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Isolation of the First Metalloxy Ketene Complexes via "Double Insertion" of Carbon Monoxide into Thorium−Silicon Bonds[†]

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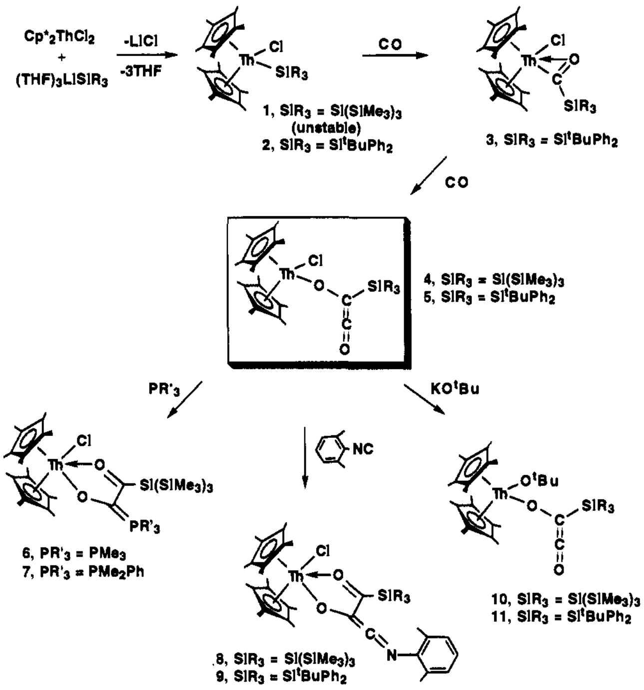
Migratory insertion reactions of carbon monoxide in early-transition-metal compounds have played an important role in development of molecular CO-activation chemistry.[1] In particular, d^0 metal complexes of the transition, lanthanide, and actinide series have often been observed to participate in CO−CO coupling reactions.[1−7] The mechanisms of these "double insertion" reactions have been the subject of much speculation, but little mechanistic information has been forthcoming. In some cases, reactivity studies have suggested the possibility that an initial η^2-acyl product of insertion couples with carbon monoxide to form a highly reactive metalloxy ketene intermediate, $(L_nMO)(R)CCO$; however, despite much effort, such ketene derivatives have never been isolated or even observed.[2,3,5] Because of their enhanced reactivity, it has been suggested that these species are activated by intramolecular coordination of the terminal ketene oxygen to the metal center (and bending of the $C{=}C{=}O$ linkage) in monometallic[2a,b] or bimetallic[5] structures. In our investigations of the chemistry of d^0 metal−silicon bonds, we have encountered carbonylation reactions which appear to involve (tantaloxy)(silyl)-[4a] and (scandoxy)(silyl)ketene[4b] intermediates. We now report the first observation and isolation of metalloxy ketene complexes, which have resulted from attempts to study the chemistry of actinide−silicon bonds.

For reasons that are currently unclear, actinide silyl complexes have proven very difficult to isolate, with the only reported success being Cp_3USiPh_3.[8] The reaction of $Cp^*_2ThCl_2$ ($Cp^* = \eta^5$-C_5Me_5) with $(THF)_3LiSi(SiMe_3)_3$ produces the yellow thorium silyl complex $Cp^*_2Th[Si(SiMe_3)_3]Cl$ (**1**, by ^1H NMR spectroscopy),[9] but decomposition to $Cp^*_2ThCl_2$, $HSi(SiMe_3)_3$, and other products has so far prevented its isolation. In an attempt to trap compound **1**, a toluene solution of $Cp^*_2ThCl_2$ and the lithium silyl was pressurized with carbon monoxide (40 psi), since d^0 metal silyl complexes are known to undergo rapid, and often clean, carbonylations. This trapping reaction provided the ketene derivative **4**[9] (Scheme 1) as pink crystals from pentane (41%). The infrared spectrum exhibits characteristic ketene absorption bands at 2044 and 1244 cm^{-1},[10] and the ^{13}C NMR spectrum contains resonances for the terminal (C_β) carbon at δ 66.77 and for the $=C_\alpha=O$ carbon at δ 223.31.[11]

Scheme 1



Molecules of **4** in the solid state (Figure 1)[12] have the ketene fragment oriented roughly in the plane bisecting the C_5Me_5 rings,

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[†] This work was initiated at the University of California, San Diego.

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(9) Selected data. **1**: ^1H NMR (benzene-d_6, 300 MHz) δ 0.44 (s, 27 H, Si*Me*), 2.09 (s, 30 H, C_5*Me*$_5$). **3**-^{13}C: $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz) δ 370.06 (η^2-$^{13}COSi^tBuPh_2$). **4**: ^1H NMR (benzene-d_6, 300 MHz) δ 0.37 (s, 27 H, Si*Me*), 2.06 (s, 30 H, C_5*Me*$_5$). Anal. C, H, Cl. IR (Nujol, CsI, cm^{-1}): ν(CCO) 2044. **4**-$^{13}C_2$: $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz) δ 1.79 (Si*Me*), 11.58 (C_5*Me*$_5$), 67.77 (d, $^1J_{CC}$ = 100 Hz, $^{13}\mathit{C}{=}^{13}C{=}O$), 223.31 (d, $^1J_{CC}$ = 100 Hz, $^{13}C{=}^{13}\mathit{C}{=}O$). **5**: ^1H NMR (benzene-d_6, 300 MHz) δ 1.28 (s, 9 H, C*Me*$_3$), 1.96 (s, 30 H, C_5*Me*$_5$). IR (Nujol, CsI, cm^{-1}) ν(CCO) 2050. **5**-$^{13}C_2$: $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz) δ 74.63 (d, $^1J_{CC}$ = 100 Hz, $^{13}\mathit{C}{=}^{13}C{=}O$), 224.55 (d, $^1J_{CC}$ = 100 Hz, $^{13}C{=}^{13}\mathit{C}{=}O$). **6**-$^{13}C_2$: ^1H NMR (benzene-d_6, 400 MHz) δ 0.38 (s, 27 H, Si*Me*), 1.00 (dd, $^2J_{PH}$ = 13.2 Hz, $^3J_{CH}$ = 2.0 Hz, 9 H, P*Me*$_3$), 2.25 (s, 30 H, C_5*Me*$_5$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz) δ 135.48 (dd, $^1J_{PC}$ = 115 Hz, J_{CC} = 67 Hz, $O^{13}\mathit{C}PMe_3$), 165.72 (dd, $^2J_{PC}$ = 61 Hz, J_{CC} = 67 Hz, $O^{13}\mathit{C}Si(SiMe_3)_3$). $^{31}P\{^1H\}$ NMR (benzene-d_6, 161.9 MHz) δ −3.59 (dd, $^1J_{PC}$ = 115 Hz, $^2J_{PC}$ = 61 Hz). **7**: Anal. C, H. **7**-$^{13}C_2$: ^1H NMR (benzene-d_6, 300 MHz) δ 0.37 (s, 27 H, Si*Me*), 1.46 (d, $^2J_{PH}$ = 13.2 Hz, $^3J_{CH}$ = 1.9 Hz, P*Me*$_2$Ph), 2.24 (s, 30 H, C_5*Me*$_5$), 7.01−7.12, 7.35−7.42 (m, 5 H, PMe$_2$*Ph*). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz) δ 134.20 (dd, $^1J_{PC}$ = 115 Hz, J_{CC} = 67 Hz, $O^{13}\mathit{C}PMe_2Ph$), 169.10 (dd, $^2J_{PC}$ = 62 Hz, J_{CC} = 67 Hz, $O^{13}\mathit{C}Si(SiMe_3)_3$). $^{31}P\{^1H\}$ NMR (benzene-d_6, 161.9 MHz) δ −0.65 (dd, $^1J_{PC}$ = 114 Hz, $^2J_{PC}$ = 61 Hz). **8**: Anal. C, H, N. IR (Nujol, CsI, cm^{-1}) ν(CCN) 2004 s. ^1H NMR (benzene-d_6, 300 MHz) δ 0.31 (s, 27 H, Si*Me*), 2.23 (s, 30 H, C_5*Me*$_5$), 2.34 (s, 6 H, *Me*$_2C_6H_3$), 6.74 (d, 2 H, *m*-$Me_2C_6\mathit{H}_3$), 6.83 (t, 1 H, *p*-$Me_2C_6\mathit{H}_3$). **8**-$^{13}C_2$: $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz) δ 130.94 (d, $^1J_{CC}$ = 57 Hz, $O^{13}\mathit{C}N(2,6\text{-}Me_2C_6H_3)$), 221.86 (d, $^1J_{CC}$ = 57 Hz, $O^{13}\mathit{C}Si(SiMe_3)_3$). **9**-$^{13}C_2$: IR (benzene-$d_6$, NaCl, cm^{-1}) ν(CCN) 2050 s. $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz) δ 129.38 (d, $^1J_{CC}$ = 60 Hz, $O^{13}\mathit{C}N(2,6\text{-}Me_2C_6H_3)$), 212.35 (d, $^1J_{CC}$ = 60 Hz, $O^{13}\mathit{C}Si^tBuPh_2$). **10**: IR (Nujol, CsI, cm^{-1}): ν(CCO) 2040 s. ^1H NMR (benzene-d_6, 300 MHz) δ 0.40 (s, 27 H, Si*Me*), 1.35 (s, 9 H, ^{t}Bu), 2.11 (s, 30 H, C_5*Me*$_5$). **10**-$^{13}C_2$: $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz) δ 64.04 (d, $^1J_{CC}$ = 100 Hz, $^{13}\mathit{C}{=}^{13}C{=}O$), 224.98 (d, $^1J_{CC}$ = 100 Hz, $^{13}C{=}^{13}\mathit{C}{=}O$). **11**-$^{13}C_2$: $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz) δ 73.39 (d, $^1J_{CC}$ = 100 Hz, $^{13}\mathit{C}{=}^{13}C{=}O$), 227.0 (d, $^1J_{CC}$ = 100 Hz, $^{13}C{=}^{13}\mathit{C}{=}O$).

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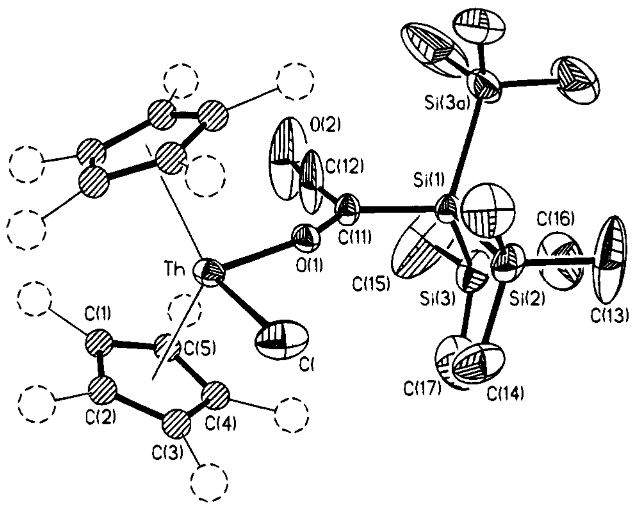

Figure 1. The molecular structure of **4** drawn with 35% thermal ellipsoids. The Cp* rings are fully disordered and are shown with methyl groups in calculated positions (dashed circles), as none were located. Important bond distances (Å) and angles (deg): Th–Cl 2.651(5), Th–O(1) 2.15(1), O(1)–C(11) 1.41(2), C(11)–C(12) 1.34(3), C(12)–O(2) 1.14(3), C(11)–Si(1) 1.87(2); Cl–Th–O(1) 100.5(3), Th–O(1)–C(11) 163(1), O(1)–C(11)–Si(1) 126(1), O(1)–C(11)–C(12) 117(1), C(11)–C(12)–O(2) 174(2), Cp*(centroid)–Th–Cp*(centroid) 130.1.

which are disordered apparently by free rotation about the Th–Cp*(centroid) axes. Overall, distances and angles for the ketene ligand are consistent with typical bonding parameters for organic ketene derivatives. For example, the C=C and C=O distances of 1.34(3) and 1.14(3) Å, respectively, correspond to analogous distances reported for $CH_2=C=O$ (1.31(1) and 1.16(1) Å).[13] Also, the structure of **4** is similar to that observed for the closely related thorium ketenimine $Cp^*_2Th(Cl)[OC(CH_2{}^tBu)=N(2,6\text{-}Me_2C_6H_3)]$,[2b] and the Th–O distance of 2.15(1) Å is identical to the Th–O distance reported for $[Cp^*_2Th(\mu\text{-}O_2C_2Me_2)]_2$.[14]

The carbonylation to give **4** appears to proceed via insertions of CO into the Th–Si bond of **1**, since both $Cp^*_2ThCl_2$ and $(THF)_3LiSi(SiMe_3)_3$ are inert toward CO. Also, we have observed analogous insertion reactions with the isolated thorium silyl $Cp^*_2Th(Si^tBuPh_2)Cl$ (**2**),[15] which undergoes carbonylation (40 psi) to the yellow-orange ketene **5**. This reaction was monitored by NMR spectroscopy (benzene-d_6) using ^{13}CO (1 atm). Under these conditions, the green η^2-silaacyl complex $Cp^*_2Th[\eta^2\text{-}^{13}CO(Si^tBuPh_2)]Cl$ (**3**-^{13}C) was observed as a transitory intermediate ($t_{1/2}$ < 1 h) by a ^{13}C NMR resonance (δ 370.06) which is quite characteristic for such species.[4,16] Gradually, this resonance is cleanly replaced by those for ketene **5**-$^{13}C_2$ (δ 74.63, 224.55; $^1J_{CC}$ = 100 Hz; ν(CCO) 2050 cm^{-1}).

Initial reactivity studies with **4** and **5** have been geared toward establishing possible similarities with processes that have previously been attributed to unobserved ketene intermediates.[2,4,5] For example, the proposed ketene intermediates $Cp^*_2Th(Cl)[OC(=C=O)CH_2{}^tBu]$,[2e] $Cp^*Cl_3TaOC(=C=O)SiMe_3$,[4a] and $Cp_2ScOC(=C=O)Si(SiMe_3)_3$[4b] are trapped by phosphines as metallacyclic ylide complexes of the type $L_nM[OC(=PR_3)C=O(R')]$. Reaction of **4** with PMe_3 and PMe_2Ph quantitatively generates the ylide complexes **6** and **7**,[9] respectively (Scheme 1). Complex **7** was isolated in 56% yield as yellow prisms from pentane. The $^1J_{PC}$ coupling constants for **6**-$^{13}C_2$ and **7**-$^{13}C_2$ (115 Hz) are in the range expected for such compounds (100–123 Hz[2a,4,17]), as are the $^1J_{CC}$ coupling constants (68 and 67 Hz, respectively), which range from 68 to 71 Hz in the previously reported Ta and Sc complexes. Analogous reactions of both **4** and **5** with $CN(2,6\text{-}Me_2C_6H_3)$ occur by attack of the nucleophile at the ketene C_α carbon, to give the dark red complexes **8** and **9**, respectively.[9]

Interestingly, **4** and **5** undergo nucleophilic attack by KO^tBu at thorium, rather than at the ketene ligand to form the enediolate complexes $Cp^*_2Th[OC(SiR_3)=C(O^tBu)O]$. As can be readily shown by IR and ^{13}C NMR spectroscopy,[9] the products of these reactions are the ketene complexes **10** and **11**, respectively. Unlike $Cp^*Cl_3TaOC(=C=O)SiMe_3$, which undergoes ene-type ether cleavage reactions with diethyl ether and methyltetrahydrofuran,[4a] compound **4** does not react with these ethers (excess, 24 h at room temperature). Thus, compounds **4** and **5** appear to have some chemical properties in common with previously proposed d^0 metalloxy ketene derivatives. More importantly, they provide concrete evidence that such species are viable intermediates, and they present the first structural and spectroscopic properties for this class of compounds.

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Supplementary Material Available: Experimental procedures and characterization data for complexes, tables of crystal, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates, and a view of the disordered molecular structure (20 pages); listing of observed and calculated structure factors (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(12) Crystal data for $Cp^*_2Th(Cl)[OC(=C=O)Si(SiMe_3)_3]$ (**4**): $C_{31}H_{57}ClO_2Si_4Th$, orthorhombic, *Pnma*, a = 26.385(5) Å, b = 16.817(3) Å, c = 9.193(3) Å, V = 4079(2) Å^3, Z = 4, D_{calcd} = 1.370 g cm^{-3}, μ (Mo Kα) = 38.61 cm^{-1}, T = 297 K. Of 4786 independent and absorption-corrected data collected (Siemens P4, 2θ(max) = 55°), 1989 were observed ($5\sigma(F_o)$). The Cp* rings are fully disordered and appear as almost featureless circular planes of electron density. The disorder was modeled by the construction of overlapping geometrically constrained forms with appropriate occupancy weighting. Only the ring centroids are reliable. All non-hydrogen atoms, except those in the Cp* rings, were anisotropically refined. Hydrogen atoms, except those of the Cp* rings, were idealized. $R(F)$ = 4.76%, and $R(wF)$ = 5.57%. All computations used the SHELXTL-PC program library (G. Sheldrick, Siemens XRD, Madison, WI).

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