properties of these complexes compared with the related series containing nitrogen donor ligands, Ru(N-N)$(SQ)_2$, suggest that the N-donor analogues exist as $Ru^{II}(SQ)_2$ species in solution but change in charge distribution to the Ru^{III}(SQ)(Cat) form in the solid state.

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Supplementary Material Available: For $Ru(PPh_3)_2(DBSQ)Cl_2$ and $Ru(PPh_3)_2(Cl_4SQ)_2$, tables giving crystal data and details of the structure determination, atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters (26 pages); listings of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of an Organotitanium Complex Containing a Planar Bis(μ-oxo)dititanium Core

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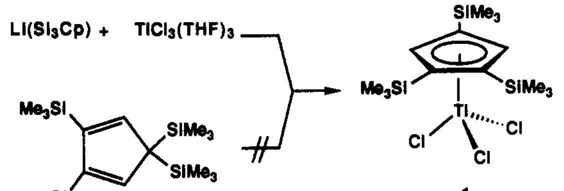
Hydrolysis of trichloro[tris(trimethylsilyl)cyclopentadienyl]titanium, $[(\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]TiCl_3$ (**1**), yields with $^1/_2$ equiv of water the μ-oxo complex $[(\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]_2Ti_2Cl_4(\mu\text{-}O)$ (**2**), which upon further reaction with water gives dinuclear $[(\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]_2Ti_2Cl_2(\mu\text{-}O)_2$ (**5**). An X-ray structural determination of **5** revealed the presence of a planar $Ti_2(\mu\text{-}O)_2$ core with Ti-O distances of 1.814 (1) and 1.835 (1) Å and angles at Ti and at O of 84.23 (3) and 95.78 (3)°, respectively. The substituted cyclopentadienyl ligands are η^5-bonded and mutually trans configurated. Compound **5** crystallizes from pentane in the monoclinic space group $C2/c$, with cell dimensions a = 21.144 (1) Å, b = 9.713 (1) Å, c = 20.686 (2) Å, β = 93.90 (1)°, V = 4238 Å^3, and D(calcd) = 1.194 g·cm^{-3} (Z = 4).

Introduction

Among the transition-metal–oxo complexes bearing $\eta^5\text{-}C_5H_5$ (Cp) or $\eta^5\text{-}C_5Me_5$ (Cp*) groups as ancillary ligands,[1] titanium–oxo complexes seem to occupy a special position. While complexes featuring a terminal oxo functionality remain unknown so far,[2] a diversity of ring[3] and cage[4] frameworks in addition to the relatively common linear Ti–O–Ti core[5] have been characterized. These organotitanium complexes can be regarded as molecular models for materials formed by the extremely complicated sol–gel processes during hydrolysis of $TiCl_4$,[6] since they are usually prepared by the reaction of metallocene derivatives L_2TiX_2 or of half-sandwich complexes of the formula $LTiX_3$ (L = Cp, Cp*; X = monoanionic ligand such as halide or alkyl) with water. We report here results of our attempts to further clarify the course of these hydrolysis reactions by modifying the steric properties of the supporting cyclopentadienyl ligand and the formation of a new dinuclear organotitanoxane with a planar $Ti_2(\mu\text{-}O)_2$ core. The cyclopentadienyl ligand systems we utilized in this study are sterically highly hindered $\eta^5\text{-}C_5H_2(SiMe_3)_3$-1,2,4 ("$Si_3Cp$")[7] and $\eta^5\text{-}C_5H_2(CMe_3)$-4-$(SiMe_3)_2$-1,2 ("$BuSi_2Cp$").[8] They have been designed to kinetically stabilize reactive intermediates and block any bimolecular condensation reactions that would lead to high-nuclearity aggregates.[8,9]

Scheme I



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Results

The key compound $(Si_3Cp)TiCl_3$ (**1**), reported briefly before,[10] is accessible by reacting $TiCl_3$ or $TiCl_3(THF)_3$ with $Li(Si_3Cp)$ in THF followed by in situ oxidation of the green titanium(III) intermediate $(Si_3Cp)TiCl_2(THF)_2$. We found that carbon tetrachloride as oxidizing agent gives reproducibly $(Si_3Cp)TiCl_3$, albeit in moderate yields. The product can be isolated as pentane-soluble, orange crystals. The $BuSi_2Cp$ analogue

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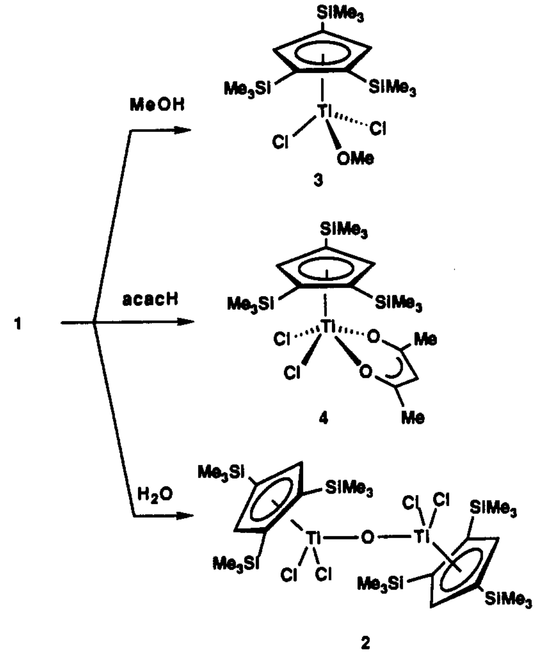
$(BuSi_2Cp)TiCl_3$ (**6**) can be prepared similarly and obtained as red crystals in ca. 40% yield. The more elegant method of treating tetrakis(trimethylsilyl)cyclopentadiene[7] with titanium tetrachloride (Scheme I) that was expected to give **1** directly with elimination of Me_3SiCl has failed so far, resulting in the formation of dark intractable material under a variety of conditions and in different solvents. It is noteworthy that nearly any trichloro(cyclopentadienyl)titanium derivative including the parent compound $CpTiCl_3$[11] as well as Cp^*TiCl_3[12] and $(Si_2Cp)TiCl_3$[13] (Si_2Cp = $\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$) can be efficiently synthesized by this procedure.

The trichloro complex **1** smoothly and cleanly undergoes nucleophilic substitution of one chloride ligand with oxygen nucleophiles. Thus, refluxing **1** in pure methanol gives the yellow dichloro methoxo complex **3** in quantitative yield, whereas 1 equiv of 2,4-pentanedione (acacH) in the presence of triethylamine gives the dichloro acetylacetonato complex **4** as orange-red crystals.



The methoxo complex **3** can be assigned the usual three-legged piano stool structure; for the acac complex **4**, however, both square-pyramidal and pentagonal-bipyramidal configurations are in principle conceivable.[14] Reaction of **1** with $^1/_2$ equiv of water yields the mono(μ-oxo)-bridged complex **2**, regardless of whether a base to trap the hydrogen chloride is added or not. Both **3** and **4** are also hydrolyzed to give this oxo complex that is isolated as pentane-soluble, dark yellow crystals. Analytical, mass spectral, and NMR spectroscopic data are in agreement with the proposed structure. In particular, the strong band at 762 cm^{-1} for the antisymmetric Ti–O–Ti vibration in the IR spectrum is diagnostic for the presence of a linear μ-oxo bridge linking two titanium fragments.[5]

Since no intermediate can be detected during the formation of **2** from the trichloride **1** by ^1H NMR spectroscopy, we assume that both the water adduct of **1**, $(Si_3Cp)TiCl_3(H_2O)$, and the hydroxo species $(Si_3Cp)TiCl_2(OH)$ are strong acids and readily dissociate to the presumably highly nucleophilic dichloro oxo anion A that attacks another molecule of **1** to give **2**. The less electrophilic zirconium do form aquo and hydroxo complexes, as has been described in the recent literature.[15]

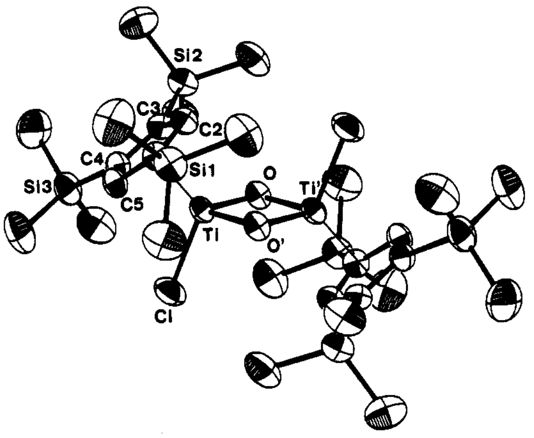
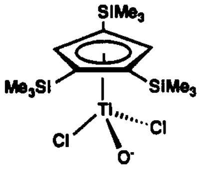


Figure 1. ORTEP representation of $[\{\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4\}TiCl]_2(\mu\text{-}O)_2$ (**5**). Atoms are drawn with 50% probability thermal ellipsoids.

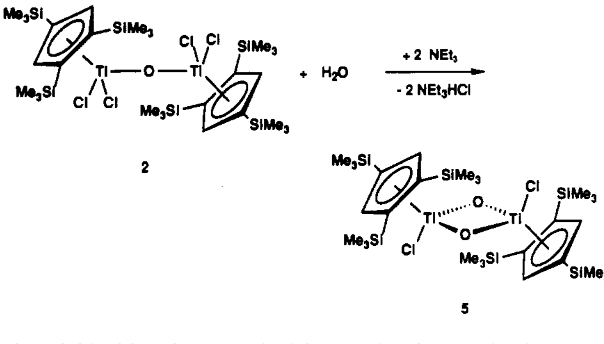
Table I. Crystallographic Data for **5**

chem formula	$C_{28}H_{58}Cl_2O_2Si_6Ti_2$	Z	4
fw	762.0	T, °C	23 ± 1 °C
cryst syst	monoclinic	D(calcd) $g \cdot cm^{-3}$	1.194
space group	$C2/c$	abs coeff (μ), cm^{-1}	62.6
a, Å	21.144 (1)	λ(Cu Kα), Å	1.541 84
b, Å	9.713 (0.6)	transm factors	0.3499–0.1207
c, Å	20.686 (2)	$R(F_o)$	0.043
β, deg	93.90 (0.7)	$R_w(F_o)$	0.047
V, Å^3	4238 (1)		



A

When the μ-oxo complex **2** is further treated with another 1 equiv of water and 2 equiv of base (eq 1) or, more directly, when the trichloride **1** is reacted with 1 equiv of water in the presence of 2 equiv of base, the new titanoxane derivative **5** is formed cleanly and can be isolated as pentane-soluble lemon yellow needlelike crystals in good yield. Elemental analysis and EI and FD mass spectra as well as molecular weight determination by vapor



(1)

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Table II. Final Positional Parameters of Compound **5** (Including Estimated Standard Deviations)

atom	x	y	z	B_{eq},[a] Å^2
Ti	0.03954 (2)	0.08607 (6)	0.03472 (3)	3.03 (1)
Cl	0.10207 (4)	0.2028 (1)	−0.03114 (4)	4.98 (2)
Si1	−0.07988 (4)	0.2885 (1)	0.11751 (5)	4.28 (2)
Si2	0.10033 (4)	−0.16633 (1)	0.16558 (5)	3.85 (2)
Si3	0.19365 (4)	0.1804 (1)	0.13218 (5)	4.70 (2)
O	0.03965 (8)	−0.0914 (2)	0.0074 (1)	3.27 (4)
C1	−0.0028 (1)	0.1919 (3)	0.1250 (2)	3.37 (7)
C2	0.0062 (1)	0.0487 (3)	0.1380 (2)	3.40 (7)
C3	0.0729 (1)	0.0147 (3)	0.1414 (1)	3.27 (7)
C4	0.1061 (1)	0.1398 (3)	0.1293 (2)	3.37 (7)
C5	0.0593 (1)	0.2453 (3)	0.1205 (2)	3.61 (7)
C11	−0.1458 (2)	0.1641 (4)	0.1036 (2)	6.1 (1)
C12	−0.0776 (2)	0.4138 (4)	0.0512 (2)	6.6 (1)
C13	−0.0869 (2)	0.3825 (5)	0.1949 (2)	7.4 (1)
C21	0.0370 (2)	−0.2920 (4)	0.1454 (2)	5.8 (1)
C22	0.1720 (2)	−0.2181 (4)	0.1258 (2)	5.7 (1)
C23	0.1153 (2)	−0.1609 (5)	0.2559 (2)	6.3 (1)
C31	0.2287 (2)	0.1266 (6)	0.2138 (2)	7.8 (1)
C32	0.2009 (2)	0.3688 (5)	0.1225 (2)	7.1 (1)
C33	0.2381 (2)	0.0951 (5)	0.0684 (2)	6.7 (1)
Cp	0.0483	0.1281	0.1308	

[a] The equivalent isotropic parameters are defined as $B_{eq} = {}^4/_3[a^2B(11) + b^2B(22) + c^2B(33) + ac\cos\beta(13)]$. Cp denotes the center of the tris(trimethylsilyl)cyclopentadienyl ligand.

pressure osmometry establish a dimeric constitution of the formula $[(Si_3Cp)TiClO]_2$. ^1H and ^{13}C NMR spectra show only one set of a typical pattern for the Si_3Cp ligand with chemical shifts significantly different from those of **2**. Moreover, the IR spectrum lacks the strong band in the region 750–800 cm^{-1} that is typical for the linear Ti–O–Ti unit,[5] while a pair of absorptions of medium intensity at 670 and 624 cm^{-1} is observed in addition to the bands due to the Si_3Cp ligand. These data suggest that complex **5** has a $Ti_2(\mu\text{-}O)_2$ unit with nonlinear Ti–O–Ti bridges, since for a four-membered ring of idealized D_{2h} symmetry two vibrational modes (B_{2u} and B_{3u}) are expected.[16] A single-crystal structure determination has confirmed the structure of two edge-sharing $(Si_3Cp)TiClO_2$ tetrahedra for **5**, which can be formally regarded as the dimer of the hypothetical mononuclear oxo species $(Si_3Cp)TiCl({=}O)$. By contrast, tetranuclear $[CpTiCl(\mu\text{-}O)]_4$[3a–c] and trinuclear $[Cp^*TiCl(\mu\text{-}O)]_3$[3e,4d] are formed under similar conditions by using $CpTiCl_3$ and Cp^*TiCl_3, respectively.

Crystals of **5** suitable for X-ray structural analysis were obtained by slow recrystallization from pentane at −40 °C. The lattice contains discrete dinuclear molecules without any significant intermolecular contacts. Figure 1 shows the molecular geometry and Table II lists the final atomic coordinates. Selected interatomic distances and angles are given in Table III. The dinuclear molecule has a crystallographically imposed center of symmetry.

Considering the Si_3Cp ligand as monodentate, the geometry around titanium is essentially tetrahedral with the Si_3Cp ring centrally bonded to the d^0 metal center in the familiar η^5 fashion. The distance of titanium to the centroid of the ring ligand of 2.026 Å is unexceptional, as are all other geometrical parameters of the ancillary Si_3Cp ligand.[9] The planar $Ti_2(\mu\text{-}O)_2$ core of C_{2h} symmetry shows only a slight distortion from a square with Ti–O distances of 1.814 (1) and 1.835 (1) Å and with angles of 84.23 (3)° at the titanium atom and 95.78 (3)° at the oxygen atom. The Ti–Ti distance of 2.707 Å is unusually short as compared with that of other dinuclear titanium complexes[17] and of titanium metal (3.212 Å[18]). The bulky Si_3Cp ligands are arranged in a trans configuration, the rings adopting a conformation relative to each other so as to minimize interannular steric repulsion between the $SiMe_3$ groups. All geometrical features of the central titanoxane core, including the short Ti–Ti distance, are comparable with those of the few known examples of complexes with a planar $Ti_2(\mu\text{-}O)_2$ unit, viz. $[Ti(acac)_2(\mu\text{-}O)]_2$[19] and $K_4[Ti(O_2C_6H_4)_2(\mu\text{-}O)]_2\cdot 9H_2O$.[20] A more distorted $Ti_2(\mu\text{-}O)_2$ ring has been reported for $[(\eta^5{:}\eta^1\text{-}C_5H_4CMe_2C_6H_4N)TiCl(\mu\text{-}O)]_2\cdot 2CH_2Cl_2$[21] and a puckered Ti_2O_2 ring has been found in the fulvene-bridged $Cp^*Ti(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2TiCp^*$.[22] Table IV summarizes the pertinent bond distances of complexes containing the $Ti_2(\mu\text{-}O)_2$ core.

Table III. Selected Bond Distances (Å) and Angles (deg) and Their Standard Deviations

Bond Distances			
Ti–Cl	2.266 (1)	Si1–C1	1.878 (1)
Ti–O	1.814 (1)	Si2–C3	1.881 (1)
Ti–O′	1.835 (1)	Si3–C4	1.889 (1)
Ti–C1	2.361 (1)	C1–C2	1.428 (2)
Ti–C2	2.324 (1)	C1–C5	1.421 (2)
Ti–C3	2.374 (1)	C2–C3	1.445 (2)
Ti–C4	2.390 (1)	C3–C4	1.434 (2)
Ti–C5	2.369 (1)	C4–C5	1.429 (2)
Ti–Cp	2.026	O–O	2.447 (1)
Ti–Ti	2.7071 (4)		
Bond Angles			
Cl–Ti–O	106.0 (0)	Si1–C1–C2	127.3 (1)
Cl–Ti–O′	104.6 (0)	Si1–C1–C5	127.9 (1)
Cl–Ti–Cp	118.1	Si2–C3–C2	120.4 (1)
O–Ti–Cp	119.7	Si2–C3–C4	132.8 (1)
O′–Ti–Cp	118.7	Si3–C4–C3	131.5 (1)
Ti–O–Ti′	95.8 (0)	Si3–C4–C5	121.6 (1)
C2–C1–C5	104.8 (2)	C3–C4–C5	106.6 (2)
C1–C2–C3	110.4 (2)	C1–C5–C4	111.4 (1)
C2–C3–C4	106.7 (2)		

Table IV. Selected Geometrical Parameters of Complexes Containing the $Ti_2(\mu\text{-}O)_2$ Unit

compd	dist, Å		ref
	Ti–O	Ti–Ti	
$[Ti(acac)_2]_2(\mu\text{-}O)_2$	1.824 (4) 1.831 (1)	2.729 (1)	19
$[\{Ti(O_2C_6H_4)_2\}_2(\mu\text{-}O)_2]^{4-}$	1.859 (1) 1.876 (1)	2.819 (1)	20
$Cp^*Ti(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2TiCp^*$	1.787 (3) 1.961 (2)	2.724 (1)	22
$[(\eta^5{:}\eta^1\text{-}C_5H_4CMe_2C_6H_4N)TiCl]_2(\mu\text{-}O)_2$	1.791 (3) 1.910 (2)	2.801 (1)	21
$[(Si_3Cp)TiCl]_2(\mu\text{-}O)_2$	1.814 (1) 1.835 (1)	2.707 (0)	this work

The analogous titanium–oxo complexes of the related $BuSi_2Cp$ ligand $[(BuSi_2Cp)TiCl_2]_2(\mu\text{-}O)$ (**7**) and $[(BuSi_2Cp)TiCl]_2(\mu\text{-}O)_2$ (**8**) can be prepared in a similar manner and characterized by analytical and spectroscopic methods. When an equimolar mixture of the mono(μ-oxo)-bridged complexes **2** and **7** is treated with exactly $^1/_2$ equiv of water per titanium and 1 equiv of triethylamine, the product isolated contains the cyclodititanoxane derivatives **5** and **8** and about 10% of the crossover product $(Si_3Cp)(BuSi_2Cp)Ti_2Cl_2(\mu\text{-}O)_2$ (**9**) according to ^1H NMR spectroscopy.[23] This result suggests that the formation of the second oxo bridge to give the four-membered ring proceeds in an intramolecular manner. The presence of **9** is accounted for by a water-catalyzed scrambling between **5** and **8** (vide infra) (eq 2).

The cyclodititanoxane **5** appears to be thermally robust showing no sign of decomposition or rearrangement to other derivatives when the melt is heated to 200 °C for several hours. Likewise,

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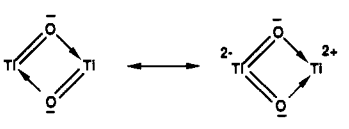
$$\underset{\mathbf{8}}{\underset{\mathbf{5}}{[(Si_3Cp)TiCl]_2(\mu\text{-}O)_2} + [(BuSi_2Cp)TiCl]_2(\mu\text{-}O)_2} \rightleftharpoons 2\ \underset{\mathbf{9}}{(Si_3Cp)(BuSi_2Cp)Ti_2Cl_2(\mu\text{-}O)_2} \quad (2)$$

when pure **5** and **8** are mixed in C_6D_6, there is no crossover observed at room temperature even after 1 week. Only when the mixture is heated to 50 °C for **5** days can a slight scrambling (ca. 30%) be detected. We found subsequently that traces of water catalyze the scrambling reaction at this temperature, and after 1 week a nearly statistical amount of the three complexes **5**, **8**, and **9** (molar ratio 1:1:2) is obtained.[24]

The degradation of the ring structure in **5** to give first the linear derivative **2** and finally the mononuclear trichloride **1** can be easily achieved by reaction with excess of trimethylchlorosilane and hydrogen chloride in ether. On the other hand, further hydrolysis of **5** by treating it with excess water and base or with aqueous ammonia results in virtually complete decomposition to give an insoluble white precipitate of titanium oxide hydrate. However, a minute amount of pale yellow crystals can be isolated from such reaction mixtures irreproducibly, which according to elemental analysis and FD mass spectrometry appears to be the chloride-free cluster $[(Si_3Cp)Ti]_4(\mu\text{-}O)_6$ with an adamantane-like cage structure. In keeping with this formulation and in analogy to the structurally completely characterized complex $(Cp^*Ti)_4(\mu\text{-}O)_6$,[4c] the IR spectrum exhibits a broad strong band at 770 cm^{-1}. Apparently, the nucleophilic substitution reaction of the chloride ligands in **5** cannot compete with the degradation of the Si_3Cp ligand, which is destabilized by the presence of good π-donating oxo ligands.

Discussion

In summary, we have synthesized and structurally characterized a new cyclodititanoxane with a planar $Ti_2(\mu\text{-}O)_2$ core.[25] The controlled hydrolysis of the trichloride **1** to give **5** rather than other higher nuclearity ring or cage compounds clearly reflects the pronounced steric bulk of the Si_3Cp ligand, since analogous reactions with less sterically hindered ancillary ligands such as Cp and Cp* yield tetra- and trinuclear titanoxane derivatives.[3,4] The steric bulk of the peripheral substituents obviously blocks further condensation and aggregation reactions. Although the ubiquitous linear or almost linear Ti–O–Ti unit seems to be favored by the π-donating effect of the oxygen atom at the electron-deficient titanium centers, a certain thermodynamic stability has to be attributed to the $Ti_2(\mu\text{-}O)_2$ unit. We speculate in the absence of molecular orbital calculations that population of states with some *transannular* bonding interactions between the titanium atoms might be involved.[26] On the basis of differing Ti–O distances, the formulation of the $Ti_2(\mu\text{-}O)_2$ unit as containing Ti–O double bonds has been implied for the complexes $[(\eta^5\text{:}\eta^1\text{-}C_5H_4CMe_2C_6H_4N)TiCl(\mu\text{-}O)]_2$[21] and $Cp^*Ti(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2TiCp^*$.[22] Considering both structural data and chemical behavior, however, we do not believe that formula B significantly contributes to the bonding of the four-membered ring in **5**.[27]



B

There is a close analogy between the dimeric titanium oxo complexes described here and the recently reported cyclodimetalloxanes of group 14 elements $(R_2E)_2(\mu\text{-}O)_2$ (E = Si, Sn). The structurally characterized derivatives, $(R_2Si)_2(\mu\text{-}O)_2$ (R = mesityl[28]) and $(R_2Sn)_2(\mu\text{-}O)_2$ (R = $CH(SiMe_3)_2$[29]), both contain bulky ligands and have striking structural similarities to the titanoxane derivatives. Thus, an unusually close *transannular* contact between the metalloid atoms E[30] is observed and the four-membered ring forms a lozenge with only slightly different E–O bond lengths. Finally, there is apparently also a comparatively short uranium(IV)–uranium(IV) bond in $[(Si_2Cp)_2U]_2(\mu\text{-}O)_2$.[31]

Experimental Section

General Consideration. All operations were performed under an inert atmosphere of nitrogen using standard Schlenk-line techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl. Pentane and hexane were purified by distillation from sodium/potassium alloy. Triethylamine was distilled from CaH_2 and stored over molecular sieves. Si_3CpH,[7] $BuSi_2CpH$,[8] $TiCl_3(THF)_3$,[32] and $(Si_3Cp)TiCl_3$[10] were synthesized as described in the literature. ^1H NMR and ^{13}C NMR spectra were recorded in C_6D_6 at 25 °C on a JEOL GX 400 spectrometer. IR spectra were obtained on a Nicolet 5 DX FT IR spectrometer using KBr pellets. Electron-impact mass spectra were taken at 70 eV on a Varian MAT 311 A instrument and field desorption mass spectra on a Finnigan MAT 90 mass spectrometer. Melting points were determined in capillary tubes under nitrogen and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Anorganisch-chemisches Institut der TU München.

$[(Si_3Cp)TiCl_2]_2(\mu\text{-}O)$ (2). A mixture of water (9 μL, 0.5 mmol) and triethylamine (140 μL, 101 mg, 1.0 mmol) in 5 mL of THF was slowly added dropwise with vigorous stirring to a solution of $(Si_3Cp)TiCl_3$ (435 mg, 1.0 mmol) in ether (20 mL) at room temperature. After the completion of the addition, all volatiles were removed in vacuo, the residue was extracted with pentane (3 × 10 mL), and the extracts were filtered. The yellow filtrate was concentrated and slowly cooled down to −78 °C to give dark yellow crystals: yield 360 mg (88%); mp 159 °C. ^1H NMR: δ 7.65 (s, 2 H, C_5H_2), 0.47 (s, 18 H, $SiCH_3$), 0.43 (s, 9 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 148.83, 146.55, 140.13 (ring-C), 1.27, 0.25 ($SiCH_3$). IR (cm^{-1}): 2961 mw, 2903 w, 1250 s, 1098 s, 985 m, 929 ms, 839 vs, 762 s, 745 s, 640 w, 632 w, 451 m, 398 ms. EI MS (*m/e*, relative intensity): 818 (M^+, 5%), 803 ($M^+ - CH_3$, 100%). Anal. Calcd for $C_{28}H_{58}Cl_4OSi_6Ti_2$: C, 41.17; H, 7.16; C, 17.36. Found: C, 41.21; H, 7.25; Cl, 16.92.

$(Si_3Cp)TiCl_2(OMe)$ (3). In 20 mL of methanol was suspended $(Si_3Cp)TiCl_3$ (435 mg, 1.0 mmol) and the mixture refluxed until all of the solid dissolved. The mixture was cooled down slowly to −40 °C to afford well-formed orange-yellow crystals: yield 410 mg (95%); mp 106 °C. ^1H NMR: δ 7.38 (s, 2 H, C_5H_2), 3.95 (s, 3 H, OCH_3), 0.35 (s, 18 H, $SiCH_3$), 0.27 (s, 9 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 142.52, 139.89, 138.89 (ring-C), 71.82 (OCH_3), 0.96, −0.38 ($SiCH_3$). IR (cm^{-1}): 2956 mw, 2917 w, 1249 s, 1115 vs, 1102 s, 999 m, 932 m, 835 vs, 755 m, 630 mw, 594 mw, 491 w, 395 ms. EI MS (*m/e*, relative intensity): 430 (M^+, 4%), 415 ($M^+ - CH_3$, 100%). Anal. Calcd for $C_{15}H_{33}Cl_2OSi_3Ti$: C, 41.66; H, 7.69; Cl, 16.39. Found: 41.59; H, 7.36; Cl, 16.08.

$(Si_3Cp)TiCl_2(H_3CCOCHCOCH_3)$ (4). A solution of $(Si_3Cp)TiCl_3$ (500 mg, 1.15 mmol) in pentane (30 mL) was treated with 2,4-pentanedione (118 μL, 115 mg, 1.15 mmol) at room temperature and then with triethylamine (160 μL, 116 mg, 1.15 mmol). A white precipitate rapidly formed, and the color of the mixture turned darker. After being stirred for 30 min, the reaction mixture was filtered and the filtrate concentrated and cooled to −78 °C to give orange-red crystals: yield 450 mg (78%); mp 121 °C. ^1H NMR: δ 7.33 (s, 2 H, C_5H_2), 5.02 (s, 1 H, COCHCO), 1.63 (s, 3 H, CH_3CO), 0.52 (s, 18 H, $SiCH_3$), 0.28 (s, 9 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 190.96 (CO), 148.36, 144.17, 141.27 (ring-C),

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102.61 (COCHCO), 25.32 (CH_3CO), 1.20, −0.49 ($SiCH_3$). IR (cm^{-1}): 2953 ms, 2899 w, 1564 s, 1534 s, 1333 w, 1291 mw, 1249 s, 1106 m, 1031 m, 983 m, 931 m, 895 m, 842 vs, 761 ms, 641 mw, 630 mw, 462 m, 432 m. EI MS (*m/e*, relative intensity): 500 (M^+, 2%), 485 ($M^+ - CH_3$, 5%), 464 ($M^+ - Cl$, 100%). Anal. Calcd for $C_{19}H_{36}Cl_2O_2Si_3Ti$: C, 45.68; H, 7.26; Cl, 14.19. Found: C, 45.58; H, 7.50; Cl, 14.09.

$[(Si_3Cp)TiCl]_2(\mu\text{-}O)_2$ (5). A solution of $(Si_3Cp)TiCl_3$ (435 mg, 1.0 mmol) in either (15 mL) was treated with water (18 μL, 1.0 mmol) at room temperature and subsequently with triethylamine (280 μL, 200 mg, 2.0 mmol). The resulting yellow suspension was stirred for 30 min, and all volatiles were evaporated. The residue was extracted with pentane (3 × 15 mL) and the filtrate concentrated until incipient crystallization. Over a period of a week, lemon yellow needles were obtained upon cooling to −78 °C: yield 320 mg (85%); mp 197 °C. ^1H NMR: δ 7.62 (s, 2 H, C_5H_2), 0.44 (s, 18 H, $SiCH_3$), 0.29 (s, 9 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 142.97, 137.72, 136.82 (ring-C), 1.11, −0.68 ($SiCH_3$). IR (cm^{-1}): 2958 mw, 2896 w, 1249 s, 990 ms, 937 m, 883 m, 838 vs, 756 s, 671 s, 657 ms, 639 ms, 624 s, 474 m, 426 w. EI MS (*m/e*, relative intensity): 762 (M^+, 5%), 747 ($M^+ - CH_3$, 100%). FD MS (*m/e*): 762 (M^+). Molecular weight (vapor-pressure osmometry in benzene): 692 (M_r = 762.0). Anal. Calcd for $C_{14}H_{29}ClOSi_3Ti$: C, 44.14; H, 7.67; Cl, 9.31. Found: C, 44.48; H, 7.91; Cl, 9.41.

$(BuSi_2Cp)TiCl_3$ (6). To a suspension of $TiCl_3(THF)_3$ (5.93 g, 16 mmol) in 70 mL of THF was added dropwise a solution of $Li(BuSi_2Cp)$ (436 mg, 16 mmol) at −95 °C. The mixture was allowed to warm up to room temperature and then refluxed for 2 h. The brownish green mixture was treated with carbon tetrachloride (1 mL, 1.59 g, 30 mmol) and refluxed for 4 h. The solvent was removed in vacuo, the residue extracted with pentane (3 × 15 mL), and the filtrate concentrated and cooled to −40 °C to afford orange-red crystals: yield 2.80 g (42%); mp 128 °C. ^1H NMR: δ 7.31 (s, 2 H, C_5H_2), 1.18 (s, 9 H, CH_3), 0.33 (s, 18 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 161.71, 147.72, 133.03, (ring-C), 34.49 ($\mathit{C}CH_3$), 30.82 ($C\mathit{C}H_3$), 0.81 ($SiCH_3$). IR (cm^{-1}): 2965 m, 2937 w, 2929 w, 2906 w, 1252 s, 857 vs, 759 m, 439 mw, 406 mw. EI MS (*m/e*, relative intensity): 418 (M^+, 2%), 403 ($M^+ - CH_3$, 100%). Anal. Calcd for $C_{15}H_{29}Cl_3Si_2Ti$: C, 42.91; H, 6.96; Cl, 25.33. Found: C, 43.35; H, 7.09; Cl, 25.16.

$[(BuSi_2Cp)TiCl_2]_2(\mu\text{-}O)$ (7). This compound was prepared from $(BuSi_2Cp)TiCl_3$ in a manner analogous to that described to prepare **2** and isolated as dark yellow flakes: 85% yield; mp 179 °C. ^1H NMR: δ 7.34 (s, 2 H, C_5H_2), 1.25 (s, 9 H, CCH_3), 0.45 (s, 18 H, $SiCH_3$). IR (cm^{-1}): 2963 m, 2901 w, 1250 s, 981 m, 861 m, 841 vs, 759 s, 731 vs, 670 m, 638 s, 454 m, 400 m. EI MS (*m/e*, relative intensity): 784 (M^+, 4%), 769 ($M^+ - CH_3$, 40%). Anal. Calcd for $C_{30}H_{58}Cl_4OSi_4Ti_2$: C, 43.92; H, 7.45; Cl, 18.07. Found: C, 45.95; H, 7.58; Cl, 17.86.

$[(BuSi_2Cp)TiCl]_2(\mu\text{-}O)_2$ (8). This compound was synthesized by using $(BuSi_2Cp)TiCl_3$ following an analogous procedure as described for the preparation of **5** and obtained as pale yellow crystals: yield 75%; mp 238 °C. ^1H NMR: δ 7.35 (s, 2 H, C_5H_2), 1.26 (s, 9 H, CCH_3), 0.47 (s, 18 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR: δ 151.94, 139.19, 129.13 (ring-C), 33.45 ($\mathit{C}H_3$), 30.76 ($C\mathit{C}H_3$), 1.20 ($SiCH_3$). IR (cm^{-1}): 2960 m, 2904 w, 1250 s, 877 ms, 850 vs, 759 ms, 668 vs, 638 s, 450 m. EI MS (*m/e*, relative intensity): 728 (M^+, 12%), 713 ($M^+ - CH_3$, 100%). Anal. Calcd for $C_{30}H_{58}Cl_2O_2Si_4Ti_2$: C, 49.37; H, 8.01; Cl, 9.72. Found: C, 49.21; H, 7.96; Cl, 9.41.

X-ray Structure Determination. Crystal data for $[(Si_3Cp)TiCl]_2(\mu\text{-}O)_2$ (**5**) are listed in Table I. The compound, obtained as lemon yellow crystals by slow cooling of *n*-pentane solution, crystallizes in the monoclinic space group $C2/c$ (No. 15; systematic absences hkl ($h + k = 2n + 1$), $h0l$ ($l = 2n + 1$; $h = 2n + 1$), $0k0$ ($k = 2n + 1$)). Cell constants were obtained from least-squares refinement by using a set of 42 reflections in the range $60.30 < 2\theta < 84.90$. Data collection was performed on an Enraf-Nonius CAD-4 four-circle diffractometer with graphite-monochromated Cu Kα radiation. An ω-scan mode in the range $2.0° < \theta < 60.0°$ was chosen with variable scan width $(1.10 + 0.30 \tan \theta)° \pm 25\%$ before and after each reflection for background determination. From 3475 measured reflections, 73 reflections with negative intensity were rejected. After merging, 3062 independent reflections with $I > 0.01$ were used and 298 parameters were refined by full-matrix least-squares. The intensity data were corrected for Lorentz and polarization effects and for a small linear decay ($16.2h = -3.3\%$). An absorption correction was applied. The structure was solved by using direct methods techniques and difference Fourier synthesis and refined with anisotropic thermal parameters for the non-hydrogen atoms. All hydrogen atoms were located and refined isotropically. Refinements converged with unweighted and weighted agreement factors $R(F_o) = 0.043$ and $R_w(F_o) = 0.047$, respectively. The refinement finished with a shift/error ratio of <0.001 in the last cycle, and the residual electron density yielded +0.52 and −0.40 e/Å^3, respectively, near the heavy atom Ti. All calculations were performed on VAX11/730 and VAX8200 computers using the STRUX-II[33] and SDP systems.[34]

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Supplementary Material Available: Listings of final positional parameters, thermal parameters, bond lengths and angles, and selected least-squares planes (and distances of atoms from these planes), stereodrawings of the molecule and unit cell, and a table of all crystal data and refinement parameters (18 pages); a listing of observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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