The First Zwitterionic, Optically Active Disilicate with Pentacoordinate Silicon**

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The study of compounds with higher coordinate silicon atoms is currently one of the main areas of research in silicon chemistry.\(^{1}\) In the past few years, ionic \(\text{\textsuperscript{2}}\text{Si}\)-silicates have been investigated particularly intensively. With the systematic elaboration of a new class of compounds, the spirocyclic zwitterionic \(\text{\textsuperscript{2}}\text{Si}\)-silicates, this area of research has recently expanded.\(^{2,3}\) These compounds are neutral molecular \(\text{\textsuperscript{2}}\text{Si}\)-silicates in which two dioila(2−) ligands and one ammonio-substituted organic group are bound to the Si coordination center. The bidentate dioila(2−) ligands thus far employed are derived from diols of the catechol and glycolic acid types. The zwitterions \(1^{+}\text{\textsuperscript{2}}\text{Si}-\) and \(2^{2+}\text{\textsuperscript{2}}\text{Si}\)- which may be classified as molecular complexes of pentacoordinate silicon, are typical examples of this class of compounds.

With the synthesis of \((+)-\text{(ammonio)methyl}b\text{is}(\mu-(R,R)-\text{tartrato})(4\text{\textsuperscript{-}})\text{-}O\text{\textsuperscript{2}}\text{Si}\text{-}O\text{\textsuperscript{2}}\text{Si}\text{-}\text{disilicate} (\text{\textsuperscript{+}})\text{-}4\), we have now succeeded in obtaining a molecular binuclear \(\text{\textsuperscript{2}}\text{Si}\text{-}\text{Si}\)-silicon complex for the first time (Scheme 1). In this compound, two tetra-

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**[\(\text{\textsuperscript{2}}\text{Si}\)-silicate]

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**Scheme 1. Synthesis of the disilicate (\text{\textsuperscript{+}})\text{-}4 from (aminomethyl)trietiarysilane 3 and (\(R,R\))-\text{tartrato} acid.

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optically active compound of pentacoordinate silicon. Its optical activity results from the presence of the two chiral (R,R)-tartarato(-) ligands and the two chiral Si(OH)₃C units.

Compound (+)-4 was prepared by reaction of (aminomethyl)triethoxysilane with (R,R)-(+)-tartaric acid (molar ratio 1:1) in aqueous solution and isolated as a 2:1 mixture of (+)-4 and (+)-4·3H₂O (yield approx. 88%). The formation of (+)-4 (100% ee, 100% de) occurred stereospecifically. Compounds (+)-4 and (+)-4·3H₂O were obtained in pure form by mechanical sorting and then characterized. The trihydrate was structurally characterized by X-ray diffraction on a single crystal, but this was not possible in the case of the water-free compound because of its poor crystal quality.

The molecular structure of (+)-4 in the crystal of (+)-4·3H₂O is shown in Figure 1. The coordination polyhedra surrounding the atoms Si1 and Si1' can be described as slightly distorted trigonal bipyramids [transformation trigonal bipyramid → square pyramid: 7.7% Si1; 10.6% Si1'] in which each of the axial positions is occupied by carbonyl oxygen atoms. Several intermolecular N···H···O and O···H···O hydrogen bonds are present in the crystal structure of (+)-4·3H₂O. The construction of the three-dimensional hydrogen-bonding system is complicated and characterized by a large acceptor excess (D/A ratio 12:30), such that generally only one of the acceptor sites on the oxygen atoms is used (exceptions: use of two acceptor sites by the carbonyl oxygen atoms O2, O2', and O6' as well as nonparticipation of the atoms O4, O4', and O5' in hydrogen bonding).

It follows from NMR spectroscopic investigations[8] that the zwiterionic binuclear complex (+)-4 is also present in solution ([D₆]DMSO, D₂O). The presence of pentacoordinate Si atoms of the type SiO₃C is clearly indicated by the characteristic ²³Si chemical shifts ([D₆]DMSO, D₂O), and the presence of tetracoordinate N atoms of the ammonium type can be indirectly confirmed by the identification of the NH₃ group by ¹H NMR spectroscopy ([D₆]DMSO, D₂O). The results presented here suggest that a rich complex chemistry of higher coordinate silicon in aqueous solution may be developed, in which diolato ligands derived from natural products (such as tartaric acid in this case) are of particular interest: it has been speculated in the literature[9] that silicon transport in biological systems might be based on higher coordinate Si species, and complexes such as the title compound could be of interest as metal systems in this respect.

Experimental Procedure

(+)-4·3H₂O: [3]δ (400 mg, 4.14 mmol) was added to a stirred solution of (R,R)-(+)-tartaric acid (622 mg, 4.14 mmol) in water (120 mL) at room temperature. The resulting clear solution was concentrated at 60°C to a volume of 100 mL, then allowed to stand undisturbed at room temperature for 96 h (formation of the first crystals ca. 24 h after the reactants were mixed). The solid formed was filtered off and washed with ethanol (3 × 10 mL) and then dried at room temperature in a nitrogen stream: yield 780 mg (ca. 88%) of a crystal mixture composed of (R,R)-tartarato(-) derivatives and (+)-4·(R,R)-tartarato(-) (ratio in roughly 2:1) (¹H NMR spectroscopic determination of the proportion of H₂O). (+)-4 and (+)-4·3H₂O were isolated in pure form by mechanical sorting under the microscope.

The compound of (+)-4 is colorless rhombic plates in colorless rhombuses in a nitrogen stream: yield 1994.

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[Zr3(Cp2O2CNiPr2)µ(µ3-O)(µ2-CCO)], the First Crystallographically Established Ketenylidene Complex; A Model for CO Reductive Cleavage on Metal Surfaces**

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The formation of carbon–carbon bonds from the C, feedstock, CO, is a fundamental reaction in organometallic chemistry. Reductive coupling of CO to give fragments containing C-C multiple bonds has been reported.[11] In these reactions, exhaustive reduction of oxygen from CO to cations of early transition metals, lanthanides, or actinides occurs. On the other hand, less extensive reductions of carbon monoxide with alkali metals or solutions of them to yield (CO)n− species, n = m = 2;[12] n = 4, = 3, = 6.[14] To our knowledge, only one case exists[15] of the intermediate reduction of CO to the ketenylidene ligand, namely in the reaction of [Tat(Bu3SiO)] with CO at low temperature and pressure, which gives an almost equimolar mixture of [TaO(Bu3SiO)] and [Ta(COO)(Bu3SiO)]; the latter compound is not isolated, but contains a terminal ketenylidene ligand according to spectroscopic data. The reaction of [Sm(C2Me5)3(thf)] with CO was reported to yield the metal-substituted ketenocarboxylic acid in [Sm(C2Me5)3(O2CCCO)-thf]2.[16]

In continuation of our studies on redox reactions with N,N-dialkylcarbamato complexes of transition elements,[17] we now report[18] that the reaction of [Zr2(CO)6] with [Zr2(O2CNuPr2)] (R = Et, Pr) in refluxing toluene affords colorless crystals of the diamagnetic compounds 1a (R = Et) and 1b (R = Pr) in satisfactory yields [Eq. (a)].

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\begin{align*}
\text{[Zr2(CO)6]} & \rightarrow \text{[Zr2(Cp2O2CNiPr2)µ(µ3-O)(µ2-CCO)]}^+ \\
& \text{[Zr2(Cp2O2CNiPr2)µ(µ3-O)(µ2-CCO)]}^+ \rightarrow \text{[Zr2(Cp2O2CNiPr2)µ(µ3-O)(µ2-CCO)]}^2+ 
\end{align*}
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Compounds 1 are poorly soluble in aliphatic hydrocarbons and slightly soluble in aromatic hydrocarbons and THF. The μ-ketenylidene derivatives 1 are characterized by a sharp IR absorption at 1303 cm−1 (in toluene or nujol mull), which shifts to 1551 cm−1 in the 13C-labeled compound prepared from [Zr2(Cp2(13CO)µ2)] and [Zr2(O2CNiPr2)]3, thus showing that the carbon atoms of the μ-ketenylidene ligand come from the carbonyl groups of the zirconium(IV) complex. No shift of the 2031 cm−1 band is observed in the compound obtained from the reaction of [Zr2(Zr(CO)µ2)] with [Zr2(CP)(13C=O)]3.

The 13C NMR spectrum of the 13C-labeled product [Zr2(Cp2(13CNiPr2)µ(µ3-O)(µ2-CCO)] shows two doublets at δ = 181.5 and 112.4 (J C-C = 78.9 Hz); the former resonance is assigned to the carbon adjacent to the oxygen atom of the ketenylidene ligand, in agreement with the reported values for bridging ketenylidene groups.[18]

Figure 1 shows the molecular structure[19] of 1b, which consists of a μ-O-bridged triangle of zirconium atoms. Two of the metal atoms (Zr1 and Zr3) are coordinated to bridging carbamates and to the cyclopentadienyl and µ-CO ligands; the third zirconium atom (Zr2) has bridging and terminal carbamato ligands. A similar essentially planar Zr3(µ2-O) moiety has been observed[19] in [Zr3(Cp2(µ2-O)(µ2-PhCOO)]2 PhCOO+ [Zr-O (mean value) 2.071(11) Å, Zr-O-Zr (mean value) 108.1(8)]; Zr...Zr (mean value) 3.354(12) Å; see caption to Fig. 1 for the corresponding values for 1b. The μ-ketenylidene ligand is substantially linear [C1-C2-O2, 179(1)°]; the C1-C2 and the C2-O2 bond lengths of 1.31(3) and 1.24(1) Å, respectively, are in accord with the reported values.[18]

The ketenylidene ligand has been assembled around a transition metal cation by four synthetic methods: a) reductive dehalogenation or dehalogenation of a metal-coordinated C=X fragment, such as the dehalogenation[11] of [C2=CCl2] by AlCl3 in the presence of CO; b) reductive cleavage (by an external reducing agent such as an alkali metal) in a trinuclear or tetracnuclear metal cluster of a CO single bond obtained by a preliminary electrolyslic activation of a metal-coordinated carbonyl group,[12] c) reaction of a low-valent metal complex with C2O3,[13] d) carbynylation of a diazomethyl complex.[14] Furthermore, a silver ketenylidene complex has been prepared[15] from a silver salt and ketene or ketene precursors. The isolation of compounds 1 corresponds to a new preparative method by which the Zr-coordinated carbonyl groups are reduced to the μ2-ketenylidene ligand without addition of an external reducing agent. The four reducing equivalents required by this process (2CO → C2O + O) are provided by zirconium(II).

The proximity of the metal atoms in 1 may establish similar conditions to those at a metal surface on which an analogous process might take place. The simplicity and the high chemoselectivity of the reaction reported in this paper, and the high