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Monocyclopentadienyl-Type Titanium Complexes with the $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]^{2-}$ Ligand. X-ray Crystal Structure of $[(TiCl)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]_2(\mu_2\text{-}O)_2$. The First Example of a Nonplanar "Ti_4O_4" Core

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Summary: The thallium compound $[Tl_2\{(C_5H_4)_2SiMe_2\}]$ *(1) was prepared by reaction of* $(C_5H_5)_2SiMe_2$ *with thallium ethoxide in diethyl ether at −78 °C. Reaction of 1 with 2 equiv of* $TiCl_4$ *produces the dinuclear compound* $[(TiCl_3)_2\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$ *(2). Controlled hydrolysis of 2 gives the dinuclear μ-oxo compound* $[(TiCl_2)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$ *(3). Complex 3 reacts with* $AlEtCl_2$ *to regenerate quantitatively complex 2. When 2 or 3 is treated with water in acetonitrile, the tetranuclear μ-oxo complex* $[(TiCl)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]_2(\mu_2\text{-}O)_2$ *(4) is obtained. The crystal and molecular structure of 4 has been determined by X-ray diffraction methods. 4 crystallizes in a triclinic space group* $P\bar{1}$ *with* $a = 9.508$ *(1) Å,* $b = 9.789$ *(1) Å,* $c = 9.808$ *(1) Å,* $\alpha = 116.09$ *(1)°,* $\beta = 94.62$ *(1)°,* $\gamma = 97.97$ *(1)°,* $V = 801.5$ *Å*^{3}*,* $Z = 1$*, and* $d_{calc} = 1.595$ *g cm*$^{-3}$*. The structure can be formally regarded as the dimer of the hypothetical dinuclear fragment* $[(TiCl)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}(\text{-}O)]$ *with a nonplanar "*Ti_4O_4*" core, not previously reported for other similar* Ti_4O_x *systems.*

One of the most important aspects in the organometallic chemistry of group 4 elements which dictates the general behavior of these metals, is their strongly oxophilic character. Thus, a large number of oxo derivatives containing M_nO_m (M = Ti, Zr) cores of different types are known. An extensive chemistry has been developed for monocyclopentadienyl oxo complexes of titanium in which oxygen acts as a double bridging ligand and different types of structural dispositions have been observed.[1,2]

Hydrolysis of the corresponding monocyclopentadienyltitanium trihalides, appears to be the generally applicable preparative method for such monocyclopentadienyl oxo derivatives. However, all of the monocyclopentadienyl oxo derivatives of titanium known so far contain independent cyclopentadienyl rings. Group 4 complexes containing cyclopentadienyl ligands bridged by an interannular group are of interest. Their main characteristics are (a) restricted mobility of the cyclopentadienyl rings, which hinders their participation in reactions involving ring C–H activation, thus modifying their chemical behavior, and (b) special stability of low oxidation states when the two rings are connected by a dimethylsilyl group. We have recently reported[3] the first dimeric monocyclopentadienyl-type μ-oxo derivative of titanium in which the two cyclopentadienyl rings are connected directly by a C–C bond (fulvalene group). Herein, we report the synthesis of $[Tl_2\{(C_5H_4)_2SiMe_2\}]$ as a reagent for the preparation of the new dinuclear monocyclopentadienyl complexes $[(TiCl_3)_2\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$ and $[(TiCl_2)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$ and the tetranuclear monocyclopentadienyl derivative $[(TiCl)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]_2(\mu_2\text{-}O)_2$. Their characterization was carried out by analysis and spectroscopic methods.

The thallium compound $[Tl_2\{(C_5H_4)_2SiMe_2\}]$ (1) was prepared in 98% yield by reaction of $(\eta^1\text{-}C_5H_5)_2SiMe_2$ with thallium ethoxide in diethyl ether at −78 °C. It was isolated as an insoluble yellow solid. Addition of 1 to a solution of $TiCl_4$, in dry toluene, gives the dinuclear complex $[(TiCl_3)_2\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$ (2) (Scheme I).

When rigorously anhydrous conditions are not observed, 2 is contaminated with variable amounts of the dinuclear μ-oxo compound $[(TiCl_2)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$ (3). This compound was obtained pure by controlled hydrolysis of 2 with a stoichiometric amount of water. Complex 2 is extremely moisture sensitive, so its manipulation under anhydrous conditions is strictly required to avoid the formation of 3, from which it is difficult to separate.

When 3 or a mixture of 2 and 3 is treated with a toluene solution of $AlEtCl_2$, pure 2 is produced. This behavior is analogous to that observed for similar titanium complexes.[3] Addition of the stoichiometric amount of water to an acetonitrile solution of 3 leads to the tetranuclear μ-oxo complex 4, which precipitates slowly as a microcrystalline yellow solid.

Complexes 2 and 3 are insoluble in alkanes and poorly soluble in toluene, benzene, chloroform, and dichloromethane. Complex 4 is insoluble in alkanes and aromatic solvents and partially soluble in chloroform and dichloromethane. All the new complexes were characterized by elemental analysis, IR and ^{1}H NMR spectroscopy (^{13}C NMR spectra were not recorded due to their poor solubility), and mass spectrometry. All analytical and spectroscopic data support the structures depicted for 2–4. The crystal structure of 4 has also been determined by X-ray diffraction methods.

The value of $\Delta\delta$ [$\Delta\delta = \delta_d - \delta_p$ (δ_d = distal protons; δ_p = proximal protons)] is 0.28 for 2; 0.33 for 3, for which the distal and proximal protons remain magnetically equivalent; and 0.23 for 4, for which the distal and proximal protons are no longer magnetically equivalent and the $\Delta\delta$ value is calculated from the mean chemical shifts of the corresponding protons signals. These values are indicative

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[1] (a) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* 1988, *28*, 339. (b) Bottomley, F. *Polyhedron* 1992, *11*, 1707.

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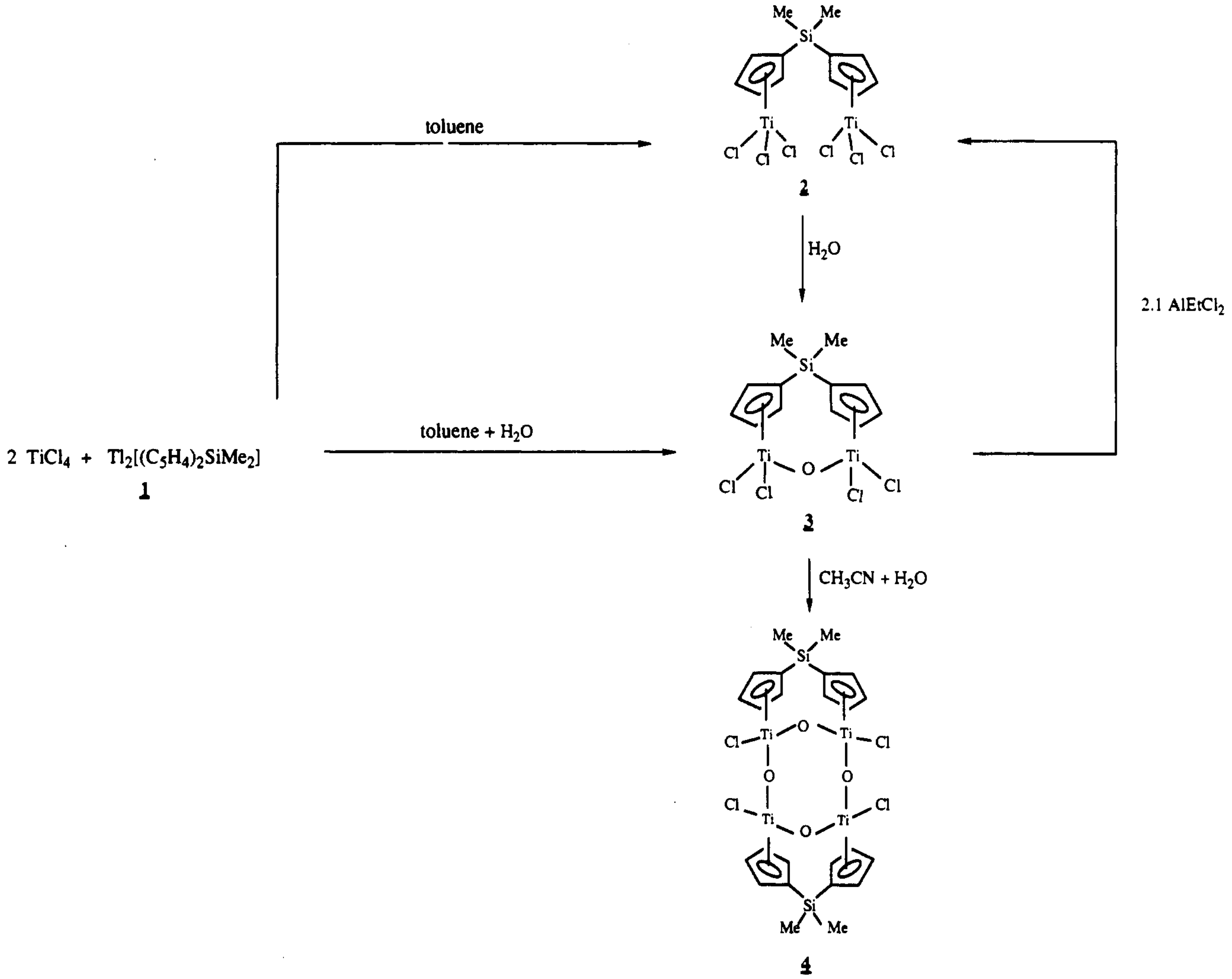
[3] Alvaro, L. M.; Cuenca, T.; Flores, J. C.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* 1992, *11*, 3301.

0276-7333/93/2312-0944$04.00/0

Scheme I



of a chelating mode of coordination for the $[(C_5H_4)_2SiMe_2]^{2-}$ ligand.[4]

Elemental analysis and the EI mass spectrum for 4 are clearly in agreement with its given formulation. One strong broad band for ν(Ti–O–Ti) due to the vibration centered at approximately 800 cm^{-1} in the IR spectrum is indicative of the presence of the μ-oxo bridge linking two titanium fragments. However, it is very difficult to differentiate between linear and nonlinear Ti–O–Ti bridges.

An ORTEP view of the molecular structure of 4 with atom labeling scheme is shown in Figure 1. The unit cell contains only one molecule with two equivalent fragments related by the center of symmetry.

The molecular structure confirms that 4 can be formally regarded as the dimer of the hypothetical dinuclear fragment $[(TiCl)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}(-O)]$, affording a tetranuclear derivative showing a nonplanar "Ti_4O_4" core with oxygen bridges between the titanium atoms. This result markedly differs from that found by Okuda[2b] for the hydrolysis of $[TiCl_3\{\eta^5\text{-}(Me_3Si)_3C_5H_2\}]$ which affords the dinuclear derivative with a planar "$Ti_2(\mu\text{-}O)_2$" core, although the bridging disposition of the ligand $[(C_5H_4)_2SiMe_2]^{2-}$ in our compound could be a favorable condition for the planar conformation of the "$Ti_2(\mu\text{-}O)_2$" framework. If the ring centroids are considered as

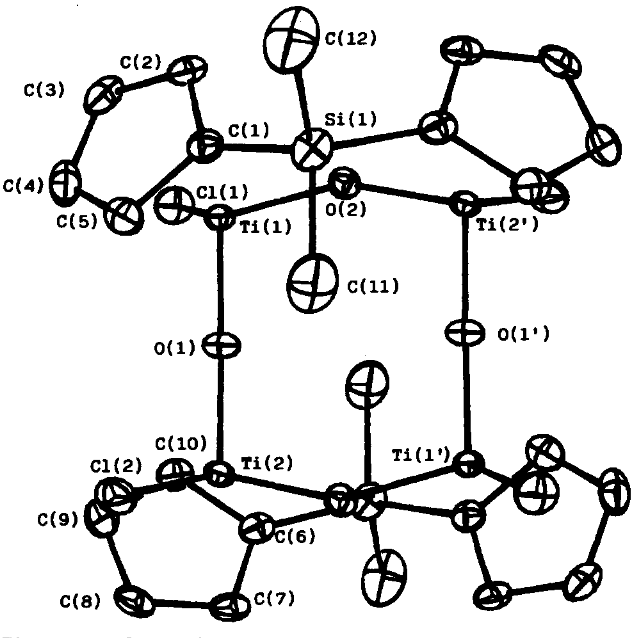


Figure 1. ORTEP view of $[(TiCl)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]_2(\mu\text{-}O)_2$ with atom labeling scheme (30% probability ellipsoids).

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[4] (a) Reddy, K. P.; Petersen, J. L. *Organometallics* **1989**, *8*, 2107. (b) Gómez, R.; Cuenca, T.; Royo, P.; Herrmann, W. A.; Herdtweck, E. *J. Organomet. Chem.* **1990**, *382*, 103. (c) Gómez, R.; Cuenca, T.; Royo, P.; Hovestreydt, E. *Organometallics* **1991**, *10*, 2516.

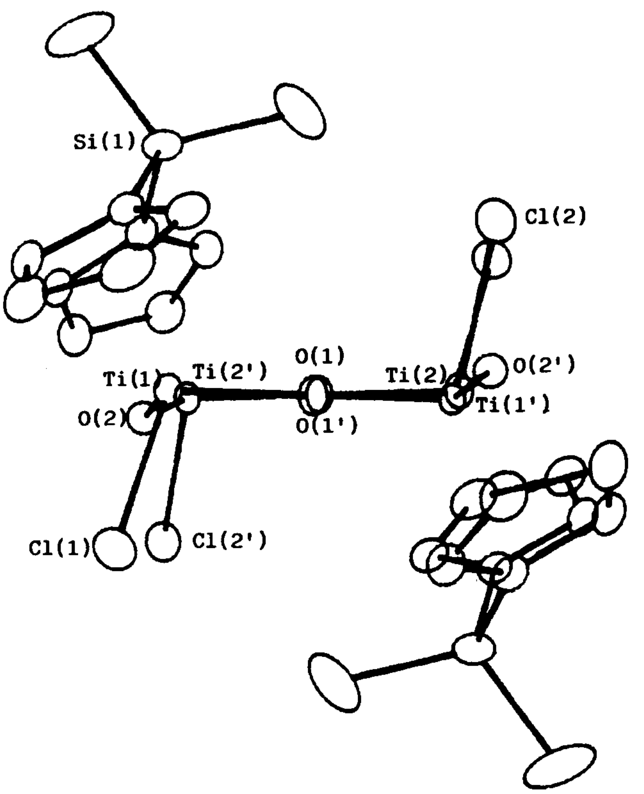

Figure 2. Molecular structure of $[(TiCl)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]_2(\mu\text{-}O)_2$ showing the nonplanar conformation for the "Ti_4O_4" core.

coordination positions, each titanium is tetrahedrally coordinated to two oxygen atoms, one chlorine atom, and one cyclopentadienyl ring, with angles between 102 and 115°. The Ti_4O_4 ring shows a "chair conformation" that has not been reported previously for similar Ti_4O_x systems. These generally exhibit a planar disposition when $x = 4$ or a tetrahedral disposition when $x = 6$, as observed for $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu\text{-}O)_6]$.[5,6] Most planar cyclic tetramers show all equal Ti–O–Ti bond angles[2a,7] (approximately 160°) but two different types of angles have been found for $[\{Ti(\eta^5\text{-}C_5HMe_4)Br(\mu\text{-}O)\}_4]$[8] (149.3 and 175.7°) and $[\{Ti(\eta^5\text{-}C_5H_4SiMe_3)(NCS)(\mu\text{-}O)\}_4]$[9] (148.8 and 171.2°), always containing a C_2 axis perpendicular to the planar Ti_4O_4 core and an alternating disposition of the cyclopentadienyl rings with respect to the plane.

The "chair conformation" of 4 also shows a C_2 axis passing through the two linear O(1) atoms and a plane of symmetry containing the two Si, O(2), and methylsilyl carbon atoms. This singular arrangement is due to the presence of the bridging *ansa*-bis(cyclopentadienyl) ligands that brings the two bridged titanium atoms near, folding the oxygen bridge to an angle of 144.5 (1)°, which is the closest value observed for this type of titanium–oxygen ring, with the exception of the tetrahedral Ti_4O_6[5,6] complex (122°) and the μ-oxo trimer $[\{Ti(\eta^5\text{-}C_5Me_5)(CH_3)(\mu\text{-}O)\}_3]$.[10] However, the oxygen atom which is not influenced by the *ansa*-cyclopentadienyl bridge shows an almost linear disposition with an angle of 176.2 (1)°. Conversely, all the titanium–oxygen distances are similar, between 1.803 and 1.811 Å, being indicative of a partial double bond which seems to be independent of the angle, in contrast to previous proposals.[11] The two O(2) atoms are located above and below at +0.315 (2) and −0.315 (2) Å with respect to the plane defined by the Ti(1), Ti(2), and O(1) atoms. The two chlorine atoms Cl(1) and Cl(2) are also located above and below with respect to this plane at +1.927 (1) and −2.022 (1) Å, instead of the usual alternating arrangement observed for similar complexes.[2a] The Ti–Cl distances, 2.2795 (8) and 2.2779 (7) Å, are in the same range as that previously reported.[7b] The rotation of the two Cp rings of the ansa ligand about the C(1)–Si(1) and C(6′)–Si(1) axes, could be evaluated by the different distances of the proximal carbon atoms to the pseudo symmetry plane defined by Si(1)–C(11)–C(12), these distances being for C(2) 1.884 (3) Å, for C(5) 2.698 (3) Å; for C(7′) 1.844 (3) Å, and for C(10′) 2.680 (3) Å.

Experimental Section

All manipulations were performed under an inert atmosphere (dinitrogen or argon) using Schlenk and high vacuum line techniques or a Model HE-63-P glovebox. Hexane was distilled from sodium/potassium amalgam, toluene from sodium, diethyl ether from sodium benzophenone ketyl and acetonitrile from CaH_2. $(C_5H_5)_2SiMe_2$[12] was prepared by the reported method. $AlEtCl_2$ (Aldrich) and TlOEt (Aldrich) were purchased and used without further purification. $TiCl_4$ (Aldrich) was distilled before use. NMR spectra were recorded on Varian FT-80A and Varian Unity FT-300 instruments. ^1H chemical shifts are referenced to Me_4Si. Mass spectra were recorded on a Hewlett Packard 5890 spectrometer. Elemental C, H analyses were carried out with a Perkin-Elmer 240B microanalyzer.

Synthesis of $[Tl_2\{(C_5H_4)_2SiMe_2\}]$ (1). To a stirred solution of 0.32 g (1.7 mmol) of $(C_5H_5)_2SiMe_2$ in 30 mL of diethyl ether at −78 °C was added dropwise a solution containing 0.24 mL (3.4 mmol) of TlOEt in 20 mL of diethyl ether. A pale precipitate was formed immediately. The reaction mixture was warmed to room temperature and stirred for 3 h, while the color of the precipitate changed to lemon-yellow. The solvent was evaporated under vacuum and the resulting solid washed several times with diethyl ether and dried under vacuum. A pale yellow powder (1.0 g) identified as 1 was obtained (98% yield).

Anal. Calcd for $C_{12}H_{14}SiTl_2$: C, 24.22; H, 2.37. Found: C, 24.22: H, 2.27. EI/MS (70 eV): $m/z = 596$ [M^+].

Synthesis of $[(TiCl_3)_2\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$ (2). A solution containing 1.05 mL (9.6 mmol) of $TiCl_4$ in 75 mL of toluene and cooled at −78 °C was rapidly added to a suspension of 2.76 g (4.6 mmol) of freshly prepared $[Tl_2\{(C_5H_4)_2SiMe_2\}]$ in 75 mL of toluene at −78 °C. The reaction mixture was warmed to room temperature and stirred for 15 h. After filtration, a red-brown solution was obtained which was evaporated to dryness to give a dark-red oil. This oil was washed with several 20-mL portions of cold hexane to yield a red solid. Subsequent recrystallization from toluene/hexane at −40 °C gave 1.19 g (50 % yield) of microcrystalline 2.

Anal. Calcd for $C_{12}H_{14}SiTi_2Cl_6$: C, 29.40; H, 2.85. Found: C, 29,37; H, 3.02. ^1H NMR: (300 MHz, C_6D_6, 25 °C) δ 0.49 (s, 6 H, CH_3–Si), 6.13 (t, $J = 2.4$ Hz, 4 H, C_5H_4), 6.41 (t, $J = 2.4$ Hz, 4

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Table I. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B* (Å^2)[a]
Ti(1)	0.63400 (4)	0.08857 (4)	0.33809 (4)	1.940 (8)
Ti(2)	0.26254 (4)	0.01843 (5)	0.38428 (4)	2.015 (8)
Cl(1)	0.63902 (8)	−0.08376 (8)	0.09030 (7)	3.62 (2)
Cl(2)	0.21330 (8)	0.26118 (7)	0.46770 (8)	3.69 (2)
Si(1)	0.7496 (1)	0.39524 (8)	0.74012 (8)	3.17 (2)
O(1)	0.4482 (2)	0.0466 (2)	0.3579 (2)	2.71 (4)
O(2)	0.7285 (2)	0.0093 (2)	0.4455 (2)	2.41 (4)
C(1)	0.7257 (3)	0.3428 (3)	0.5309 (3)	2.53 (5)
C(2)	0.8303 (3)	0.3029 (3)	0.4300 (3)	2.93 (6)
C(3)	0.7705 (4)	0.2789 (3)	0.2845 (3)	3.72 (6)
C(4)	0.6292 (4)	0.3051 (3)	0.2911 (3)	3.99 (7)
C(5)	0.6014 (3)	0.3457 (3)	0.4409 (3)	3.33 (6)
C(6)	0.1750 (3)	−0.2448 (3)	0.2239 (3)	2.73 (5)
C(7)	0.0531 (3)	−0.1791 (3)	0.2765 (3)	3.08 (6)
C(8)	0.0334 (3)	−0.0737 (3)	0.2208 (3)	3.53 (7)
C(9)	0.1412 (3)	−0.0713 (3)	0.1301 (3)	3.60 (6)
C(10)	0.2261 (3)	−0.1772 (3)	0.1294 (3)	3.04 (6)
C(11)	0.5710 (4)	0.4075 (4)	0.8047 (4)	6.07 (9)
C(12)	0.8793 (6)	0.5812 (4)	0.8425 (4)	7.0 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$.

Table II. Selected Bond Distances (Å) and Bond Angles (deg)

Ti(1)–Cl(1)	2.2779 (7)	Ti(2)–Cl(2)	2.2795 (8)
Ti(1)–O(1)	1.803 (2)	Ti(2)–O(1)	1.806 (2)
Ti(1)–O(2)	1.811 (2)	Ti(2)–O(2)	1.803 (2)
Ti(1)–C(1)	2.349 (2)	Ti(2)–C(6)	2.331 (2)
Ti(1)–C(2)	2.382 (2)	Ti(2)–C(7)	2.369 (2)
Ti(1)–C(3)	2.394 (3)	Ti(2)–C(8)	2.398 (3)
Ti(1)–C(4)	2.365 (3)	Ti(2)–C(9)	2.376 (2)
Ti(1)–C(5)	2.342 (2)	Ti(2)–C(10)	2.346 (2)
Si(1)–C(1)	1.868 (2)	Si(1)–C(6)	1.876 (3)
Si(1)–C(11)	1.861 (4)	Si(1)–C(12)	1.847 (4)
Ti(1)–Ti(2)	3.44 (3)	Ti(1)–Ti(2′)	3.61 (3)
Cl(1)–Ti(1)–O(1)	102.89 (5)	Cl(2)–Ti(2)–O(1)	102.65 (6)
Cl(1)–Ti(1)–O(2)	102.15 (5)	Cl(2)–Ti(2)–O(2)	103.43 (6)
O(1)–Ti(1)–O(2)	104.36 (9)	O(1)–Ti(2)–O(2)	103.55 (9)
Ti(1)–O(1)–Ti(2)	176.2 (1)	Ti(1)–O(2)–Ti(2)	144.5 (1)

H, C_5H_4); (300 MHz, $CDCl_3$, 25 °C) δ 0.80 (s, 6 H, CH_3–Si), 7.09 (br, 4 H, C_5H_4), 7.23 (br, 4 H, C_5H_4).

Compound **2** was always contaminated with **3** (as identified in the ^1H NMR spectrum) when rigorous exclusion of moisture during the reaction was not maintained.

Synthesis of [$(TiCl_2)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}$] (3). To a suspension of 2.76 g (4.6 mmol) of freshly prepared [$Tl_2\{(C_5H_4)_2SiMe_2\}$] in 75 mL of toluene cooled at −78 °C was added rapidly with vigorous stirring a solution of 1.05 mL (9.6 mmol) of $TiCl_4$ in 75 mL of toluene. The reaction mixture was warmed to room temperature and stirred for 25 h. After filtration, a dark-red solution was obtained. Deoxygenated and distilled water (83 μL, 4.6 mmol) was added by syringe to this solution at room temperature, and the mixture obtained was stirred for 20 h. After filtration, the solution was evaporated to dryness to give a dark-red oil, which was washed several times with small portions of cold hexane, to give a pale green powder. Recrystallization from toluene/hexane at −30 °C yielded **3** as a microcrystalline solid (1 g, 49% yield).

Anal. Calcd for $C_{12}H_{14}SiTi_2Cl_4O$: C, 32.76; H, 3.21. Found: C, 33.00; H, 3.31. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.13 (s, 6 H, CH_3–Si), 6.27 (t, *J* = 2.4 Hz, 4 H, C_5H_4), 6.60 (t, *J* = 2.4 Hz, 4 H, C_5H_4). EI/MS (70 eV): *m/z* = 438 [M^+].

Reaction of [$(TiCl_2)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}$] (3) with $AlEtCl_2$. To a solution of 1.07 g (2.4 mmol) of **3** in 40 mL of toluene at −78 °C was added with stirring 2.8 mL (5.1 mmol) of a 1.8 M solution of $AlEtCl_2$ in toluene. The solution immediately turned an intense red. It was then warmed to room temperature and stirred 30 min. After filtration, the solution was evaporated to give a dark-red oil which was washed with 20-mL portions of cold hexane. Recrystallization from toluene/hexane at −25 °C gave pure **2** as a microcrystalline solid (1 g, 83 % yield). In a similar manner, addition of a toluene solution of $AlEtCl_2$ to a mixture of **2** and **3**, obtained when strictly anhydrous conditions for the reaction between $TiCl_4$ and Tl[$(C_5H_4)_2SiMe_2$] were not employed (the **2**/**3** ratio can be deduced from the ^1H NMR spectrum) and when the same procedure described above was followed, gave pure samples of **2**.

Table III. Crystal Data, Experimental Data, and Structure Refinement Procedures for Compound 4

formula	$Ti_4O_4Cl_4Si_2C_{24}H_{28}$
cryst habit	prismatic
color	pale yellow
cryst size	0.2 × 0.25 × 0.15
symmetry	triclinic, $P\bar{1}$
unit cell determination	least squares fit from 25 reflns θ < 12°
unit cell dimensions	
a, *b*, *c*, Å	9.508 (1), 9.789 (1), 9.808 (1)
α, β, γ, deg	116.09 (1), 94.62 (1), 97.97 (1)
packing	
V, Å^3; *Z*	801.5; 1
D_{cal}, g cm^{-3}	1.595
M_w	771.07
F(000)	388
μ, cm^{-1}	13.90
technique	Enraf-Nonius CAD4, four-circle diffractometer; bisecting geometry, graphite-oriented monochromator; Mo Kα, W/θ scans; θ_{max} = 30°
no. of reflns	
measured	4930
independent	4420
observed	2923 [2σ(I) criterium]
range of *hkl*	−13 to +13; −13 to +13; 0 to 13
std reflns	2 reflections every 120 min, no variation
R	0.032
R_w	0.039
goodness of fit indicator	1.21
largest parameter shift/error	0.03
max peak in final diff map, e Å^{-3}	0.50
min peak in final diff map, e Å^{-3}	0.26

Synthesis of [$\{(TiCl)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}\}_2(\mu\text{-}O)_2$] (4). A 63-μL (3.5-mmol) aliquot of deoxygenated and distilled water was added by syringe to a stirred solution of 1.56 g (3.5 mmol) of [$(TiCl_2)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}$] in 50 mL of acetonitrile. The reaction mixture was maintained at room temperature for 3 h. A yellow microcrystalline solid was slowly formed. The volume was reduced to 10 mL and the resulting solution cooled to 0 °C to give yellow crystals. Subsequent recrystallization from chloroform at −40 °C yielded **4** as a crystalline solid (1 g, 73% yield).

Anal. Calcd for $C_{12}H_{14}SiTi_2Cl_2O_2$: C, 37.44; H, 3.67. Found: C, 38.11; H, 3.74. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.52 (s, 3 H, CH_3–Si), 0.61 (s, 3 H, CH_3–Si), 6.68 (m, 2 H, C_5H_4), 6.77 (m, 2 H, C_5H_4), 6.94 (m, 2 H, C_5H_4), 6.98 (m, 2 H, C_5H_4). EI/MS (70 eV): *m/z* = 315 [{M/2} − Cl^+].

X-ray Data Collection and Structural Analysis of 4. A single crystal of **4** suitable for X-ray structural determination was obtained by crystallization of a chloroform solution at −50 °C and sealed in a Lindemann tube under a nitrogen atmosphere. Final atomic coordinates and equivalent isotropic thermal parameters only for independent non-hydrogen atoms are presented in Table I. Selected bond distances and angles are given in Table II.

Crystallographic and experimental details are given in Table III. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by a combination of direct methods and Fourier synthesis and refined (on *F*) by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically.

The hydrogen atoms were found in the Fourier difference map and refined on cycle isotropically for the hydrogen atoms of the methyl groups and with fixed thermal parameters for the hydrogen atoms of the cyclopentadienyl rings. Final values of $R = 0.032$ and $R_w = 0.039$ with $R_w = [\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2]^{1/2}$ and $w = 4F_o^2/[\sigma(F_o)^2]^2$ were obtained. Anomalous dispersion corrections and atomic scattering factors were taken from ref 13. Calculations were performed with the SDP Enraf-Nonius package,[14] MULTAN,[15] and DIRDIF[16] on a Microvax II computer.

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Supplementary Material Available: Tables of hydrogen atom positional and isotropic thermal parameters, non-hydrogen atom anisotropic thermal parameters, and all bond distances and angles for 4 (13 pages). Ordering information is given on any current masthead page.

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