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Synthesis and structure of hexaphenyltrisiloxanediolates of sodium, titanium, and iron

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The syntheses and single-crystal X-ray structures of several well-defined hexaphenyltrisiloxanediolates of sodium, titanium, and iron are reported. All these compounds contain eight-membered MSi_3O_4 rings (M = Na, Ti, Fe). Treatment of 1,1,3,3-tetraphenyldisiloxane-1,3-diol, $(HO)SiPh_2OSiPh_2(OH)$ (**1**), with excess metallic Na in THF afforded the sodium-hexaphenyltrisiloxandiolate reagent $[Ph_2Si(OSiPh_2O)_2]_2$-$Na_4(THF)_4$ (**3a**) in 68% yield. Single crystals suitable for X-ray diffraction were obtained for the diglyme solvate $[Ph_2Si(OSiPh_2O)_2]_2Na_4(diglyme)_2$ (**3b**) which was prepared in 76% yield by recrystallization of **3a** from diglyme (=ethylene-bis(2-methoxyethyl)ether). Readily accessible **3a** has been demonstrated to be a highly useful precursor for new transition metal hexaphenyltrisiloxanediolates (=metallacyclotetrasiloxanes). Reaction of **3a** with an excess of $TiCl_4$ in THF provided the titanacyclotetrasiloxane derivative $[Ph_2Si(OSiPh_2O)_2]TiCl_2(THF)_2$ (**4**) with octahedral coordination around titanium. Similar reaction of **3a** with $FeCl_3$ in THF afforded the anionic spirocyclic iron(III) complex $[Na(DME)_3][\{Ph_2Si(OSiPh_2O)_2\}_2Fe]$ (**5**) as yellow-brown crystals in 71% yield. An iron(III) analog of **4**, the anionic ferracyclotetrasiloxane complex $[Li(DME)_3][Ph_2Si(OSiPh_2O)_2FeCl_2]$ (**6**) was prepared in moderate yield (53%) by deprotonation of 1,1,3,3,5,5-hexaphenyl-1,3,5-trisiloxanediol, $Ph_2Si(OSiPh_2OH)_2$ (**2**), with *n*-butyllithium followed by reaction with $FeCl_3$ in DME. The molecular and crystal structures of **3b**, **4**, **5**, and **6** have been determined by X-ray diffraction.

Introduction

Well-defined metal siloxides (metallasiloxanes) comprising an M—O—Si functionality are of broad interest due to their diverse potential applications [1]. For example, metal siloxides have been shown to be excellent molecular models for silica-supported heterogeneous metal catalysts [2]. Moreover, they serve as useful precursors for new materials [3], nanoparticles [4], well-defined surface species [5], and homogeneous catalysts [6]. It has also been demonstrated that siloxide ligands can support highly reactive metal complexes in low oxidation states (*e.g.* Co(I), Ti(III), Sm(II), U(III) *etc.*) [7]. Useful silanol precursors range from simple triorganosilanols, R_3SiOH [1,8], through silanediols, $R_2Si(OH)_2$ [9], α,ω-oligosiloxanediols, $HO(R_2SiO)_nH$ [10], and silanetriols, $RSi(OH)_3$ [11], to more complex systems such as trisilanols, *e.g.* $MeSi(R_2SiOH)_3$ [12], and incompletely condensed polyhedral oligosilsesquioxanes (=POSS), *e.g.* $R_7Si_7O_9(OH)_3$ [1,13].

A very simple, though highly useful and versatile precursor for a large variety of metal siloxides is the readily accessible 1,1,3,3-tetraphenyldisiloxane-1,3-diol, $(HO)SiPh_2OSiPh_2(OH)$ (**1**), which forms stable complexes with virtually every metallic element across the Periodic Table ranging from lithium to uranium [1,14]. Pioneering work in this field has been reported *e.g.* by Sullivan and co-workers [1,14]. 1,1,3,3-Tetraphenyl-disiloxane-1,3-diol is easily prepared in 51% isolated yield by the controlled hydrolysis of dichlorodiphenylsilane [15]. As a minor product (18% yield), the higher homologue 1,1,3,3,5,5-hexaphenyl-1,3,5-trisiloxanediol, $Ph_2Si(OSiPh_2OH)_2$ (**2**), is formed in the same reaction. Notably, the dianionic tetraphenyldisiloxanediolate ligand, $[O(Ph_2SiO)_2]^{2-}$, is not always just a stable spectator ligand. Under certain reaction conditions, the $[O(Ph_2SiO)_2]^{2-}$ dianion can undergo fragmentation under formation of diphenylsilanediolate ligands, $[Ph_2SiO]^{2-}$ [16], or chain extension to afford hexaphenyltrisiloxanediolate ligands [14a,17-19]. This phenomenon has been studied in great detail by Sullivan and co-workers [18]. According to these authors (and in analogy with accepted mechanisms for the base-catalyzed ring-opening polymerization of cyclosiloxanes), the ring-expansion process can be initiated by (*a*) nucleophilic attack at a silicon atom in a six-membered metallasiloxane ring by free

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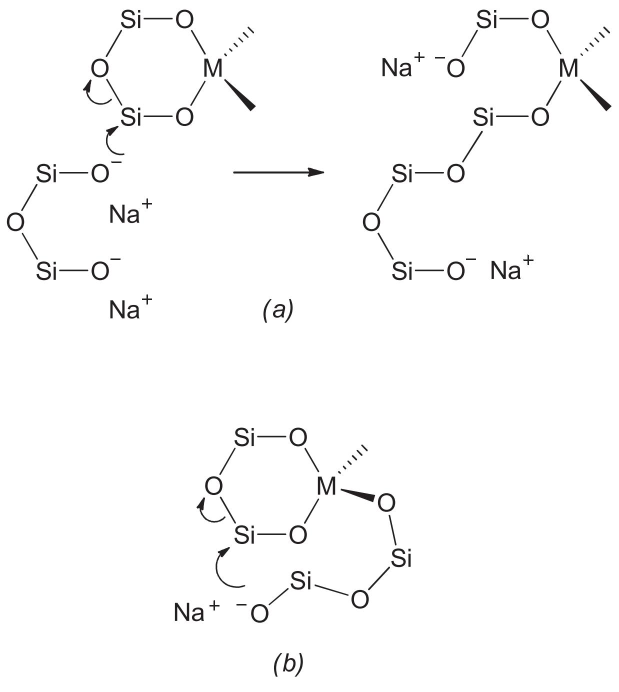
disiloxanediolate, or by (*b*) attack by a dangling disiloxanediolate coordinated only at one end to the metal center as illustrated in Scheme 1 [18]. However, the individual occurrence of such ring-expnasion processes is virtually unpredictable. Thus the following statement cited from Ref. [18] appears to be valid until today: “The data accumulated so far suggest no particular correlation between the occurrence of ring expansion and the nature of the disiloxanediolate reagent or the metal chloride. The persistent occurrence of ring expansion for certain combinations of metal chloride and disiloxanediolate reagent (even in the presence of an excess of metal chloride) over a wide range of reaction conditions may suggest formation of intermediate species where stereochemical arrangements of disiloxanediolate ligands are subtly different from those which do not undergo ring expansion”.

Complexes containing the chelating 1,1,3,3,5,5-hexaphenyl-1,3,5-trisiloxanediolate dianion as ligand have previously been reported *e.g.* for magnesium [14a], titanium [17], hafnium [18], and uranium [19]. In these cases, the *tri*siloxanediolate ligand is formed by chelate ring-enlargement (chain extension) reactions starting from *di*siloxanediolate precursors. As mentioned above, the outcome of such reactions is often unpredictable. We report here the straightforward synthesis of two sodium-hexaphenyltrisiloxanediolate reagents and their use as precursors for the synthesis of new hexaphenyltrisiloxanediolate complexes of titanium and iron.

Results and discussion

Treatment of 1,1,3,3-tetraphenyl-disiloxane-1,3-diol, (HO)$SiPh_2OSiPh_2(OH)$ (**1**), with an excess of freshly cut sodium metal pieces in THF according to Scheme 2 resulted in evolution of hydrogen and formation of a colorless solution. Removal of unreacted sodium, concentration of the filtrate and cooling to 4 °C afforded colorless, needle-like crystals in 68% yield, which were shown to be the THF solvate of disodium-hexaphenyltrisiloxanediolate, $[Ph_2Si(OSiPh_2O)_2]_2Na_4(THF)_4$ (**3a**). In accordance, the ^{29}Si NMR spectrum showed two resonances at δ −46.6 and −50.7 ppm in an intensity ratio of 2:1. The presence of coordinated THF was clearly seen in the ^{1}H NMR spectrum which displayed two multiplets at δ 3.60 and 1.72 ppm. Well-formed, colorless, rod-like single crystals of **3a** could be obtained by repeated recrystallization from THF. However, an X-ray diffraction study showed that these crystals were always heavily twinned and full refinement of the crystals structure was impossible due to multiple disorder problems. However, the X-ray crystal structure analysis clearly showed the basic structural motif of the molecular structure of **3a**. The molecule is dimeric with the central Na_4O_4 heterocubane structure to which the chelating hexaphenyltrisiloxanediolate dianions and four THF ligands are attached as shown in Scheme 2. Thus the overall structure of $[Ph_2Si(OSiPh_2O)_2]_2Na_4(THF)_4$ (**3a**) closely resembles that of the previously reported acetonitrile solvate of the dilithium derivative of hexaphenyltrisiloxanediol, $[Ph_2Si(OSiPh_2O)_2]_2Li_4(MeCN)_4$. The latter compound was, however, formed in a rather serendipitous manner upon treatment of the gadolinium disiloxanediolate complex $[\{(Ph_2SiO)_2O\}Li(THF)_2]_2GdN(SiMe_3)_2$ with $Ph_2Si(OH)_2$ [19b], whereas high yields of **3a** could be readily prepared by employing the straightforward synthetic protocol illustrated in Scheme 2. Thus, compound **3a** represents the first readily available hexaphenyltrisiloxanediolate transfer reagent which should be useful as precursor for new metallacyclotetrasiloxanes of transition metals.



Scheme 1. Formation of ring-expanded products from disilioxanediolate precursors (adapted from Ref. [18]).

Further in the course of this study it was discovered that single-crystals of a disodium-hexaphenyltrisiloxanediolate suitable for X-ray diffraction could be obtained be recrystallization of **3a** from ethylene-bis(2-methoxyethyl)ether (= diglyme) as shown in Scheme 2. The recovery of the resulting diglyme adduct of disodium-hexaphenyltrisiloxanediolate (**3b**) in this recrystallization process was 76%. A ^{1}H NMR spectrum of $[Ph_2Si(OSiPh_2O)_2]_2Na_4(diglyme)_2$ (**3b**) revealed the complete replacement of the coordinated THF by the tridentate chelating diglyme (three multiplets at δ 3.61, 3.51, and 3.34 ppm). Two ^{29}Si NMR resonances at δ −46.7 and −50.9 ppm in an intensity ratio of 2:1 clearly showed that the hexaphenyltrisiloxanediolate moieties had remained unchanged. The molecular structure of **3b** together with selected bond lengths and angles is shown in Fig. 1, while the crystallographic data are listed in Table 1. Full structural details can be found in the Supplementary data. The single-crystal X-ray structure determination revealed that upon coordination of diglyme the structure core had changed from a heterocubane to a ladder-type arrangement. Ladder-like structures are very common in the structural chemistry of lithium amidinates and guanidinates [20]. In the case of **3b**, the ladder-like core consists of a centrosymmetric arrangement of three slightly trapezoidal, four-membered Na_2O_2 rings connected through Na–O bonds. This arrangement formally results from opening up one face of the heterocubane structure present in **3a**. A very similar folded ladder arrangment has also been reported for the pyridine adduct of dilithium-diphenyldisiloxanediolate, $[O(Ph_2SiOLi(py))_2]_2$ [21]. The Na–O distances in **3b** are in the range of 2.200(4) to 2.396(4) Å. The coordination of the two diglyme ligands in **3b** is quite unusual. Each coordinated diglyme molecule acts as chelating ligand toward one of the outer sodium ions, while the oxygen of the remaining methoxyethyl functional group is coordinated to one of the central sodium ions in the ladder arrangement. This way each sodium ion acquires a distorted tetrahedral coordination geometry. This reflects the larger ionic radius of Na^+ as compared to Li^+ as in $[O(Ph_2SiOLi(py))_2]_2$ in which the central lithium ions are four-coordinate, while the outer two lithiums are only tricoordinate by being bonded to two siloxide oxygen atoms and one pyridine ligand [21].

Since the THF adduct **3a** has now become readily accessible in multigram quantities, it has been employed as precursor for new transition metal hexaphenyltrisiloxanediolates (= metallacyclotetrasiloxanes). Treatment of **3a** with an excess of $TiCl_4$ in