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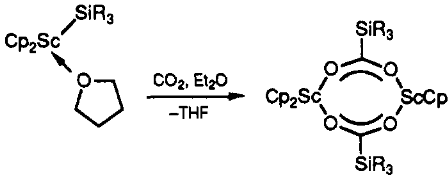
Communications

Carbon Dioxide Activation by a Transition-Metal–Silicon Bond. Formation of Silanecarboxylate Complexes $[Cp_2Sc(\mu\text{-}O_2CSiR_3)]_2$

Recent work in our laboratory has demonstrated the reactivity of d^0 M–Si bonds toward unsaturated species. Depending on the nature of the early transition-metal silyl complex, insertions of carbon monoxide,[1] isonitriles,[1b,d,g] organic carbonyl compounds,[2] and ethylene[3] can be observed. In contrast, numerous attempts to observe insertion of a heterocumulene into the M–Si bond of group 4 or 5 transition-metal silyl derivatives have proven unsuccessful. For example, $Cp^*Cl_3TaSiMe_3$ failed to react with CO_2 or PhNCO,[2] and $Cp_2Zr(SiMe_3)Cl$ is unreactive toward CO_2, CS_2, and PhNCO.[1b] The zirconium silyl $CpCp^*Zr[Si(SiMe_3)_3]Cl$ ($Cp^* = \eta^5\text{-}C_5Me_5$) gave an unidentified mixture of products after prolonged reaction with CO_2 or PhNCO.[1d] Recently, it was reported that the anionic silyl complex $PPN[(CO)_5WSiMe_3]$ does not react with CO_2 even at pressures above 1000 psi, but that SO_2 does react via insertion into the W–Si bond.[4] We now report that insertion of CO_2 into the Sc-Si bonds of $Cp_2Sc(SiR_3)(THF)$ (**1**, $R_3 = (SiMe_3)_3$; **2**, $R_3 = {}^tBuPh_2$) occurs readily to form the dimeric silanecarboxylate complexes $[Cp_2Sc(\mu\text{-}O_2CSiR_3)]_2$ (**3**, $R_3 = (SiMe_3)_3$; **4**, $R_3 = {}^tBuPh_2$).

Syntheses of yellow **1** and **2** from $[Cp_2ScCl]_2$ and lithium silyls follow analogous procedures for other d^0 $M\text{-}SiR_3$ derivatives.[1b-g,5] When CO_2 is bubbled through diethyl ether or benzene solutions of these silyl complexes, colorless solutions containing dimeric insertion products form rapidly (<1 min, eq 1). Compound **3** was isolated by crystallization from the reaction solvent, and **4** was crystallized by diffusion of layered pentane into a concentrated toluene solution. Compound **3** was independently prepared by the reaction of $HO_2CSi(SiMe_3)_3$[6] with **1**. Spectroscopic properties for **3** and **4** are very similar,[7] and the dimeric nature of **3** was established by X-ray crystallography (vide infra). The $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ infrared stretching frequencies for **3** occur at 1486 and 1349 cm^{-1}, respectively. These relatively low values are apparently the result of silyl substitution, since the dimeric acetate $[Cp_2Sc(\mu\text{-}O_2CMe)]_2$ exhibits analogous infrared bands at 1580 and 1445 cm^{-1}.[8] The difference between the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ stretching frequencies for **3** (135 cm^{-1}) is consistent with bidentate or bridging carboxylate ligands.[9] The relatively downfield ^{13}C NMR chemical shifts for the carboxylate carbons of **3** and **4** (δ 200.81 and 196.55, respectively) may also be attributed to the presence of a silyl group.[1b]



(1)

3, $R_3 = (SiMe_3)_3$

4, $R_3 = {}^tBuPh_2$

X-ray crystallography provided a somewhat imprecise structure for **3** (Figure 1).[10] However, the structure solution clearly reveals dimeric $[Cp_2ScO_2CSi(SiMe_3)_3]_2$ units. To our knowledge no structures of the type $[Cp_2Sc(O_2CR)]_n$ are available for comparison, but the structure of $(\eta^5\text{-}C_5Me_5)_2Sc(\eta^2\text{-}O_2CC_6H_4CH_3)$ has been determined to be monomeric with a bidentate carboxylate group.[11] The related lanthanide complex $[Cp_2Yb(\mu\text{-}O_2CC_6F_5)]_2$ has a structure similar to that of **3**.[12] Also, the structure of a related complex with μ-silanecarboxylate ligands, $[Cu(\mu\text{-}O_2CSiPhMe_2)_2\cdot H_2O]_2$, has been reported.[13]

Subsequent crystallizations from the mother liquors that yield

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(5) $LiSi^tBuPh_2$ was generated in solution by reaction of lithium metal with $ClSi^tBuPh_2$ in tetrahydrofuran. Compounds **1** and **2** were prepared in pentane solvent and purified via crystallization from toluene: Campion, B. K.; Heyn, R. H.; Tilley, T. D. Manuscript in preparation.

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(7) Data for **3**: mp 236–238 °C. Anal. Calcd for $C_{20}H_{37}O_2ScSi_4$: C, 51.5; H, 7.99. Found: C, 51.3; H, 7.96. ^1H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.40 ($SiMe_3$), 6.25 (Cp). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 2.21 ($SiMe_3$), 112.24 (Cp), 200.81 (CO_2Si). For **4**: mp 224–225 °C. Anal. Calcd for $C_{27}H_{34}O_2ScSi$: C, 70.7; H, 6.37. Found: C, 70.4; H, 6.41. IR (Nujol, CsI, cm^{-1}): 1510 s, 1389 s, $\nu(CO_2)$. ^1H NMR (benzene-d_6, 300 MHz, 23 °C): δ 1.28 (^{t}Bu), 5.98 (Cp), 7.24 (m, 12 H, Ph), 7.82 (m, 8 H, Ph). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 18.85 ($SiCMe_3$), 27.89 ($SiCMe_3$), 112.15 (Cp), 128.3, 131.5, 132.2, 136.6 ($SiPh_2$), 196.55 (CO_2Si). For **5**: ^1H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.34 (s, 27 H, $SiMe_3$), 6.12 (s, 10 H, Cp). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 1.46 ($SiMe_3$), 112.35 (Cp).

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(10) Due to inability to model a small amount of electron density well removed from molecules of **3**, the structure solution is somewhat incomplete. However, the quality of the structure determination is sufficient to establish connectivity. Structure solution in space group $R\bar{3}$, R_F = 10.72%, R_{wF} = 15.01%. Full details are provided in the supplementary materials.

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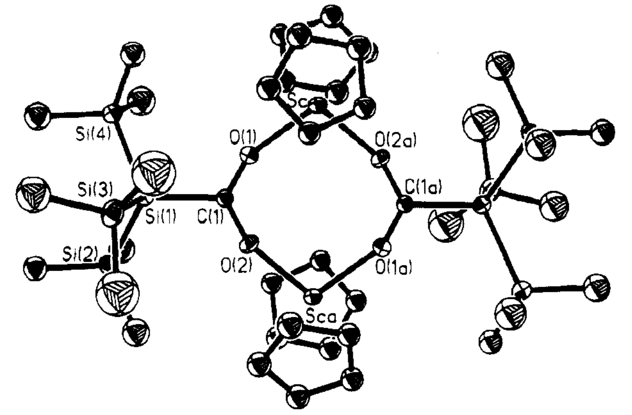

Figure 1. ORTEP view of $\{Cp_2Sc[\mu\text{-}O_2CSi(SiMe_3)_3]\}_2$ (3) with thermal ellipsoids drawn at the 20% probability level.

3 result in isolation of samples containing small amounts of an additional product, 5.[7] Compound 5 could not be isolated in pure form, but ^1H NMR spectroscopy shows that Cp and $Si(SiMe_3)_3$ groups are present in a 2:1 ratio. It therefore seemed that 5 could be formulated as a siloxide, $[Cp_2ScOSi(SiMe_3)_3]_x$, generated by expulsion of CO from 3. Analogous CO elimination reactions have been observed for the esters $(Me_3Si)_3SiCO_2R$ (R = Me, $SiPh_3$, $SiMe_3$, $Si(SiMe_3)_3$),[6] and for the copper(II) complexes $Cu(O_2CSiR_3)_2{\cdot}H_2O$ (SiR_3 = $SiPh_3$, $SiMePh_2$, $SiMe_2Ph$, $SiPh_2SiPh_3$).[14] Consistent with this, reaction of 1 with $^{13}CO_2$ produced a mixture of 3-^{13}C and 5, and no incorporation of carbon-13 into 5 could be detected (by ^{13}C NMR spectroscopy). However, 3 does not decompose to a measurable extent when heated to 95 °C for 60 h (by ^1H NMR, benzene-d_6). We are therefore reluctant at this time to definitely assign a structure to 5.

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Supplementary Material Available: Details concerning the structure solution and refinement and tables of crystal data, data collection, and refinement parameters, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and their isotropic thermal parameters (9 pages); listings of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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Catalysis of the Autoxidation of Aqueous Sulfur Dioxide Using $[Ni^{III}(cyclam)]$: Evidence for a Novel Radical Chain Mechanism

Sulfur dioxide is a menance to the environment, and transition-metal-catalyzed autoxidation offers a potentially cost-effective means for its abatement.[1] Aqueous catalyst solutions have been described with pH > 1.5 using iron,[2,3] manganese,[3] cobalt,[4] and copper[5] species. $[Ni^{III}(cyclam)]$ was selected as an oxidant (E^0 ~ 0.96 V) and found to exhibit distinctive catalytic properties in this regard.[6] Two equivalents of $[Ni^{III}(cyclam)]$ were consumed per equivalent of S(IV) in acidic (pH < 1) anaerobic solutions to produce 2 equiv of $[Ni^{II}(cyclam)]$ and 1 equiv of S(VI).[10] Oxygenated solutions furnished the catalytic output of sulfate.[11] Kinetic evidence is presented now for a novel mechanism of sulfur dioxide autoxidation with $[Ni^{III}(cyclam)]$ serving as the radical chain carrier.

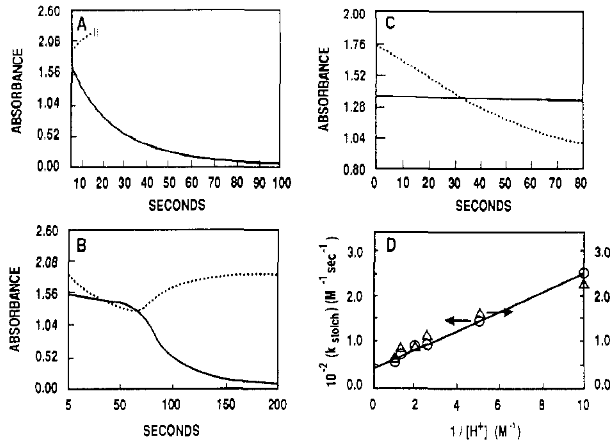

Figure 1. Temporal profiles (A–C: (--) λ = 206 nm; (—) λ = 308 nm; path length = 1 cm) and kinetic comparison (D) of stoichiometric oxidation and catalytic autoxidation of excess S(IV) using $[(cyclam)Ni^{III}]$ (T = 25 °C). (A) Pseudo first-order rate behavior for stoichiometric reaction $\{p_{Ar} \sim 101$ kPa $[HBF_4] = 1.0$ M; $[(cyclam)Ni^{III}]_0 = 1.4 \times 10^{-4}$ M; $[S(IV)]_0 = 5.0 \times 10^{-4}$ M$\}$. (B) Reaction under deficiency of dioxygen $\{p_{O_2} \sim 21$ kPa; $[HBF_4] = 1.0$ M; $[(cyclam)Ni^{III}] = 1.2 \times 10^{-4}$ M; $[S(IV)] = 1.0 \times 10^{-3}$ M$\}$. (C) Reaction under excess dioxygen $\{p_{O_2} \sim$ 450 kPa; $[HClO_4] = 1.0$ M; $[(cyclam)Ni^{III}]_0 = 1.2 \times 10^{-4}$ M; $[S(IV)]_0 = 1.0 \times 10^{-3}$ M$\}$. (D) Comparison between rate constants for the stoichiometric reaction of $[(cyclam)Ni^{III}]$ with S(IV) and the $[(cyclam)Ni^{III}]$-catalyzed autoxidation of S(IV) in aqueous perchloric acid $\{[(cyclam)Ni^{III}]_0 = 1.2 \times 10^{-4}$ M; $[S(IV)]_0 = 1.0 \times 10^{-3}$ M; $\mu = 1.0$ M $(LiClO_4)\}$: (○) stoichiometric reaction; (△) catalytic reaction.

Analogous reactions in 1.0 M acid under either argon or dioxygen have been monitored spectroscopically to determine the relationship between the stoichiometric and catalytic reactions. Wavelengths of 206 and 308 nm were chosen to follow $[Ni^{III}(cyclam)]$ ($\epsilon_{206} = 2800\ M^{-1}\ cm^{-1}$; $\epsilon_{308} = 11\,070\ M^{-1}\ cm^{-1}$), $[Ni^{II}(cyclam)]$ ($\epsilon_{206} = 10\,200\ M^{-1}\ cm^{-1}$; $\epsilon_{308} = 17\ M^{-1}\ cm^{-1}$), and

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(10) See the supplementary data, Tables 1 and 2, for the stoichiometric and catalytic stoichiometries, respectively.

(11) Reaction of a solution containing initially 1.0×10^{-4} M $[Ni^{III}(cyclam)]$ and 0.10 M HCl to which 0.10 M S(IV) was added (slowly) under p_{O_2} ~ 260 kPa led to the complete conversion of S(IV) to S(VI) [isolated as Na_2SO_4 from solution adjusted to pH 8; IR (KBr) ν = 1130 br s, 720 s cm^{-1}] with $[(cyclam)Ni^{III}(Cl)(H_2O)]^{2+}$ remaining spectroscopically unchanged ($\epsilon_{308} \sim 13\,700\ M^{-1}\ cm^{-1}$). Absence of dithionate ($S_2O_6^{2-}$) absorptions (ν = 1245 s, 1000 s cm^{-1}) requires it to be <2%.

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