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Role of Siloxides in Transition Metal Chemistry and Homogeneous Catalysis

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The role of siloxide ligands in the chemistry and catalysis of transition metals is reviewed. The first part deals with recent aspects of low-valent transition metal siloxide chemistry, while the second part describes some developments in the chemistry of transition metal siloxides in high oxidation states, in particular with regard to the stability of the M–OSi bond. The third part highlights applications of well-defined late and early transition metal siloxides as "single site" catalysts in homogeneous catalysis. Special emphasis is placed on the steric and electronic influence of the siloxide ligand on the activity, selectivity, and stability of the catalytically active metal species.

Introduction

There has been considerable interest in recent years in the chemistry and structures of well-defined metal siloxides, which are also referred to as metalla- or metallosiloxanes and metal silanolates. These molecular compounds have found widespread application as precursors for novel materials[1] and heterogeneous catalysts,[2] and as model compounds for silica-supported metal catalysts.[3] The vast majority of main group metals, and many transition metals, lanthanides, and actinides are already known to form either homoleptic metal siloxides of formula $M(OSiR_3)_x$ or heteroleptic complexes of the form $L_yM(OSiR_3)_x$. Most of these metal siloxides are derived either from silanols [R_3SiOH], silanediols [$R_2Si(OH)_2$], α,ω-siloxanediols [$HO\text{-}(R_2SiO)_n\text{-}H$], silanetriols [$RSi(OH)_3$], or from incompletely condensed polyhedral oligosilsesquioxanes such as $R_7Si_7O_9(OH)_3$.[4] The synthesis and characterization of these complexes as well as their precursor compounds is well documented in the literature.[5] Therefore, it is not the goal of this review to recount all the efforts being made in this area but rather to take a more general view of the role of the siloxide ligand as an ancillary ligand in transition metal chemistry and homogeneous catalysis. Particular attention will be given to the steric and electronic influence of siloxide ligands on the structure, stability, and catalytic activity of the supported transition metal fragments.

Electronic Properties of R_3SiO^- Ligands

What are the main properties of siloxide ligands that allow them to electronically interact with metals and how do these interactions compare with those of the alkoxides? (1) The siloxide oxygen atom may form polar covalent bonds to metal atoms or may support ionic bonds, depending on the relative electropositivity of the metal and the electronic nature of the R groups bound to silicon. (2) Siloxides (R_3SiO^-) are similar to alkoxides (RO^-) and, in principle, are capable of binding to the metal through a σ-bond and by π-donation of the two p orbitals of oxygen, provided that the Si–O–M angle is close to 180°. The fact that M–O distances are shorter for M–O–R groups that have M–O–C angles approaching 180° is generally accepted to be due to strong ligand-to-metal π-bonding. The case of siloxides, however, should be approached with caution, since silicon is more electropositive than carbon; therefore Si–O–M angles are generally larger than C–O–M angles. (3) Moreover, the bonding between the p_π orbital of the oxygen atom and the d_π orbital of the metal atom (Op_π-to-Md_π bonding) is reduced relative to that in aliphatic alk-

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oxides due to backbonding of the Op orbitals into fairly low-lying and vacant silicon–carbon σ^* orbitals of π symmetry. This, in turn, decreases the overall donating power of siloxides and consequently increases the electrophilicity of the metal center relative to that in aliphatic alkoxides. In fact, IR spectroscopic studies on a series of molybdenum complexes of formula $[Mo(OR)_3(NO)]_2$ performed by Chisholm and co-workers support this view.[6] The $\nu_{(NO)}$ values increase from 1630 cm^{-1} (R = tBu), through 1640 cm^{-1} (R = iPr) and 1660 cm^{-1} (R = SitBuMe$_2$) to 1670 cm^{-1}, where $(RO)_3$ = (cyclohexyl)$_7Si_7O_9(O)_3$, which shows the siloxide groups to be weaker donors than aliphatic alkoxides. This could be confirmed by Caulton and co-workers, who reported IR spectroscopic data that indicate the ($\sigma + \pi$) ligand donor power of the group X in compounds of formula X–RuH(CO)(PtBu$_2$Me)$_2$ to be as follows: X = OEt > OCPh$_3$ > OSiMe$_3$ > OSiMe$_2$Ph > OSiPh$_3$ > OH > OCH$_2$CF$_3$ > OPh.[7] Both studies also suggest that the overall electron-releasing properties of R_3SiO^- can be fine-tuned by proper choice of R. A good estimate of the donor properties of R_3SiO^- can be obtained from the relative acidity of its protonated form, R_3SiOH, which progressively decreases as R becomes more electropositive, consistent with the order in acidity: (Siloxy)$_3$SiOH > (Alkoxy)$_3$SiOH > (Aryl)$_3$SiOH > (Alkyl)$_3$SiOH > (Silyl)$_3$SiOH.

General Aspects

In general, transition metal siloxides can be prepared by deprotonation of silanols with transition metal alkyls, hydrides, alkoxides, and amides, or by reactions between alkali metal siloxides and transition metal halides by salt metathesis. The latter route is important for the synthesis of mid to late transition metal siloxides. Alkali metal siloxides can be synthesized readily from reactions of the metal or the metal hydride with silanols in polar solvents (Scheme 1).

$$2R_3SiOH + 2M \longrightarrow 2R_3SiOM + H_2 \qquad (M = Na, K)$$

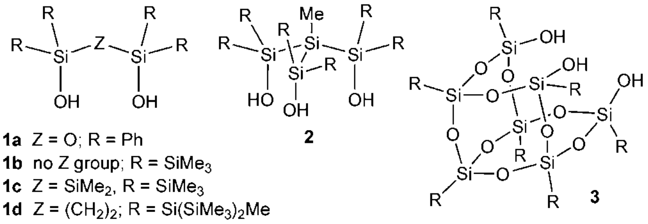
$$yR_3SiOM + TMX_n \longrightarrow (R_3SiO)_yTMX_{n-y} + yMX \qquad (X = halide)$$

$$yR_3SiOH + TMX_n \longrightarrow (R_3SiO)_yTMX_{n-y} + yXH \qquad (X = R, OR, NR_2)$$

Scheme 1. Synthetic routes to transition metal siloxides.

By far the most popular monoanionic siloxide ligands used in the coordination chemistry of structurally well-defined metal siloxides are Ph_3SiO^-, $(tBuO)_3SiO^-$, and tBu_3SiO^- (silox). In particular, the latter is a thermally very robust siloxide with unusual steric properties, even though the large-scale preparation of the starting material, tBu$_3$SiOH, is challenging and requires multistep synthesis.[8] Ph$_3$SiOH and (tBuO)$_3$SiOH, on the other hand, are less sterically demanding but commercially available. From a steric point of view, potentially interesting but less frequently used silanols are Mes$_3$SiOH,[9] [Me(Me$_3$Si)$_2$Si]$_3$SiOH,[10] bowl-shaped (3.5-Mes$_2$–C$_6$H$_3$)$_3$SiOH,[11] and (Ph$_2$MeSiCH$_2$CH$_2$)$_3$SiOH.[12]

Cyclic metal siloxides have also been employed, mainly to improve the stability of the M–O bond towards metal–ligand cleavage. The most frequently investigated are trianionic $[R_7Si_7O_9(O)_3]^{3-}$ derived from the "incompletely condensed" POSS, $R_7Si_7O_9(OH)_3$ (**3**), and dianionic $[(OSiPh_2)_2O]^{2-}$, derived from either $Ph_2Si(OH)_2$ or (HO)SiPh$_2$OSiPh$_2$(OH) (**1a**). The latter silanols often unselectively react with metal salts or alkyls by self condensation and/or ring expansion to afford mainly eight-membered polycyclic metal siloxides or undesired cyclic polysiloxanes. As reported recently by Krempner et al., the design of disilanols **1b–d**[13] and trisilanols **2**,[14] where the SiOH moieties are linked together either directly or via silicon- and carbon-containing spacer groups (Z), avoids "self condensation" and gives much better control over ring size in cyclic metal siloxides (Scheme 2).



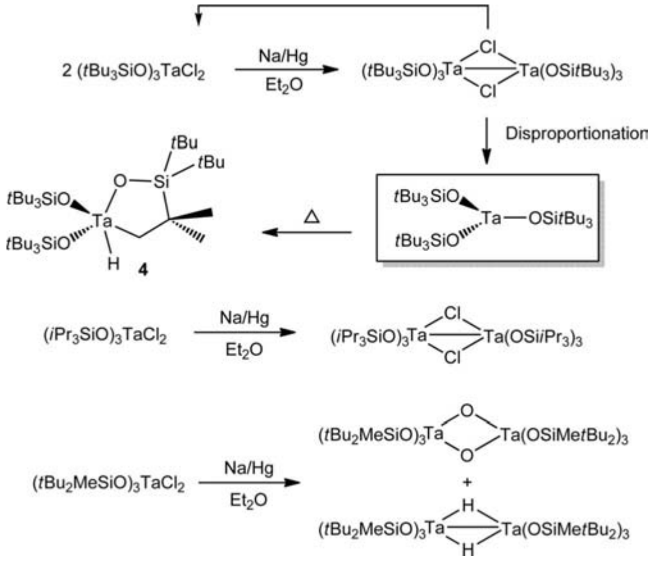
1a Z = O; R = Ph
1b no Z group; R = SiMe$_3$
1c Z = SiMe$_2$, R = SiMe$_3$
1d Z = (CH$_2$)$_2$; R = Si(SiMe$_3$)$_2$Me

Scheme 2. Structures of various disilanols and trisilanols.

Low-Valent Transition Metal Siloxides

Wolczanski, in his paper on the coordination chemistry of the monoanionic ligand tBu_3SiO^- (also referred to as "silox"), noted: "The most interesting feature of the silox ligand is its ability to stabilize reduced early transition metal centers."[8] In fact, a variety of low-coordinate monomeric Ti^{III}, V^{III}, Ta^{III}, Mo^{III} [as (tBu$_3$SiO)$_3$M] and Nb^{III}, W^{III} [as (tBu$_3$SiO)$_3$ML (L = CO, PMe$_3$)] compounds have been stabilized with the help of silox.[8,15] A striking example is (tBu$_3$SiO)$_3$Ta, a relatively stable monomeric tantalum(III) siloxide obtained from reduction of (tBu$_3$SiO)$_3$TaCl$_2$ with sodium amalgam.[16] The reduction is proposed to proceed via Ta^{IV}, through the formation of the dichloride-bridged [(tBu$_3$SiO)$_3$Ta]$_2$(μ-Cl)$_2$, which instantly disproportionates into (tBu$_3$SiO)$_3$Ta and (tBu$_3$SiO)$_3$TaCl$_2$ as a result of steric strain caused by the bulky silox groups (Scheme 3). According to detailed experimental and computational studies, diamagnetic (tBu$_3$SiO)$_3$Ta has a singlet ground state with a $(d_{z^2})^2$ electron configuration that is 14 kcal/mol lower in energy than the lowest lying triplet state. The stability of (tBu$_3$SiO)$_3$Ta is attributed to the extreme bulk of the three silox groups, which prevent the empty metal-based d_{xz} and d_{yx} orbitals from being attacked by any donor. Note that cyclometalation to **4** occurs only slowly in solution (benzene, $t_{1/2}$ = 90 h, 25 °C) and the solid state.

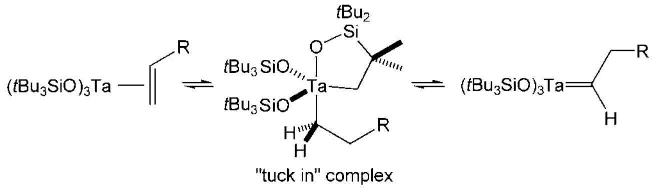
Wolczanski et al. have also shown that the steric properties of the siloxide ligand can significantly affect the reduction chemistry of the various dichloridotantalum siloxides (Scheme 3).[17] For example, the significantly smaller



Scheme 3. Reduction of various tantalum siloxides.

ligand $i\mathrm{Pr_3SiO^-}$ enables reduction to the dimer, but disproportionation to the tantalum(III) siloxide did not take place. In the case of the bulkier $t\mathrm{Bu_2MeSiO^-}$, reduction and disproportionation occurred, but the intermediate complex, $(t\mathrm{Bu_2MeSiO})_3\mathrm{Ta}$, proved unstable and subsequently reacted with solvent molecules to form $[(t\mathrm{Bu_2MeSiO})_3\mathrm{Ta}]_2(\mu\text{-H})_2$ and $[(t\mathrm{Bu_2MeSiO})_3\mathrm{TaO}]_2$ as the major products.

Another notable aspect of the chemistry of low-coordinate Ta and Nb siloxides, $(t\mathrm{Bu_3SiO})_3\mathrm{M}$ (M = Ta, Nb), is their ability to activate hydrocarbons (Scheme 4).[18] At elevated temperatures, $(t\mathrm{Bu_3SiO})_3\mathrm{Ta(olefin)}$, derived from the reaction of various terminal and cyclic olefins with $(t\mathrm{Bu_3SiO})_3\mathrm{Ta}$, is slowly converted into the alkylidine complex $(t\mathrm{Bu_3SiO})_3\mathrm{Ta{=}CRH}$. The rearrangement proceeds through oxidative addition of $\mathrm{Ta^{III}}$, which results in the formation of a "tuck in" $\mathrm{Ta^{V}}$ intermediate that is stable enough to be structurally characterized by X-ray crystallography.



Scheme 4. Stoichiometric activation of hydrocarbons.

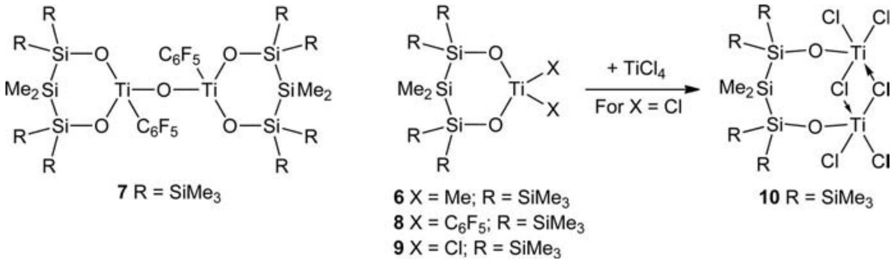
Despite extensive shielding by the bulky silox ligands, the metal often retains its high reactivity with respect to formal oxidation as exemplified by $(t\mathrm{Bu_3SiO})_3\mathrm{Mo(PMe_3)}$ and $(t\mathrm{Bu_3SiO})_3\mathrm{W(PMe_3)}$ (Scheme 5).[19] Both complexes were prepared by reduction of $(t\mathrm{Bu_3SiO})_3\mathrm{MCl}$ with sodium amalgam in the presence of $\mathrm{PMe_3}$. Upon treatment with $\mathrm{P_4}$, formation of the corresponding phosphide complexes $(t\mathrm{Bu_3SiO})_3\mathrm{M{\equiv}P}$ rapidly occurred with formal oxidation of M from (3+) to (6+).

Scheme 5. Formation of $\mathrm{Mo^{III}}$ siloxides and a $\mathrm{Mo^{VI}}$ phosphidosiloxide.

Transition Metal Siloxides in High Oxidation States

Numerous examples of well-defined transition metal siloxides in high oxidation states have been reported, and the structural chemistry of these molecular compounds is well documented in the literature. The siloxides $\mathrm{Cr(OSiEt_3)_4}$,[20] $\mathrm{V(OSiPh_3)_4}$,[21] and $\mathrm{(Cy_8Si_8O_{13})_2Ce(py)_3}$[22] provide examples of oxophilic metal compounds in oxidation state 4+. The related halides $\mathrm{CeX_4}$ and $\mathrm{CrX_4}$ are thermodynamically unstable, and in the case of the more stable $\mathrm{VCl_4}$, oxidation to $\mathrm{OVCl_3}$ can readily occur at ambient conditions. Note that $\mathrm{V(OSiPh_3)_4}$ is conveniently formed upon oxidation of $\mathrm{Li[V(OSiPh_3)_4]}$ in air! Also remarkable is the ease of formation of a uranium siloxide exclusively in oxidation state 6+ from reactions of the low-oxidation-state uranium precursors, $\mathrm{(COT)_2U}$ (COT = η_8-$\mathrm{C_8H_8}$) or $\mathrm{UCl_4}$ with $\mathrm{(HO)SiPh_2OSiPh_2(OH)}$.[23]

The ability of siloxide ligands to effectively stabilize highly electrophilic and oxophilic metals in high oxidation states is thought to be primarily due to their good σ- and π-donor properties; the stronger the donor properties of the ligand the stronger the M–O bond, which is reflected in a shortening of the M–O distances. M–O–Si angles that are close to 180° could indicate the involvement of $\mathrm{O_{p\pi}}$-to-$\mathrm{M_{d\pi}}$ backbonding, which also should result in shorter M–O distances. However, the M–O–Si angles in metal siloxides are generally large as a result of repulsive interactions between the metal and silicon, both of which are partially positively charged. Table 1 shows the average M–O, Si–O distances, and Si–O–M angles of selected $\mathrm{Ti^{III}}$ and $\mathrm{Ti^{IV}}$ complexes supported by linear triphenylsiloxide or cyclic disiloxide ligands (Scheme 6). From a comparison of these data, the following conclusions can be drawn: (1) Generally, in ionic alkaline or alkaline earth metal siloxides, such as $\mathrm{Ph_3SiO^-K^+}$(18-crown-6) (**5**), the Si–O bond can be extremely short because of oxo anion to silicon backbonding; the more the positive and negative charges are separated, the shorter the Si–O bond. (2) For a polar covalent Ti–O bond, the Si–O distance decreases as the Ti–O distance increases and vice versa regardless of whether the Ti–O bond is more ionic or more covalent. (3) There seems to be no correlation between the Si–O–Ti bond angles and the Ti–O distances, which would indicate a significant involvement of $\mathrm{O_{p\pi}}$-to-$\mathrm{Ti_{d\pi}}$ backbonding. For example, cyclic Ti siloxides **6**–**9** with acute angles have shorter Ti–O bonds than the linear triphenylsiloxides **13**–**17** with larger Si–O–Ti angles. (4) As can be seen from the Ti–O distances of cyclic titanium disiloxides **6**–**10**, increasing the group electronegativity of the metal fragment, $\mathrm{TiX_2}$, shortens the Ti–O distance



7 R = $SiMe_3$

6 X = Me; R = $SiMe_3$
8 X = C_6F_5; R = $SiMe_3$
9 X = Cl; R = $SiMe_3$

10 R = $SiMe_3$

Scheme 6. Cyclic titanium disiloxides.

and lengthens the Si–O bond. (5) Comparing Ti^{III} species **11** and **12** with the structurally related Ti^{IV} complexes **13**, **14**, and **16** reveals that increasing the oxidation state of the metal from Ti(3+) to Ti(4+) strengthens the Ti–O but weakens the Si–O bond.

Table 1. Selected average atom distances [pm] and angles [°] of various titanium siloxides (CN = coordination number).

Compound	Ref.	CN	Ti–O	Si–O	Ti–O–Si
$Ph_3SiO^-K^+$(18-crown-6) (**5**)	[24]	7	–	157	–
$Me_2Si[R_2SiO]_2TiMe_2$ (**6**)	[25]	4	178	168	143
$\{Me_2Si[R_2SiO]_2TiC_6F_5\}_2O$ (**7**)	[25]	4	176	170	144
$Me_2Si[R_2SiO]_2Ti(C_6F_5)_2$ (**8**)	[26]	4	175	171	145
$Me_2Si[R_2SiO]_2TiCl_2$ (**9**)	[25]	4	174	171	146
$Me_2Si[R_2SiO]_2[TiCl_3]_2$ (**10**)	[25]	6	172	172	168
$(Ph_3SiO)_3Ti(THF)_2$ (**11**)	[27]	5	190	161	164
$(Ph_3SiO)_3Ti(Pyr)_2$ (**12**)	[27]	5	190	162	171
$(Ph_3SiO)_4Ti$ (**13**)	[28]	4	179	163	164
$(tBuPh_2SiO)_4Ti$ (**14**)	[29]	4	178	165	171
$(Ph_3SiO)_2Ti(O_2CNiPr_2)_2$ (**15**)	[30]	6	180	164	157
$(Ph_3SiO)_2TiCl_2(THF)_2$ (**16**)	[31]	6	178	164	168
$Ph_3SiOTi(OCH_2CH_2)_3N$ (**17**)	[32]	5	183	161	180

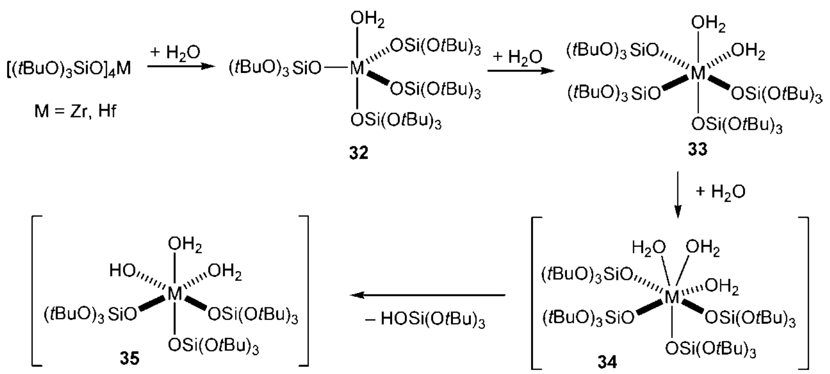
Similar conclusions can be drawn from a series of structurally related but sterically crowded W and Mo tri-*tert*-butylsiloxides (Table 2). The M–O distances in most of these complexes decrease as the oxidation state of the metal increases, whereas the Si–O distances become longer, consistent with increasingly covalent interactions between oxygen and the metal. Again, there seems to be no correlation between Si–O–M angles and the M–O distances, which is believed to be a hint for $O_{p\pi}$-to-$M_{d\pi}$ backbonding. Note that the nonbonding W···Si and Mo···Si distances are within the surprisingly narrow range of 348–353 pm, whereas the M–O [182–196 pm] and the Si–O [162–172 pm] distances vary to a larger extent. This suggests that, whenever the nonbonding M···Si distances of a series of structurally related metal siloxides are nearly constant, the diametrically opposed change in M–O and Si–O distances is driven by electronic rather than steric effects. However, these correlations are only valid for small substituents, since the nonbonding W···Si and Mo···Si distances can increase significantly upon introducing bulkier groups. Nonetheless, it can be concluded from these data that the stability of the M–O bond in metal siloxides is closely related to the electrophilicity of the metal (coordination number and oxidation state).

Table 2. Selected average atom distances [pm] and angles [°] of various Mo and W siloxides (M = Mo, W; Si···M = nonbonding Si–M distance).

Compound	Ref.	M–O	Si–O	Si···M	M–O–Si
$[tBu_3SiONa]_4$ (**18**)	[33]	–	161	–	–
$(tBu_3SiO)_3W(PMe_3)$ (**19**)	[19]	191	165	351	162
$(tBu_3SiO)_3WCO$ (**20**)	[19]	188	167	351	165
$(tBu_3SiO)_3WMe$ (**21**)	[34]	186	167	348	161
$(tBu_3SiO)_3WCl$ (**22**)	[34]	186	169	349	158
$(tBu_3SiO)_3W{=}O(Cl)$ (**23**)	[35]	184	170	351	165
$(tBu_3SiO)_3WCl_2$ (**24**)	[34]	182	172	353	170
$(tBu_3SiO)_3Mo(PMe_3)$ (**25**)	[19]	193	164	353	166
$(tBu_3SiO)_3MoEt$ (**26**)	[34]	188	165	351	170
$(tBu_3SiO)_3MoCl$ (**27**)	[34]	187	167	351	166
$(tBu_3SiO)_2Mo(PMe_3)_2$ (**28**)	[36]	196	162	352	164
$(tBu_3SiO)_2Mo = NtBu(Cl)$ (**29**)	[37]	188	165	352	171
$(tBu_3SiO)_2MoCl_2(PMe_3)$ (**30**)	[36]	183	169	348	161
$(tBu_3SiO)_2MoCl_3(THF)$ (**31**)	[36]	183	171	353	172

One of the most serious problems in homogeneous catalysis is catalyst deactivation at elevated temperatures and/or in moist air. Particularly, water can block the active site in a catalyst system by formation of inactive metal oxide species, and even more seriously, it can cause metal–ligand cleavage. Clearly, the thermodynamics and kinetics of these undesired cleavage processes are mainly governed by the metal and its oxidation state, but they can also be controlled by the electronic and steric nature of the ancillary ligand.[38]

Bradley et al. investigated the partial hydrolysis of transition metal alkoxides and trimethylsiloxides to soluble, oligomeric, and polymeric oxo(alkoxide)s and oxo(siloxide)s. They found that the rate of hydrolysis for metal siloxides is lower than that for metal alkoxides.[39] Tilley et al. studied reactions of water with $[(tBuO)_3SiO]_4M$ (M = Zr, Hf) in various ratios of metal siloxide to water (Scheme 7).[40] In the presence of excess water, complete hydrolysis to $(tBuO)_3SiOH$ occurred in THF at room temperature, whereas careful addition of one or two equivalents of water produced the isolable aqua complexes **32** and **33**. Kinetic studies on the rate of hydrolysis of these aqua complexes led to two important findings. First, the aqua ligands bound to the metal are quite labile and undergo rapid exchange at room temperature. Second, the mechanism of hydrolysis appears to be associative with intermediate formation of heptacoordinate $[(tBuO)_3SiO]_4M(H_2O)_3$ (**34**), which



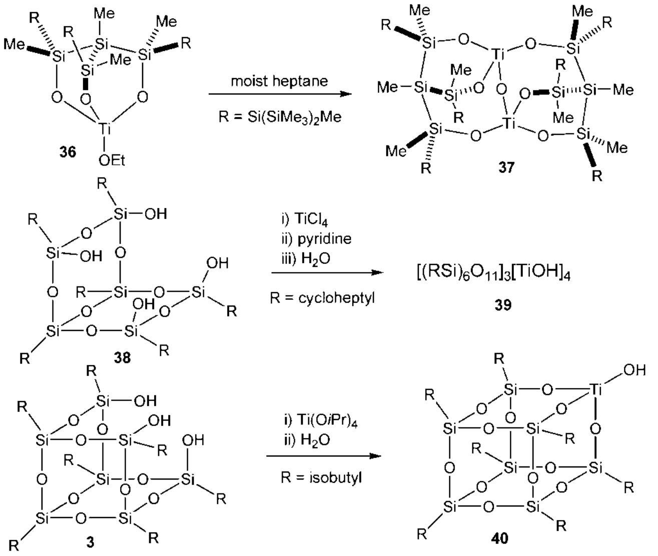
Scheme 7. Formation and hydrolysis of Zr and Hf aqua complexes.

subsequently releases $(t\text{BuO})_3\text{SiOH}$ and generates the reactive metal hydroxide **35**. The latter species forms oligomeric and polymeric oxo(siloxide)s by condensation, similar to what is observed in the hydrolysis of trimethylsiloxides.

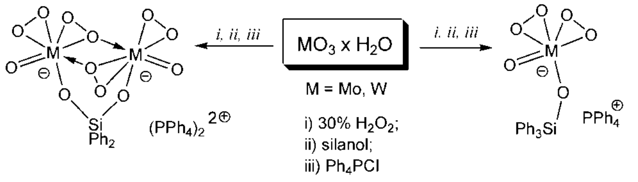
The importance of steric effects with regard to hydrolysis of metal siloxides cannot be overemphasized. For instance, the sterically overloaded vanadyl chloride $(t\text{Bu}_3\text{SiO})_2\text{-V=O(Cl)}$ could be converted in aqueous methanol into the vanadyl ester $(t\text{Bu}_3\text{SiO})_2\text{V=O(OMe)}$, and its anhydride, $[(t\text{Bu}_3\text{SiO})_2\text{V=O}]_2\text{O}$, was formed in good yields by treatment with aqueous KOH.[41] The hydrolytic stability of $[(t\text{Bu}_3\text{SiO})_2\text{V=O}]_2\text{O}$ is remarkable, as no V–OSi bond cleavage was observed even after a few hours in boiling aqueous KOH.

Hydrolytic cleavage of the M–OSi bond can also be suppressed by incorporating bulky tripodal siloxide ligands (Scheme 8). For instance, titanium ethoxide **36** readily hydrolyzes in moist solvents to form dinuclear siloxide **37**, which itself is fairly stable towards moisture.[14c] The reaction of tetrasilanol **38** with TiCl_4, followed by addition of pyridine and water, resulted in the formation of the tetranuclear TiOH cluster **39**, which was found to be thermally stable up to 250 °C and stable in water and protic oxidizing media.[42] By a similar synthetic approach, the air and moisture stable monomeric TiOH species **40** supported by a tripodal silsesquioxane could be synthesized and isolated in high yields.[43] Compounds **39** and **40** did not show the tendency to form Ti–O–Ti bonds by condensation and elimination of water. Moreover, both complexes were found to efficiently catalyze alkene epoxidations with aqueous H_2O_2 as the oxidizing agent (cyclooctene was epoxidized with selectivities and conversions higher than 90% with 1.5 mol-% of **39**).[5a] Following the mechanism of hydrolysis proposed for group 4 metal siloxides (vide supra), the hydrolytic stability of these complexes can reasonably be explained by unfavorable changes in entropy; protonation and subsequent elimination of silanol from tridentate metal siloxides is entropically less favored than from metal siloxides that bear monodentate siloxide ligands.

Bregeault et al.[44] reported on the synthesis and structures of a series of siloxide-supported peroxomolybdates and -tungstates obtained by oxidation of WO_3 and MoO_3 with H_2O_2 in the presence of various silanols (Scheme 9). Upon adding phosphonium chlorides, water-stable phosphonium salts could be isolated, which showed promising activities as catalysts in the epoxidation of various cycloalkenes. The catalysts can be recovered from solution without any sign of decomposition if excess H_2O_2 is used.

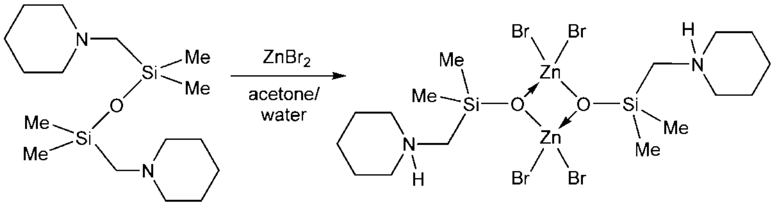


Scheme 8. Hydrolytically stable titanium siloxides.



Scheme 9. Siloxide-supported peroxomolybdates and -tungstates.

An alternative approach to hydrolytically stable metal siloxides involving the formation of zwitterions has been reported recently by Strohmann et al.[45] (Scheme 10). Reactions of ZnBr_2 with various amino-substituted disiloxanes produced hydrolytically stable zwitterionic zinc siloxides as a result of hydrolytic cleavage of the Si–O–Si bond. Whether the zwitterionic approach can be applied to the synthesis of hydrolytically stable d^0 early transition metal siloxides needs yet to be established.



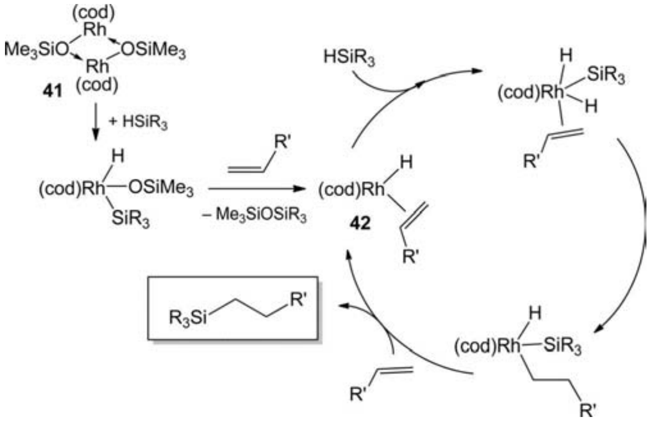
Scheme 10. Formation of a zwitterionic zinc siloxide.

Transition Metal Siloxides in Homogeneous Catalysis

Transition metal siloxides derived from "incompletely condensed" polyhedral oligosilsesquioxanes (POSS) have been used extensively as model compounds to mimic known heterogeneous silica-supported metal catalysts, and catalytic applications in the field of olefin polymerization and olefin epoxidation were reported in the literature.[3,5e,5f,5h,5i] Relatively little is known about structurally well-defined transition metal siloxides as homogeneous "single-site" catalysts in C–C and Si–C bond forming and C–C bond activation reactions of small organic molecules and organosilanes.

The hydrosilylation of olefins is one of the most important Si–C bond formation reactions in organosilicon chemistry.[46] Recently, Marciniec and co-workers have reported that dimeric rhodium siloxide [(cod)Rh(μ-OSiMe$_3$)]$_2$ (**41**) is a much more effective catalyst in the hydrosilylation of aliphatic and aromatic olefins, vinylsilanes, and allyl alkyl ethers than the respective rhodium complex [(cod)Rh(μ-Cl)]$_2$ and the commercially available Pt-Karsted catalyst most frequently used in hydrosilylation chemistry.[47] The hydrosilylation of olefins with [(cod)Rh(μ-OSiMe$_3$)]$_2$ as the precatalyst proceeds by initial oxidative addition of the HSiR$_3$ followed by subsequent elimination of R$_3$SiOSiMe$_3$ to generate the square-planar 16e$^-$ alkene complex **42** as the actual catalytically active species (Scheme 11).[47a] Immobilizing [(cod)Rh(μ-OSiMe$_3$)]$_2$ on silica gives the well-defined and highly active hydrosilylation catalyst [(cod)Rh(OSi≡)].[48] Curiously, this catalyst system does not bleach significantly even after more than ten cycles, which implies the mechanistic pathway of the hydrosilylation to be different from that of the homogeneous system that involved elimination of R$_3$SiOSiMe$_3$!

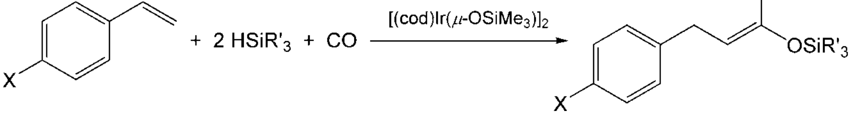
The same authors have also shown that dimeric iridium siloxide [(cod)Ir(μ-OSiMe$_3$)]$_2$ is a very active and selective catalyst in the silylcarbonylation of various *para*-substituted styrenes,[49] a reaction that gives access to enol silyl ethers of acylsilanes, important intermediates in organic and organosilicon synthesis (Scheme 12).[50] It also has been noted that both activity and selectivity with [(cod)Ir(μ-OSiMe$_3$)]$_2$ are much better than with the previously used catalysts Ir$_4$(CO)$_{12}$ or [Ir(μ-Cl)(CO)$_3$]$_n$, which require a ten-fold excess of styrene relative to HSiR$_3$ and afford only 50% yields of the silylcarbonylation products.[51]



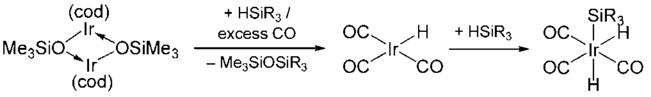
Scheme 11. Proposed mechanism of hydrosilylation with rhodium siloxides.

Investigations regarding the mechanism of the reaction revealed [(cod)Ir(μ-OSiMe$_3$)]$_2$ to be a precatalyst, which in the presence of CO and HSiR$_3$ generates HIr(CO)$_3$ as the actual catalytically active species. The formation of HIr(CO)$_3$ is thought to occur by replacement of cyclooctadiene (cod) by excess CO and simultaneous oxidative addition of HSiR$_3$ followed by subsequent elimination of R$_3$SiOSiMe$_3$ (Scheme 13), which is similar to the formation of rhodium alkene complex **42** (vide supra). HIr(CO)$_3$ readily inserts HSiR$_3$ to form (H)$_2$Ir(CO)$_3$SiR$_3$, which is also involved in the catalytic cycle of the silylcarbonylation of olefins.

In an attempt to increase the reservoir of simple and atom-economic addition reactions, Trost and co-workers recently performed Lewis acid catalyzed reactions of propargyl and allenic alcohols with imines and aldehydes.[52] For example, reactions of allenic alcohols with various aromatic and aliphatic aldehydes in the presence of 5 mol-% O=V-

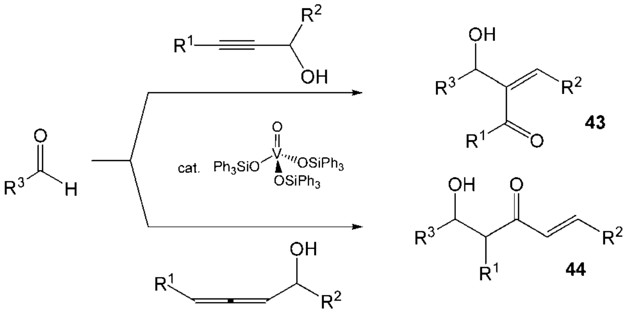


Scheme 12. Silylcarbonylation of *para*-substituted styrenes.



Scheme 13. Proposed formation of $HIr(CO)_3$ and $(H)_2Ir(CO)_3SiR_3$.

$(OSiPh_3)_3$ gave the desired aldol products **43** and **44** in good to excellent yields (Scheme 14). Remarkably, $O=V(OSiMe_3)_3$ gave much slower reactions and poor yields, whereas the more electron-rich vanadium catalyst $O=V(O\text{-}iPr)_3$ did not show any activity at all. Similar results were observed when propargylic alcohols were employed in reactions with aldehydes and imines.

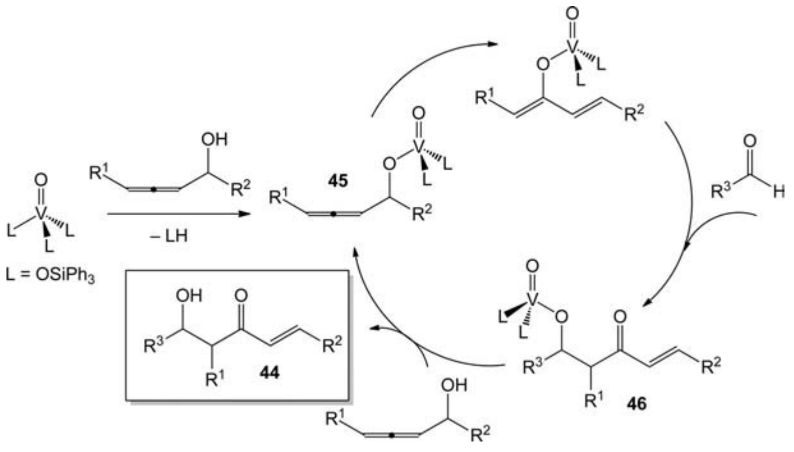


Scheme 14. Reaction of propargylic and allenic alcohols with aldehydes.

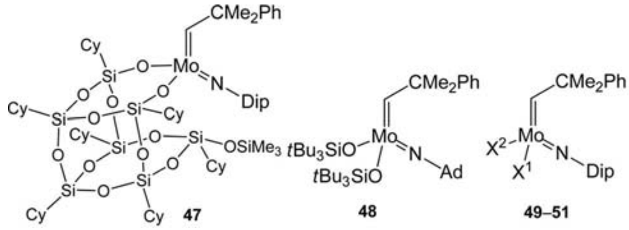
The proposed mechanism for the addition of allenic alcohols and aldehydes is shown in Scheme 15 and indicates that one of the siloxide groups of the precatalyst $O=V(OSiPh_3)_3$ acts as a leaving group to generate the actual catalytic species **45**.[53] Whether one or more siloxide groups are replaced by excess allenic alcohol remains unclear, since no studies regarding the structure of the catalyst in its resting state have been reported. It is worth noting, however, that of the catalysts studied with the formula $O=V[OSi(C_6H_4\text{-p-}X)_3]_3$ (X = H, Cl, F), $O=V[OSi(C_6H_4\text{-p-}Cl)_3]_3$ is the most active in the related vanadium-catalyzed addition of propargyl alcohols and imines.[52d] This suggests that the activity and selectivity of the catalysts is a function of the electronic properties of the remaining siloxide groups. Thus, it seems that in these aldol-type reactions catalyzed by vanadium siloxide, the siloxide groups may act as both ancillary ligands and leaving groups!

It is known that the performance of Schrock-type alkene metathesis catalysts of general formula $(RO)_2M=CHR(=NR)$ (M = Mo, W) is very sensitive to the steric and electronic nature of the alkoxide ancillary ligands. Best results have been achieved with the bulky but also strongly σ-electron-withdrawing fluorinated alkoxide, $CH_3(CF_3)_2CO^-$.[54] Feher et al. have shown that the silsesquioxane-based Mo siloxide **47** (Scheme 16) exhibits comparable activities in olefin metathesis.[55] This was ascribed to both the strongly electron-withdrawing character of the silsesquioxane ligand and the acute M–O–Si angles in structurally related complexes, which are believed to limit the extent of $O_{p\pi}$-to-$M_{d\pi}$ backbonding. However, on the basis of a competitive study regarding the alkylidene activity of a series of linear Mo siloxides, **48**–**51** (Scheme 16), toward various olefins, it is unclear whether siloxide ligands have a beneficial effect in olefin metathesis.[56] Some selected data are summarized in Table 3 and reveal the alkylidene activities of the complexes **47**–**51** toward olefins to be in the following order: **47** >> **49** ≈ **50** > **51b**–**f** > **51a** >> **48**. Interestingly, sterically crowded Mo siloxide **48** is completely inactive in the presence of ethene at 120 °C. Even in the presence of neat 1-hexene or 1-octene, only 5% consumption of **48** occurred at 120 °C. However, **48** initiates the polymerization of 100 equiv. of norbornene at 23 °C to give polynorbornene in 56% yield. Compound **48** is also relatively stable in the presence of air, moisture, and heat; it does not decompose even at 240 °C in $[D_4]$*o*-dichlorobenzene!

In comparison to the diverse applications of alkene metathesis in organic synthesis, the related alkyne metathesis is much less commonly used, primarily because nonterminal alkynes are very often required as substrates. Another drawback of the reaction is that highly air- and moisture-sensitive Schrock-type alkylidynes are required as catalysts, which makes this synthetic methodology less user-friendly for the organic community. Very recently, however, Fuerstner et al. reported on the synthesis and catalytic



Scheme 15. Mechanism for the addition of allenic alcohols and aldehydes.



49 $X^1 = X^2 = Ph_3SiO$
50 $X^1 = X^2 = tBuMe_2SiO$
51a $X^1 = tBu_3SiO$, X^2 = pyrrolide
51b $X^1 = tBu_3SiO$, $X^2 = OCMe_2CF_3$
51c $X^1 = tBu_3SiO$, $X^2 = OCMe(CF_3)_2$
51d $X^1 = tBu_3SiO$, $X^2 = OC(CF_3)_3$
51e $X^1 = tBu_3SiO$, $X^2 = OPh$
51f $X^1 = tBu_3SiO$, $X^2 = OC_6F_5$

Scheme 16. Various molybdenum imido alkylidenes that contain siloxides.

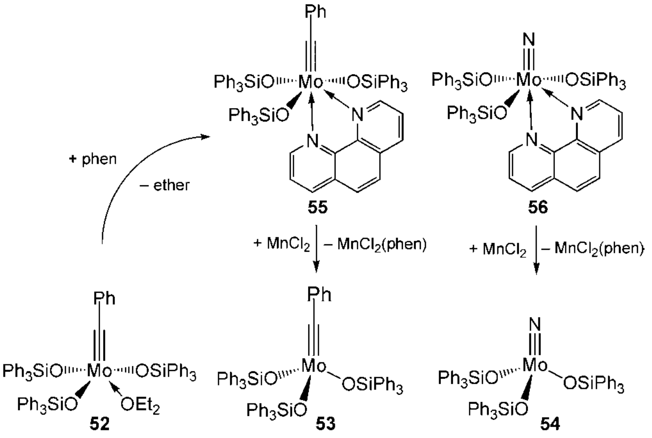
Table 3. Alkylidene activities of the Mo siloxides **47** and **48**–**51**.

Compound	c[a]	Solvent	Olefin	T [°C]	t[b]
47[c]	17	C_6D_6	1-pentene (20 equiv.)	25	[d]
48[e]	55	toluene	ethene (5 atm)	120	[f]
48[e]	55	$C_6Cl_2D_4$	ethene (1 atm)	240	12
49, **50**[e]	46	C_6D_6	ethene	22	12
49, **50**[e]	46	C_6D_6	1-hexene	22	12
51a[e]	55	C_6D_6	ethene (1 atm)	120	12
51b–**f**[e]	55	C_6D_6	ethene (1 atm)	60	≈ 4

[a] Concentration of **47** and **48**–**51** in mM. [b] Time taken for complete consumption in hours. [c] Data taken from ref.[55] [d] Complete consumption within a few minutes. [e] Data taken from ref.[56] [f] No consumption.

application of a set of new Mo nitrides and alkylidynes that contain triphenylsiloxides as ancillary ligands (Scheme 17).[57] These siloxides were shown to be active alkyne metathesis catalysts that combine easier handling with high activity, selectivity, and functional group tolerance. Of the Mo siloxides **52**–**56**, ether adduct **52** – even though air- and moisture-sensitive – is one of the most active alkyne metathesis catalysts known to date; it operates at low loadings and is distinct from other systems in terms of its selectivity profile. The stability of the Mo siloxide catalysts **52**–**54** can significantly be improved by formation of their 1,10-phenanthroline adducts **55** and **56**. Adduct **55** is stable in air at least for hours, whereas **56** seems to be indefinitely stable in air and can be handled on the benchtop without any precautions, even though both are catalytically inactive at room temperature. The more active species **52**–**54** can conveniently be regenerated from **55** as well as **56** upon adding $MnCl_2$ and heating the mixtures at 80 °C.

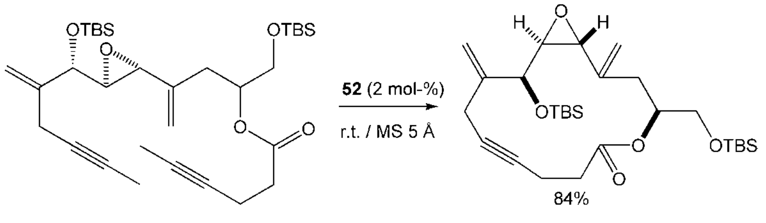
As noted by the authors: "The compatibility of the new catalysts is outstanding. Esters, ethers, various silyl ethers, thioethers sulfonates, amides, carbamates, ketones, acetals, epoxides, nitro groups, and trifluoromethyl groups are generally well-tolerated, even if they are oriented toward the reacting alkyne."[57b] Particularly **52** is worth mentioning, as it exhibits high reactivity and exceptional tolerance for functional groups, which is evident from the reaction shown in Scheme 18, in which the substrate bears a variety of polar and potentially labile functional groups. Even more exciting is the fact that **52** has been used very recently as an efficient catalyst in the high-yield synthesis of key intermediates for the concise total synthesis of the cell migration inhibitor lactimidomycin and the ecklonia lactones A and B.[58]



Scheme 17. User-friendly Mo siloxide catalysts for alkyne metathesis.

Conclusions

Siloxide ligands are able to coordinate to a large variety of transition metal fragments in various oxidation states and coordination numbers to form well-defined mononuclear metal siloxides of general formula $[R_3SiO]_mMX_n$. In particular tBu$_3$SiO-, (silox), is an extremely bulky and robust ancillary ligand that has been used to stabilize a variety of low-valent, coordinatively unsaturated metal species. Even thermally and hydrolytically stable metal siloxides supported by silox have been reported. However, as an ancillary ligand in catalysis, silox seems to block the active



Scheme 18. Synthesis of a precursor for amphidinolide V.

metal site by its bulkiness so efficiently that only poor activities are observed, as seen in olefin metathesis. The most promising results in terms of activity and selectivity arise from the use of simple $\mathrm{Ph_3SiO^-}$ derived from cheap $\mathrm{Ph_3SiOH}$. Particularly, work by Fuerstner et al. and Trost et al. using simple vanadium and molybdenum triarylsiloxides can truly be considered as a breakthrough in the application of robust and well-defined transition metal siloxides as "single site" catalysts for organic transformations. On the basis of these promising results, the chemistry and catalysis of transition metal siloxides is expected to be a highly emerging area of research within the next decade.

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[1] R. Murugavel, M. G. Walawalkar, M. Dan, H. W. Roesky, C. N. R. Rao, *Acc. Chem. Res.* **2004**, *37*, 763–774.

[2] K. L. Fujdala, R. L. Brutchey, T. D. Tilley, *Top. Organomet. Chem.* **2005**, *16*, 69–115.

[3] J.-M. Basset, R. Psaro, D. Roberto, R. Ugo (Eds.), *Modern Surface Organometallic Chemistry*, Wiley-VCH, Weinheim, **2009**.

[4] For reviews on silanols see: a) P. D. Lickiss, *Adv. Inorg. Chem.* **1995**, *42*, 147–262; b) P. D. Lickiss in *The Chemistry of Organo Silicon Compounds*, John Wiley & Sons, New York, **2001**, vol. 3, p. 695; c) V. Chandrasekhar, R. Boomishankar, S. Nagendran, *Chem. Rev.* **2004**, *104*, 5847–5910.

[5] For reviews on metal siloxides see: a) M. H. Chisholm, *Chemtracts: Inorg. Chem.* **1992**, *4*, 273–301; b) P. D. Lickiss, *Adv. Inorg. Chem.* **1995**, *42*, 147; c) R. Murugavel, A. Voigt, M. G. Walawalkar, H. W. Roesky, *Chem. Rev.* **1996**, *96*, 2205; d) L. King, A. C. Sullivan, *Coord. Chem. Rev.* **1999**, *189*, 19; e) V. Lorenz, A. Fischer, S. Gießmann, J. W. Gilje, Y. Gun′ko, K. Jacob, F. T. Edelmann, *Coord. Chem. Rev.* **2000**, *206–207*, 321; f) H. C. L. Abbenhuis, *Chem. Eur. J.* **2000**, *6*, 25–32; g) B. Marciniec, H. Maciejewski, *Coord. Chem. Rev.* **2001**, *223*, 301–305; h) R. Duchateau, *Chem. Rev.* **2002**, *102*, 3525; i) R. W. J. M. Hanssen, R. A. Van Santen, H. C. L. Abbenhuis, *Eur. J. Inorg. Chem.* **2004**, 675–583; j) B. Marciniec, *Coord. Chem. Rev.* **2005**, *249*, 2374–2390; k) V. Lorenz, F. T. Edelmann, *Adv. Organomet. Chem.* **2005**, *53*, 101–153; l) M. Veith, *Adv. Organomet. Chem.* **2006**, *54*, 49–72; m) M. M. Levitsky, B. G. Zavin, A. N. Bilyachenko, *Russ. Chem. Rev.* **2007**, *76*, 847–866; n) M. M. Levitskii, V. V. Smirnov, B. G. Zavin, A. N. Bilyachenko, A. Yu. Rabkina, *Kinet. Catal.* **2009**, *50*, 490–507; o) V. Lorenz, A. Edelmann, S. Giebmann, C. G. Hrib, S. Blaurock, F. T. Edelmann, *Z. Anorg. Allg. Chem.* **2010**, *636*, 2172–2191.

[6] a) M. H. Chisholm, F. A. Cotton, M. W. Extine, R. L. Kelly, *J. Am. Chem. Soc.* **1978**, *100*, 3354–3358; b) M. H. Chisholm, C. M. Cook, W. E. Streib, *Inorg. Chim. Acta* **1992**, *198–200*, 63–77.

[7] a) J. T. Poulton, K. Folting, W. E. Streib, K. G. Caulton, *Inorg. Chem.* **1992**, *31*, 3190–3191; b) J. T. Poulton, M. P. Sigalas, O. Eisenstein, K. G. Caulton, *Inorg. Chem.* **1993**, *32*, 5490–5501; c) J. T. Poulton, M. P. Sigalas, K. Felting, W. E. Streib, O. Eisenstein, K. G. Caulton, *Inorg. Chem.* **1994**, *33*, 1476–1485.

[8] P. T. Wolczanski, *Polyhedron* **1995**, *14*, 3335–3362.

[9] O. Wrobel, F. Schaper, H. H. Brintzinger, *Organometallics* **2004**, *23*, 900–905.

[10] S. Chtchian, R. Kempe, C. Krempner, *J. Organomet. Chem.* **2000**, *613*, 208–219.

[11] a) K. Goto, T. Okumura, T. Kawashima, *Chem. Lett.* **2001**, 1258–1259; b) I. Shimo, T. Okumura, K. Goto, T. Kawashima, *J. Organomet. Chem.* **2007**, *692*, 2115–2119.

[12] V. Amo, R. Andres, E. De Jesus, J. F. De la Mata, J. C. Flores, R. Gomez, M. P. Gomez-Sal, J. F. C. Turner, *Organometallics* **2005**, *24*, 2331–2338.

[13] a) D. Hoffmann, H. Reinke, C. Krempner, *J. Organomet. Chem.* **2002**, *662*, 1–8; b) D. Hoffmann, H. Reinke, C. Krempner in *Organosilicon Chemistry V: From Molecules to Materials* (Eds.: N. Auner, H. Weiss), Wiley-VCH, Weinheim, **2003**, pp. 420–424; c) C. Krempner, H. Reinke, K. Weichert, A. Spannenberg, *Polyhedron* **2004**, *23*, 2475–2479; d) C. Krempner in *Organosilicon Chemistry VI: From Molecules to Materials* (Eds.: N. Auner, H. Weiss), Wiley-VCH, Weinheim, **2005**, pp. 337–343; e) C. Krempner, H. Reinke, K. Weichert in *Organosilicon Chemistry VI: From Molecules to Materials* (Eds.: N. Auner, H. Weiss), Wiley-VCH, Weinheim, **2005**, pp. 344–347; f) C. Krempner, R. Ludwig, A. Flemming, R. Miethchen, M. Koeckerling, *Chem. Commun.* **2007**, 1810–1812; g) C. Krempner, H. Reinke, K. Weichert, *Eur. J. Inorg. Chem.* **2007**, 1067–1071; h) C. Krempner, H. Reinke, K. Weichert, *Organometallics* **2007**, *26*, 1386–1392; i) C. Krempner, H. Reinke, K. Weichert, *Polyhedron* **2007**, *26*, 3633–3637; j) K. Weichert, B. Carlson, H. Reinke, C. Krempner, *Dalton Trans.* **2010**, *39*, 11513–11515.

[14] a) C. Krempner, J. Kopf, C. Mamat, H. Reinke, A. Spannenberg, *Angew. Chem.* **2004**, *116*, 5521; *Angew. Chem. Int. Ed.* **2004**, *43*, 5406–5408; b) U. Jaeger-Fiedler, M. Koeckerling, R. Ludwig, A. Wulf, C. Krempner, *Angew. Chem.* **2006**, *118*, 6907; *Angew. Chem. Int. Ed.* **2006**, *45*, 6755–6759; c) C. Krempner, U. Jaeger-Fiedler, M. Koeckerling, H. Reinke, *Organometallics* **2009**, *28*, 382–385.

[15] P. T. Wolczanski, *Chem. Commun.* **2009**, 740–757.

[16] R. E. LaPointe, P. T. Wolczanski, J. F. Mitchell, *J. Am. Chem. Soc.* **1986**, *108*, 6382–6384.

[17] A. R. Chadeayne, P. T. Wolczanski, E. B. Lobkovsky, *Inorg. Chem.* **2004**, *43*, 3421–3432.

[18] K. F. Hirsekorn, A. S. Veige, M. P. Marshak, Y. Koldobskaya, P. T. Wolczanski, T. R. Cundari, E. B. Lobkovsky, *J. Am. Chem. Soc.* **2005**, *127*, 4809–4830.

[19] D. S. Kuiper, P. T. Wolczanski, E. B. Lobkovsky, T. R. Cundari, *J. Am. Chem. Soc.* **2008**, *130*, 12931–12943.

[20] J. S. Basi, D. C. Bradley, *Proc. Chem. Soc.* **1963**, 305.

[21] M. Rost, H. Goerls, W. Imhof, W. Seidel, K. Thiele, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1994–2000.

[22] Y. K. Gun′ko, R. Reilly, F. T. Edelmann, D. Stalke, *Angew. Chem.* **2001**, *113*, 1319; *Angew. Chem. Int. Ed.* **2001**, *40*, 1279.

[23] a) V. Lorenz, A. Fischer, W. Bruser, F. T. Edelmann, K. Jacob, T. Gelbrich, P. G. Jones, *Chem. Commun.* **1998**, 2217–2218; b) V. Lorenz, A. Fischer, K. Jacob, W. Bruser, F. T. Edelmann, *Chem. Eur. J.* **2001**, *7*, 848–857.

[24] M. J. McGeary, K. Folting, W. E. Streib, J. C. Huffman, K. G. Caulton, *Polyhedron* **1991**, *10*, 2699–709.

[25] C. Krempner, M. Koeckerling, H. Reinke, K. Weichert, *Inorg. Chem.* **2006**, *45*, 3203–3211.

[26] C. Krempner, K. Weichert, H. Reinke, *Acta Crystallogr., Sect. E* **2007**, *63*, m356–m357.

[27] M. Veith, T. Voigt, V. Huch, *Z. Anorg. Allg. Chem.* **2006**, *632*, 243–247.

[28] B. F. G. Johnson, M. C. Klunduk, C. M. Martin, G. Sankar, S. J. Teate, T. J. Meurig, *J. Organomet. Chem.* **2000**, *596*, 221–225.

[29] D. Mansfeld, M. Schuermann, M. Mehring, *Appl. Organomet. Chem.* **2005**, *19*, 1185–1188.

[30] D. B. Dell′Amico, F. Calderazzo, S. Ianelli, L. Labella, F. Marchetti, G. Pelizzi, *J. Chem. Soc., Dalton Trans.* **2000**, 4339–4342.

[31] B. Schweder, H. Gorls, D. Walther, *Inorg. Chim. Acta* **1999**, *286*, 14–23.

[32] W. M. P. B. Menge, J. G. Verkade, *Inorg. Chem.* **1991**, *30*, 4628–31.

[33] H.-W. Lerner, S. Schulz, M. Bolte, *Organometallics* **2002**, *21*, 3827–3830.

[34] D. S. Kuiper, R. E. Douthwaite, A.-R. Mayol, P. T. Wolczanski, E. B. Lobkovsky, T. R. Cundari, O. P. Lam, K. Meyer, *Inorg. Chem.* **2008**, *47*, 7139–7153.

[35] A. S. Veige, L. M. Slaughter, E. B. Lobkovsky, P. T. Wolczanski, N. Matsunaga, S. A. Decker, T. R. Cundari, *Inorg. Chem.* **2003**, *42*, 6204–6224.

[36] D. S. Kuiper, P. T. Wolczanski, E. B. Lobkovsky, T. R. Cundari, *Inorg. Chem.* **2008**, *47*, 10542–10553.

[37] D. C. Rosenfeld, P. T. Wolczanski, K. A. Barakat, C. Buda, T. R. Cundari, F. C. Schroeder, E. B. Lobkovsky, *Inorg. Chem.* **2007**, *46*, 9715–9735.

[38] a) D. C. Bradley, D. G. Carter, *Can. J. Chem.* **1961**, *39*, 1434–1443; b) D. C. Bradley, D. G. Carter, *Can. J. Chem.* **1962**, *40*, 15–21; c) D. C. Bradley, C. Prevedorou-Demas, *J. Chem. Soc.* **1964**, 1580–1584; d) D. C. Bradley, *Coord. Chem. Rev.* **1967**, *2*, 299–318.

[39] D. Hoebbel, M. Nacken, H. Schmidt, V. Huch, M. Veith, *J. Mater. Chem.* **1998**, *8*, 171–178.

[40] C. G. Lugmair, T. D. Tilley, *Inorg. Chem.* **1998**, *37*, 764–769.

[41] M. Weidenbruch, C. Pierrard, H. Pesel, *Z. Naturforsch. Teil B* **1978**, *33*, 1468–1471.

[42] R. A. Van Santen, H. C. L. Abbenhuis, M. L. W. Vorstenbosch, *PCT Int. Appl.* **1998**, 31 pp.

[43] a) H. Al Ghatta, H. C. L. Abbenhuis, L. Cornelis, *PCT Int. Appl.* **2008**, 28 pp; b) H. Al Ghatta, H. C. L. Abbenhuis, *PCT Int. Appl.* **2008**, 28 pp.

[44] a) J.-Y. Piquemal, C. Bois, J.-M. Bregeault, *Chem. Commun.* **1997**, 473–474; b) J.-Y. Piquemal, S. Halut, J.-M. Bregeault, *Angew. Chem.* **1998**, *110*, 1149; *Angew. Chem. Int. Ed.* **1998**, *37*, 1146–1149.

[45] a) C. Daeschlein, J. O. Bauer, C. Strohmann, *Angew. Chem.* **2009**, *121*, 8218; *Angew. Chem. Int. Ed.* **2009**, *48*, 8074–8077; b) C. Daeschlein, C. Strohmann, *Z. Naturforsch. Teil B* **2009**, *64*, 1558–1566.

[46] a) B. Marciniec, *Silicon Chem.* **2002**, *1*, 155–175; b) B. Marciniec in *Applied Homogeneous Catalysis with Organometallic Compounds*, *Vol 1, 2nd Ed.* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2002**, pp. 491–512.

[47] a) B. Marciniec, P. Kryzanowski, E. Walczuk-Gusciora, W. Duczmal, *J. Mol. Catal. A* **1999**, *144*, 263–271; b) B. Marciniec, E. Walczuk, P. Blazejewska-Chadyniak, D. Chadyniak, M. Kujawa-Welten, S. Krompiec in *Organosilicon Chemistry V: From Molecules to Materials* (Eds.: N. Auner, H. Weiss), Wiley-VCH, Weinheim, **2003**, pp. 415–419.

[48] a) B. Marciniec, K. Szubert, M. J. Potrzebowski, I. Kownacki, K. Leszczak, *Angew. Chem.* **2008**, *120*, 551; *Angew. Chem. Int. Ed.* **2008**, *47*, 541–544; b) B. Marciniec, K. Szubert, R. Fiedorow, I. Kownacki, M. J. Potrzebowski, M. Dutkiewicz, A. Franczyk, *J. Mol. Catal. A* **2009**, *310*, 9–16.

[49] a) B. Marciniec, I. Kownacki, M. Kubicki, *Organometallics* **2002**, *21*, 3263–3270; b) I. Kownacki, B. Marciniec, K. Szubert, M. Kubicki, *Organometallics* **2005**, *24*, 6179–6183; c) I. Kownacki, B. Marciniec, P. Eilbracht, *Appl. Catal. A* **2010**, *390*, 94–101.

[50] a) P. C. Page, K. Bulman, S. Sukhbinder, S. Rosenthal, *Chem. Soc. Rev.* **1990**, *19*, 147–95; b) I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063–2192; c) B. Marciniec, C. Pietraszuk, I. Kownacki, M. Zaidlewicz in *Comprehensive Organic Functional Group Transformations II* (Eds.: A. R. Katritzky, R. J. K. Taylor), Elsevier Science, Amsterdam, **2005**, pp. 941–1023.

[51] N. Chatani, S. Ikeda, K. Ohe, S. Murai, *J. Am. Chem. Soc.* **1992**, *114*, 9710–9711.

[52] a) B. M. Trost, S. Oi, *J. Am. Chem. Soc.* **2001**, *123*, 1230–1231; b) B. M. Trost, C. Jonasson, M. Wuchrer, *J. Am. Chem. Soc.* **2001**, *123*, 12736–12737; c) B. M. Trost, C. Jonasson, *Angew. Chem.* **2003**, *115*, 2109; *Angew. Chem. Int. Ed.* **2003**, *42*, 2063–2066; d) B. M. Trost, C. K. Chung, *J. Am. Chem. Soc.* **2006**, *128*, 10359–10359.

[53] The proposed catalytic cycle shown in Scheme 15 is slightly modified from the original one in ref.[52a] for the following reason: In ref.,[52a] the proposed catalytic cycle for the addition of allenic alcohols and aldehydes involves $O{=}V(OSiPh_3)_3$ as the catalyst, which is regenerated upon reaction of intermediate **46** with Ph_3SiOH. However, considering that the allenic alcohol is in 25-fold excess to Ph_3SiOH, it is more likely that the allenic alcohol reacts with **46** to generate intermediate **45** as the actual catalytic species.

[54] a) C. J. Schaverien, J. C. Dewan, R. R. Schrock, *J. Am. Chem. Soc.* **1986**, *108*, 2771–2773; b) R. R. Schrock, R. T. DePue, J. Feldman, C. J. Schaverien, J. C. Dewan, A. H. Liu, *J. Am. Chem. Soc.* **1988**, *110*, 1423–1435; c) R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare, M. ORegan, *J. Am. Chem. Soc.* **1990**, *112*, 3875–3886; d) H. H. Fox, J.-K. Lee, L. Y. Park, R. R. Schrock, *Organometallics* **1993**, *12*, 759–768; e) D. H. McConville, J. R. Wolf, R. R. Schrock, *J. Am. Chem. Soc.* **1993**, *115*, 4413–4414; f) J. H. Oskam, R. R. Schrock, *J. Am. Chem. Soc.* **1993**, *115*, 11831–11845.

[55] a) F. J. Feher, T. L. Tajima, *J. Am. Chem. Soc.* **1994**, *116*, 2145–2146; b) F. J. Feher, T.-L. Hwang, J. J. Schwab, A. J. Shaka, J. W. Ziller, *Magn. Reson. Chem.* **1997**, *35*, 730–734.

[56] a) F. Blanc, C. Copret, J. Thivolle-Cazat, J.-M. Basset, A. Lesage, L. Emsley, A. Sinha, R. R. Schrock, *Angew. Chem.* **2006**, *118*, 1238; *Angew. Chem. Int. Ed.* **2006**, *45*, 1216–1220; b) K. M. Wampler, R. R. Schrock, A. S. Hock, *Organometallics* **2007**, *26*, 6674–6680.

[57] a) M. Bindl, R. Stade, E. K. Heilmann, A. Picot, R. Goddard, A. Fuerstner, *J. Am. Chem. Soc.* **2009**, *131*, 9468–9470; b) J. Heppekausen, R. Stade, R. Goddard, A. Fuerstner, *J. Am. Chem. Soc.* **2010**, *132*, 11045–11057.

[58] a) K. Micoine, A. Fuerstner, *J. Am. Chem. Soc.* **2010**, *132*, 14064–14066; b) V. Hickmann, M. Alcarazo, A. Fuerstner, *J. Am. Chem. Soc.* **2010**, *132*, 11042–11044.

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