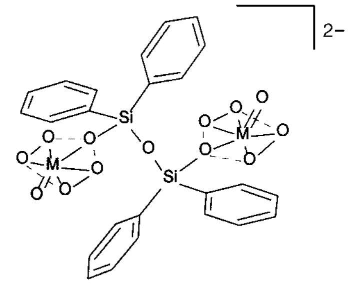
Several unsuccessful attempts to prepare heterosiloxanes of molybdenum or tungsten by conventional methods have been reported.[5] However, compounds containing Mo-O-Si moieties are formed by the reaction of sodium triphenylsilanolate with the dimethylformamide complex of $[MoO(OH)_2Cl_2]$.[6] As far as silanediols are concerned, the eight-membered metallasiloxane $[(tBu)_2SiO_2Mo(=O)_2]_2$, which may be considered as a model for metal oxides supported on silica surfaces, was isolated by Roesky et al.[7] With the dilithium salt $[LiOSi(tBu)_2]_2O$ and MoO_2Cl_2, the twelve-membered cyclic molybdenum(VI) siloxane, $[MoO_2(OSi(tBu)_2OSi(tBu)_2O)]_2$ was prepared.[8] The two molybdenum centers are bridged by two disilanolato moieties.

Diphenylsilanediol ($Ph_2Si(OH)_2$) and 1,1,3,3-tetraphenyldisiloxane-1,3-diol ($[Ph_2Si(OH)]_2O$) tend to undergo self-condensation in reactions with metal derivatives; on the other hand, tris(neopentyl)nitridomolybdenum(VI) reacts with Ph_3SiOH or $[Ph_2Si(OH)]_2O$ at 60 °C to yield imidotris(neopentyl) complexes.[9] Recently, two anionic polyoxoperoxo species $(PPh_4)_2[Ph_2SiO_2\{M_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (M = Mo, W) were synthesized in high yield by simple procedures involving $Ph_2Si(OH)_2$, $H_2O_2/H_2O/EtOH$, $MO_3 \cdot H_2O$, and PPh_4Cl.[10] These compounds were proposed as models for neutral $\{M_2O_2(\mu\text{-}O_2)_2(O_2)_2\}$ units grafted on silica surface through geminal silanol groups. Thus, organosilanols can be used to model silica-supported metal–oxo(peroxo) species; the novel anionic species may be synthesized by nondemanding reactions involving the various silanol groups of silica-based materials.

The reactions of triphenylsilanol (Ph_3SiOH, **1**) and $[Ph_2Si(OH)]_2O$ (**2**) with an aqueous solution of $[MO(O_2)_2(H_2O)_2]$ (M = Mo, W) lead to mononuclear anionic diperoxo species **3** and **4** and dinuclear complexes **5** and **6**, respectively, in fair to nearly quantitative yields. The new molybdenum- and tungsten–siloxane complexes were fully characterized by elemental analysis, vibrational and ^{29}Si NMR spectroscopies, and single-crystal X-ray diffraction studies.[11] The molecular structure of the complex anions **3** (M = Mo) and **4** (M = W) are shown in Figure 1.



3 (M = Mo), **4** (M = W)



5 (M = Mo), **6** (M = W)

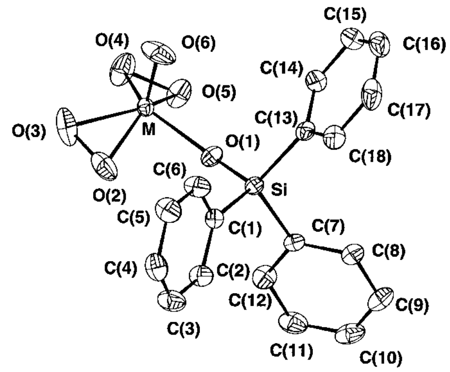


Figure 1. CAMERON representation[22] of $[Ph_3SiO\{MO(O_2)_2\}]^-$ showing the atom-labeling scheme. Selected bond lengths [Å] and angles [°] for **3** (M = Mo) [**4** (M = W)]: M–O(1) 1.933(4) [1.925(4)], M–O(2) 1.886(6) [1.898(8)], M–O(3) 1.895(6) [1.892(7)], M–O(4) 1.920(5) [1.925(7)], M–O(5) 1.907(5) [1.897(6)], M–O(6) 1.680(4) [1.690(6)], O(2) –O(3) 1.407(9) [1.38(1)], O(4) –O(5) 1.421(7) [1.422(9)], Si–O(1) 1.617(4) [1.616(5)], Si–C(1) 1.872(6) [1.882(8)], Si–C(7) 1.860(5) [1.860(7)], Si–C(13) 1.869(6) [1.851(7)]; O(1)-M-O(2) 84.6(3) [84.2(3)], O(1)-M-O(5) 84.2(2) [84.7(3)], O(3)-M-O(4) 87.4(3) [88.0(3)], O(2)-M-O(3) 43.7(3) [42.8(3)], O(4)-M-O(5) 43.6(2) [43.7(3)], Si-O(1)-M 145.4(3) [147.8(3)].

The metal center in **3** and **4** is surrounded by one silanolato ligand $(C_6H_5)_3SiO$ and two peroxo groups that are side-bound in a η^2 fashion. An interesting feature of these very unusual anionic complexes is the slightly distorted pentagonal-*monopyramidal* configuration of the six-coordinate Mo (or W) atom, since molybdenum(VI) or tungsten(VI) centers are seven-coordinate in most oxodiperoxo complexes;[12] there have only been two previous reports of compounds containing six-coordinate metal centers that describe an oxodiperoxo vanadate (1 –).[13] The coordination of two-electron donor ligands L (usually H_2O, hexamethylphosphoramide (HMPA), etc.) does not occur, although water was not excluded from the recrystallization solvent.

The axial position is occupied by an oxo ligand with a normal M–O bond length.[12] The M atoms are not located in the mean basal plane defined by the O atoms of the two peroxo groups and the silanolato group (deviation 0.55 [0.56] Å for Mo(1) [W(1)]; ca. 0.38 Å in a seven-coordinate complex). The oxygen atoms are 0.15 [0.16] Å from the mean basal plane. The Si–O and Si–C bond lengths are similar to those in metallasiloxanes.[14] The O–O bond lengths in the peroxo groups (1.38 (1) and 1.423 (9) Å) for **4** correspond to published values,[12] but are significantly shorter than those in $[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$ (1.45 (2)–1.56 (2) Å);[15] such long bonds seem to be essential for the easy transfer of active oxygen to olefinic substrates.

The reaction of **2** with $[MoO(O_2)_2(H_2O)_2]$ in aqueous H_2O_2 leads to the dianionic species **5**, in which the two Mo atoms are also coordinated by six oxygen atoms in a pentagonal *monopyramidal* arrangement (Figure 2). Each girdle (basal plane) is generated again by two peroxo groups and one oxygen atom of the (μ-$OSiPh_2OSiPh_2O$) ligand. One of the O–O bonds is 1.353 (8) Å long and amongst the shortest reported.[12] The oxygen atoms that define the mean basal plane are coplanar to within 0.16 Å. The apical position of the girdle axis is occupied by the terminal oxo ligand O^{2-}. As for the octahedral coordination in polyoxometalates, the Mo atoms are displaced by 0.58 Å towards the oxo ligand. One side of the anion is related to the other by an inversion center at O(7). The coordination environment about the silicon atoms is tetrahedral. An analogous complex was synthesized

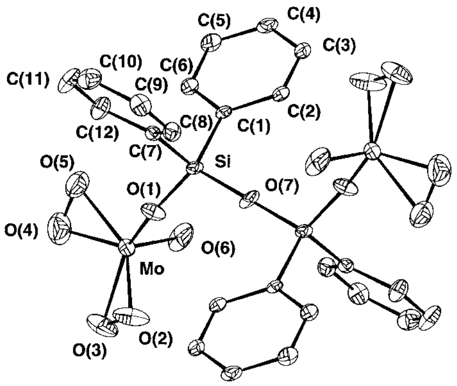


Figure 2. CAMERON representation[22] of $[(Ph_2SiO\{MoO(O_2)_2\})_2O]^{2-}$ (**5**) showing the atom labelling scheme. Selected bond lengths [Å] and angles [°]: Mo–O(1) 1.925(3), Mo–O(2) 1.907(5), Mo–O(3) 1.915(4), Mo–O(4) 1.840(6), Mo–O(5) 1.876(6), Mo–O(6) 1.697(4), O(2)–O(3) 1.439(7), O(4)–O(5) 1.353(8), Si–O(1) 1.600(3), Si–C(1) 1.863(4), Si–C(7) 1.856(5), Si–O(7) 1.609(1); O(1)-Mo-O(2) 84.5(2), O(1)-Mo-O(5) 84.1(2), O(3)-Mo-O(4) 85.7(3), O(2)-Mo-O(3) 44.2(2), O(4)-Mo-O(5) 42.7(3), Si-O(1)-Mo 150.7(2).

with $WO_3 \cdot H_2O$, but crystals suitable for an X-ray crystal structure determination could not be obtained. Comparison of the $\tilde{\nu}_{O-O}$ and $\tilde{\nu}_{Si-O}$ vibrations (IR and Raman) in the solid state and in solutions of MeCN suggests that the overall structure of the four anions is conserved in solution.

The Mo^{VI} and W^{VI} oxoperoxo complexes **3**–**6** are also active species in olefin oxidation and form epoxides as primary products; slight heating (optimum 40–60°C) is necessary to activate these anionic species. In all cases, the extent of increasing activity of homogeneous ("$H_2O_2/H_2O/$*t*BuOH") or phase-transfer catalysis systems depends on the silicon-based auxiliary anion. The replacement of phenyl by alkyl groups favors the reaction, as does use of phase-transfer agents with long alkyl chains (C_{16}–C_{18}). The yields and turnover numbers of the reaction depend inter alia on the [M]:[≡Si–O ligand]:[onium salt] ratio; it is important to avoid a large excess of the latter.[1c, 16] Spectroscopic data (Raman and/or NMR) show that the complexes are recovered without any change if excess H_2O_2 is used. Work is currently in progress to optimize conversions and selectivities and to compare the complexes with analogues in the chemistry of grafted silica surfaces and mesoporous materials.[1m]

In the solid state most of the diperoxo and some monoperoxo complexes are pentagonal-bipyramidal species. In solution, based on ab initio calculations[17] and spectral data, a distorted octahedral arrangement is favored. The work reported here shows that other structural types can be stabilized in the solid state and in solution for molybdenum and tungsten compounds as they are for anionic oxo(diperoxo)vanadium(v) species.[13]

Experimental Section

$[Ph_2Si(OH)]_2O$ (**2**) was synthesized as described in reference [18].

(Ph_4P)-**3** [(Ph_4P)-**4**]: MoO_3 (0.72 g, 5 mmol) [$WO_3 \cdot H_2O$ (1.25 g, 5 mmol)] was added to a 30% solution of hydrogen peroxide (4 mL, 35 mmol). After 1 h at 60°C the solution was cooled to room temperature [followed by centrifugation (15 min at 2000 rpm)] and then slowly added to a solution of **1** (1.38 g, 5 mmol) in ethanol (16 mL). NaOH (5 M, 1 mL) was added dropwise, and the solution stirred for 45 min. The complex anion was then precipitated by slow addition of PPh_4Cl (1.87 g, 5 mmol) in ethanol (2 mL). The pale yellow [white] solid was isolated by filtration, washed with water and Et_2O, and then dried under air. Yield = 85% [87%]; correct elemental analysis.

$(Ph_4P)_2$-**5** [$(Ph_4P)_2$-**6**]: MoO_3 (0.36 g, 2.5 mmol) [$WO_3 \cdot H_2O$ (0.62 g, 2.5 mmol)] was treated with a 30% solution of hydrogen peroxide (2 mL, 17 mmol). After 1 h at 60°C cooling of the solution [followed by centrifugation (15 min at 2000 rpm)] and dropwise addition of a solution of **2** (0.52 g, 1.25 mmol) in ethanol (4 mL) and of NaOH (5 M, 1 mL) gave a solution, which was stirred for 45 min. Slow addition of PPh_4Cl (0.94 g, 2.5 mmol) in ethanol (1 mL) gave a pale yellow [white] precipitate, which was treated as above. Yield = 95% [60%]; correct elemental analysis.

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1617, $\lambda = 71.069$ pm, $T = 293$ K, $\mu(\mathrm{Mo_{K\alpha}}) = 0.462$ mm^{-1}, crystal dimensions $0.4 \times 0.3 \times 0.25$ mm^3, $2 \leq 2\theta \leq 50°$; of 7153 measured reflections, 6525 were unique; 462 parameters refined in full matrix, $R1 = 0.039$ with 3411 reflections ($I > 3\sigma(I)$), $wR2 = 0.041$, $w = 1$, min./max. residual electron density $-290/480$ e nm^{-3}. (Ph$_4$P)-**4**: $C_{42}H_{35}O_6PSiW$, $M_r = 878.644$, monoclinic, space group $P2_1/c$ (no. 14); $a = 1089.2(2)$, $b = 1744.0(4)$, $c = 1989.7(3)$ pm, $\beta = 100.05(1)°$, $V = 3.722(2)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.57$ Mg m^{-3}, $F(000) = 1747$, $\lambda = 71.069$ pm, $T = 293$ K, $\mu(\mathrm{Mo_{K\alpha}}) = 3.29$ mm^{-1}, crystal dimensions $0.25 \times 0.25 \times 0.15$ mm^3, $2 \leq 2\theta \leq 56°$; of 7144 measured reflections, 6519 were unique; 462 parameters refined in full matrix, $R1 = 0.032$ with 4031 reflections ($I > 3\sigma(I)$), $wR2 = 0.037$, $w = 1$, min./max. residual electron density $-910/790$ e nm^{-3}. (Ph$_4$P)$_2$-**5**: $C_{72}H_{60}O_{13}P_2Si_2Mo_2$, $M_r = 1443.261$, monoclinic, space group $P2_1/c$ (no. 14); $a = 1305.0(2)$, $b = 1560.2(3)$, $c = 1676.9(6)$ pm, $\beta = 103.90(2)°$, $V = 3.314(1)$ nm^3, $Z = 2$, $\rho_{calcd} = 1.45$ Mg m^{-3}, $F(000) = 1469$, $\lambda = 71.069$ pm, $T = 293$ K, $\mu(\mathrm{Mo_{K\alpha}}) = 1.025$ mm^{-1}, crystal dimensions $0.5 \times 0.6 \times 0.2$ mm^3, $2 \leq 2\theta \leq 56°$; of 8624 measured reflections, 7973 were unique; 503 parameters refined in full matrix, $R1 = 0.045$ with 4724 reflections ($I > 3\sigma(I)$) and $wR2 = 0.047$, $w = 1$, min./max. residual electron density $-640/870$ e nm^{-3}. The data were collected on a Enraf-Nonius CAD4 four circle diffractometer (ω-2θ scans). All measurements were made at room temperature; two standard reflections showed no significant variation in intensity. Corrections were made for Lorentzian and polarization effects; an extinction correction was also applied;[19] an empirical absorption correction on the basis of Ψ scan data was introduced. The structures were solved by direct methods (SHELXS-86 program)[20] and subsequent Fourier difference techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found on difference Fourier maps; their positions were not refined and they were given one overall isotropic thermal parameter. Refinements were carried out by minimizing the function $\Sigma w(|F_O| - |F_C|)^2$, where F_O and F_C are the observed and calculated structure factors (program CRYSTALS).[21] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100828. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Solution and Solid-State Studies of a Chiral Zinc–Sulfonamide Complex Relevant to Enantioselective Cyclopropanations**

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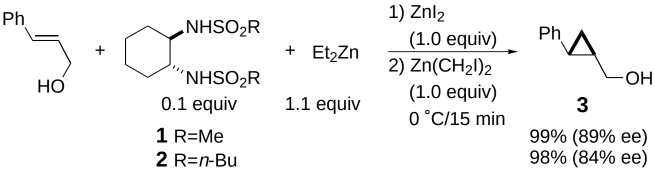
Sulfonamide derivatives of chiral amines and diamines have recently emerged as an important class of auxiliaries and catalysts in enantioselective transformations.[1] Chiral sulfonamides serve admirably as ligands for a number of different metals and have been employed in a wide variety of synthetically useful reactions, for example, cyclopropanation (Zn),[2] addition of dialkylzinc to aldehydes (Ti),[3–6] Mukaiyama aldol reaction (lanthanides),[7] enantiotopic group differentiation (Li),[8] Diels–Alder reactions (Al),[9] and enantioselective allylation of aldehydes (B).[10] In each of these systems, it is generally assumed that the metal is covalently bound to sulfonamide nitrogen atoms. Indeed, Corey et al. have provided an X-ray crystal structure of a chiral diazaaluminolidine prepared from *N,N'*-(1,2-diphenylethylene)bis(trifluoromethanesulfonamide) and trimethylaluminum, which clearly shows that the aluminum atom is bound in just such a manner.[11] Our interest in this area derives from the demonstration that chiral bis(sulfonamide)s which, when pretreated with diethylzinc, are effective catalysts for the enantioselective cyclopropanation of allylic alcohols.[12] Herein we provide reaction data, elemental analyses, spectroscopy studies, and an X-ray crystal structure in support of a catalyst structure which, among other interesting features, contains a zinc atom bound to both sulfonamide nitrogen atoms.

Although our previous studies have shown (*R,R*)-*N,N'*-cyclohexane-1,2-diyl)bis(methanesulfonamide) (**1**) to be the optimal cyclopropanation catalyst (Scheme 1), we selected the analogous and equipotent bis(*n*-butanesulfonamide) **2** for these structural studies owing to its superior solubility (e.g. in CH_2Cl_2: **1**: ≈ 1 mg mL^{-1} CH_2Cl_2; **2**: > 40 mg mL^{-1}).

We first established the chemical composition of the catalyst, which according to earlier studies requires the combination of **1** with diethylzinc.[12c] Therefore, a solution of **2** in dichloromethane was treated with diethylzinc (1.0 equiv, room temperature), and the solvent removed in



Scheme 1. Bis(sulfonamide)-catalyzed enantioselective cyclopropanation.

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