Dinuclear Titanium Metallocene-Type Complexes with the Bridging (Dimethylsilylidene)bis(cyclopentadienyl) Ligand. X-ray Structures of $[\{TiCl_2(\eta^5\text{-}C_5Me_5)\}_2\{\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$ and of $[\{TiCl(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}O)\{\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$

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Treatment of $Tl_2[Me_2Si(C_5H_4)_2]$ with 2 equiv of $Cp'TiCl_3$ ($Cp' = \eta^5\text{-}C_5H_5$; $\eta^5\text{-}C_5Me_5$) affords the corresponding chloro derivatives $[TiCl_2(\eta^5\text{-}C_5H_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**1**) and $[TiCl_2(\eta^5\text{-}C_5Me_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**2**). **1** and **2** are metallocene type dinuclear complexes which contain the bridging (dimethylsilylidene)bis(cyclopentadienyl) ligand. Compounds **1** and **2** react with LiR (R = Me, $CH_2PPh_2{\cdot}TMEDA$) to yield the alkyl complexes $[TiMe_2(\eta^5\text{-}C_5H_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**3**) and $[TiR_2(\eta^5\text{-}C_5Me_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (R = Me (**4**); CH_2PPh_2 (**5**)). Hydrolysis of **1** produces the μ-oxo derivative $[TiCl(\eta^5\text{-}C_5H_5)]_2(\mu\text{-}O)[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**6**). Compound **6** may also be obtained by reduction of **1** with 1 equiv of Na/Hg and subsequent treatment with oxygen. All new compounds were characterized by elemental (C, H) analysis, IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy, and mass spectrometry. Molecular structures of **2** and **6** were determined by single-crystal X-ray diffraction methods. Crystals of **2** are orthorhombic, space group $Pna2_1$ (No. 33) with $Z = 4$ in a unit cell of dimensions $a = 28.32(1)$ Å, $b = 14.023(6)$ Å, and $c = 8.431(5)$ Å. Crystals of **6** are monoclinic, space group $P2_1/n$ (No. 14), with $Z = 4$ in a unit cell of dimensions $a = 7.835(2)$ Å, $b = 18.291(4)$ Å, $c = 15.415(2)$ Å, and $\beta = 96.22(1)°$.

Introduction

The (dimethylsilylidene)bis(cyclopentadienyl) ligand $[Me_2Si(\eta^5\text{-}C_5H_4)_2]^{2-}$ ($DMSCp_2$) is capable of coordination to metallic centers as a chelating (I) or as a bridging group (II) (Figure 1).

The chemistry of mononuclear, type I, compounds with symmetric and asymmetric rings bridged by a SiR_2 fragment and their potential applications as catalysts in stereo- and enantioselective hydrogenation and polymerization of olefins have been extensively studied.[1] Recently we have reported the synthesis of similar halo- and alkyltitanium(IV),[2] -(III),[3] and -(II)[4] derivatives as well as some aspects of their chemical behavior. Dinuclear, type II, compounds are also well represented[5] although they are less well-known for group 4d metals, except for zirconium[6] and some new monocyclopentadienyl titanium derivatives.[7]

For compounds in which the ligand $DMSCp_2$ bonds to the planar $[M_2(\mu\text{-}X)_2]^{4-}$ fragment, Fischer[8] has predicted, from geometrical considerations, which of the two compounds should be favored. Such predictions can be taken into account to evaluate the required distortion of the angles C(Cp)–Si–C(Cp) and Cent–C(Cp)–Si (α and β respectively) for the metal to choose between the chelating or bridging dispositions. We have prepared the first examples of dinuclear metallocene type complexes of titanium with the bridging ligand $DMSCp_2$ and report here our results as well as the crystal structures of two representative complexes.

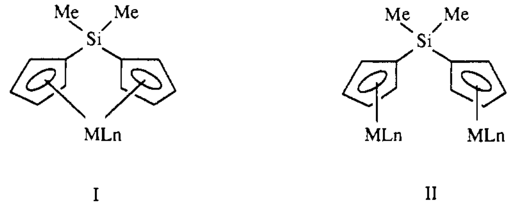

Figure 1. Coordination modes of the (dimethylsilylidene)bis(cyclopentadienyl) ligand.

Results and Discussion

Overnight reaction of $Tl_2[Me_2Si(C_5H_4)_2]$[7] with 2 equiv of $Cp'TiCl_3$ ($Cp' = \eta^5\text{-}C_5H_5$; $\eta^5\text{-}C_5Me_5$) in toluene at room temperature was found to be a suitable method to obtain the chloro derivatives $[TiCl_2(\eta^5\text{-}C_5H_5)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**1**) and $[TiCl_2(\eta^5\text{-}C_5Me_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**2**) in good yields (eq 1).

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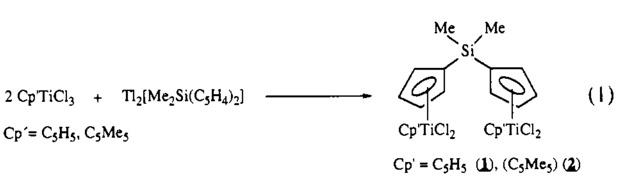
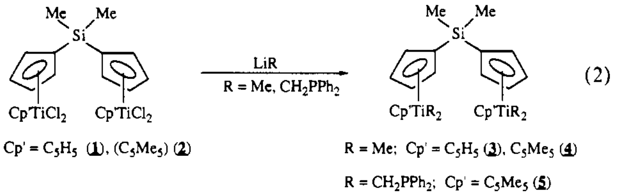
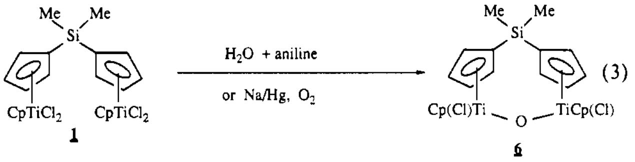


Treatment of **1** and **2** with 4.5 equiv of alkyllithium, LiR (R = Me, CH_2PPh_2), in toluene at low temperature and subsequent warming to room temperature, affords the corresponding tetraalkyl derivatives $[TiMe_2(\eta^5\text{-}C_5H_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**3**), $[TiMe_2(\eta^5\text{-}C_5Me_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**4**), and $[Ti(CH_2PPh_2)_2(\eta^5\text{-}C_5Me_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**5**) with yields between 70 and 75% (eq 2).



$[TiCl(\eta^5\text{-}C_5H_5)]_2(\mu\text{-}O)[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**6**) may be prepared in two ways: (i) by hydrolysis of **1** in the presence of aniline, and (ii) by reduction[9] of **1** with sodium amalgam and subsequent "in situ" treatment of the reaction mixture with oxygen. In both cases compound **6** may be obtained pure from the crude product by recrystallization from toluene/hexane at −30 °C.



All the new isolated compounds are soluble in chlorinated solvents (chloroform, dichloromethane) as well as in aromatic hydrocarbons (benzene, toluene). Their solubilities range in the order: **3**, **4**, **5** > **1**, **2** > **6**. Compound **5** is also slightly soluble in hexane. They are air stable and may be stored for months under dry nitrogen or argon, **3**–**5** being the least stable. A unique behavior is observed for compounds **3** and **4**. When pure, both are yellow solids and remain unchanged when heated or exposed to light. However, when they are handled, either as solids or in solution, a fast blackening often occurs, and unidentified paramagnetic products are obtained.

^1H NMR spectra of compounds **1**–**5** show the expected resonances for the bridging $DMSCp_2$ protons that appear as two sets of pseudotriplets due to an AA'BB' system. In **6** these protons appear as four multiplets corresponding to an ABCD system because substitution of chlorine by the Ti–O–Ti bridge makes the cyclopentadienyl protons unequivalent, although the methyl protons of the silylidene bridging groups remain equivalent. Various spectral aspects may be drawn from the analysis of the ^1H NMR spectra of these compounds. Values of $\Delta\delta = [\delta_d - \delta_p]$, where δ_d and δ_p are the chemical shifts for "distal protons" (BB') and "proximal protons" [AA'], respectively, are 0.25 for compound **1**, 0.91 for **2**, 0.03 for **3**, 0.82 for **4**, 0.54 for **5**, and 0.45 (estimated average from the shifts of the corresponding protons) for **6**. These values are found to be smaller than those observed for complexes containing $DMSCp_2$ as a chelating ligand {$\Delta\delta$ 1.65 for $TiCl_2[Me_2Si(C_5H_4)_2]$,[1d] 1.86 for $TiMe_2[Me_2Si(C_5H_4)_2]$,[2b] and 2.27 for $Ti(CH_2PPh_2)_2[Me_2Si(C_5H_4)_2]$[10]}, which supports the validity of this spectral parameter to distinguish between the bridging or chelating disposition of the $DMSCp_2$ ligand. The other relevant feature is the fact that in the mononuclear complexes $\Delta\delta$ decreases as the steric hindrance around the metallic center is reduced while the opposite is observed for the dinuclear complexes. It is important to note that values for $\Delta\delta$ are relatively smaller for normal cyclopentadienyl dinuclear derivatives than for pentamethylcyclopentadienyl analogues.

A second spectral feature that differentiates the mono- and dinuclear complexes is related to the chemical shifts observed for methyl protons of the bridging silyl groups in the $DMSCp_2$ ligand. In mononuclear complexes (chelating ligand), these protons generate signals at higher fields (δ −0.01 to 0.00) than in dinuclear complexes (bridging ligand) (δ 0.16 to 1.44). This effect may be attributed to the greater rigidity in the mononuclear complexes and therefore to a more efficient shielding of these protons by the conjugated π system in the neighboring rings. The lower rigidity in the dinuclear complexes favors the rotation around the Si–C_{ipso}(Cp) bond, thus reducing the shielding effect of the π system (confirmed by structure of **2**, *vide infra*).

The methylene protons of the (diphenylphosphino)methyl group in compound **5** exhibit a diastereotopic behavior (ABX system). The ^1H NMR spectrum shows two sets of signals at δ 1.45 and δ 0.58 (similar to those observed for the mononuclear complex and other analogues[11]). The {^1H, ^1H} NMR COSY 2D spectrum clearly shows the correlation between these methylene protons.

The ^{13}C NMR spectra show the ring carbon atoms of the $DMSCp_2$ ligand as three signals assigned to carbons C_{ipso}, $C_{2,5}$ and $C_{3,4}$,[12] the first being of lowest intensity (not observed in some compounds). Again an important difference is found between mononuclear complexes with chelating $DMSCp_2$ ligand and dinuclear complexes with the bridging ligand. The C_{ipso} signal appears, in the mononuclear derivatives at higher fields than the other two ($C_{2,5}$ and $C_{3,4}$) whereas in the dinuclear derivatives the reverse is true.

The ^{31}P NMR (C_6D_6) of compound **5** shows a singlet at δ 9.91 as expected for a noncoordinated phosphorus atom.

The mass spectra of all compounds are in agreement with their dinuclear nature. The infrared spectrum of compound **6** shows the $\nu_{Ti-O-Ti}$ absorption band at 725 cm^{-1}.

Crystal Structures of [{TiCl$_2$(η^5-C$_5$Me$_5$)}$_2${μ-η^5-η^5-(C$_4$H$_4$)$_2$SiMe$_2$}] (2) and of [{TiCl(η^5-C$_5$H$_5$)}$_2$(μ-O){μ-η^5-η^5-C$_5$H$_4$)$_2$SiMe$_2$}] (6). An Ortep view of the molecular structure of compound **2** with the atomic labelling scheme is shown in Figure 2. Final atomic coordinates and equivalent isotropic thermal parameters are presented in Table I. Selected bond distances and angles are given in Table II.

The molecular structure of **2** shows a dinuclear compound with two Cp^*TiCl_2 ($Cp^* = C_5Me_5$) units bound by a $DMSCp_2$ bridging ligand.

Each metallic center shows a metallocene type pseudotetrahedral geometry assuming that the ring centroids occupy a unique coordination position, comparable to the structures for Cp_2TiCl_2[13] and $CpCp^*TiCl_2$.[14] The angles are in agreement with those expected for this coordination, except the Cl(3)–Ti(2)–Cl(4) [91.7(3)°] angle, which is slightly closer than those observed for mononuclear metallocenes (94–100°).

The angles between the planes of the rings of the bridging ligand and the Cp* on Ti(1) and Ti(2) of 58 and 52°, respectively, are similar to those found for other metallocene type structures. The chlorine atoms are located exactly on the bisecting planes, and the Cp (bridge) and Cp* are equidistant from these planes,

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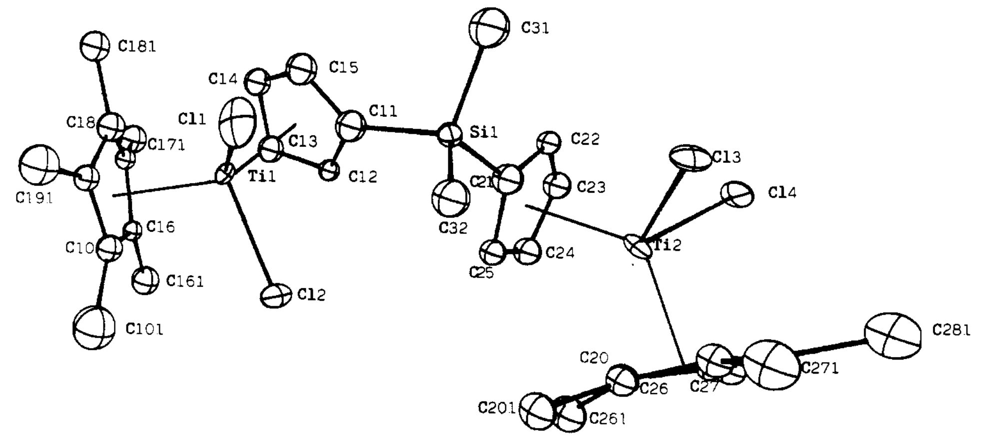

Figure 2. Ortep view of molecular structure of compound **2** with the atomic labeling scheme

Table I. Positional Parameters for Compound **2** and Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2
Ti(1)	0.2989(1)	0.0868(4)	–0.306	3.4(1)
Ti(2)	0.4917(1)	–0.2555(4)	–0.2001(6)	3.2(1)
Cl(1)	0.2538(2)	–0.0281(6)	–0.172(1)	7.3(2)
Cl(2)	0.3271(3)	–0.0114(6)	–0.510(1)	7.5(2)
Cl(3)	0.4410(2)	–0.3170(5)	–0.0091(9)	5.1(2)
Cl(4)	0.5584(2)	–0.2903(5)	–0.0432(8)	5.0(2)
Si(1)	0.3799(3)	–0.1059(6)	–0.0922(9)	4.2(2)
C(11)	0.3617(9)	0.017(2)	–0.135(3)	5.9(8)*
C(12)	0.3832(7)	0.079(2)	–0.254(3)	7.8(6)*
C(13)	0.3661(9)	0.173(2)	–0.254(3)	4.6(7)*
C(14)	0.3362(9)	0.175(2)	–0.107(3)	5.5(7)*
C(15)	0.3354(9)	0.088(2)	–0.049(3)	5.5(7)*
C(16)	0.2776(7)	0.198(2)	–0.510(3)	3.2(6)*
C(17)	0.2737(8)	0.256(2)	–0.367(3)	3.1(6)*
C(18)	0.2400(8)	0.195(2)	–0.285(3)	4.4(7)*
C(19)	0.2177(8)	0.140(2)	–0.382(3)	3.7(7)*
C(10)	0.2429(7)	0.125(2)	–0.516(3)	2.8(6)*
C(21)	0.4422(8)	–0.116(2)	–0.151(3)	4.5(7)*
C(22)	0.4834(8)	–0.104(2)	–0.054(3)	4.0(6)*
C(23)	0.5241(9)	–0.097(2)	–0.143(3)	5.1(7)*
C(24)	0.5112(8)	–0.101(2)	–0.308(4)	5.3(7)*
C(25)	0.4608(8)	–0.111(2)	–0.314(4)	4.2(6)*
C(26)	0.5027(8)	–0.290(2)	–0.474(3)	4.3(7)*
C(27)	0.5335(8)	–0.348(2)	–0.392(3)	3.1(6)
C(28)	0.5089(7)	–0.419(2)	–0.309(3)	3.8(6)
C(29)	0.4615(8)	–0.395(2)	–0.330(3)	4.3(6)*
C(20)	0.4556(8)	–0.323(2)	–0.435(3)	3.8(6)*
C(31)	0.377(1)	–0.112(2)	0.125(4)	7.7(9)*
C(32)	0.3416(9)	–0.193(2)	–0.194(4)	5.8(7)*
C(161)	0.310(1)	0.226(2)	–0.650(3)	7.0(9)*
C(171)	0.2988(9)	0.339(2)	–0.334(4)	6.0(8)*
C(181)	0.224(1)	0.240(2)	–0.125(4)	7.3(8)*
C(191)	0.174(1)	0.075(2)	–0.341(4)	7.1(9)*
C(101)	0.229(1)	0.067(2)	–0.654(4)	8.0(1)*
C(261)	0.514(1)	–0.229(2)	–0.614(4)	7.0(8)*
C(271)	0.5871(9)	–0.339(2)	–0.413(3)	5.6(8)*
C(281)	0.530(1)	–0.494(2)	–0.200(4)	7.3(9)*
C(291)	0.422(1)	–0.464(2)	0.277(4)	6.7(9)*
C(201)	0.4111(9)	–0.291(2)	–0.520(4)	5.8(8)*

[a] Starred values denote atoms that were refined isotropically. Values for 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) for Compound **2**[a]

Ti(2)–Cl(1)	2.345(9)	Ti(2)–Cl(3)	2.324(9)
Ti(1)–Cl(2)	2.348(9)	Ti(2)–Cl(4)	2.357(8)
Ti(1)–Cp(11)	2.057	Ti(2)–Cp(21)	2.110
Ti(1)–Cp(12)	2.124	Ti(2)–Cp(22)	2.111
Si(1)–C(11)	1.84(3)	Si(1)–C(21)	1.84(3)
Si(1)–C(31)	1.84(3)	Si(1)–C(32)	1.85(3)
Cl(1)–Ti(1)–Cl(2)	97.8(3)	Cl(3)–Ti(2)–Cl(4)	91.7(3)
Cl(1)–Ti(1)–Cp(11)	103	Cl(3)–Ti(2)–Cp(21)	107
Cl(1)–Ti(1)–Cp(12)	106	Cl(3)–Ti(2)–Cp(22)	106
Cl(2)–Ti(1)–Cp(11)	104	Cl(4)–Ti(2)–Cp(21)	106
Cl(2)–Ti(1)–Cp(12)	106	Cl(4)–Ti(2)–Cp(22)	106
Cp(11)–Ti(1)–Cp(12)	132	Cp(21)–Ti(2)–Cp(22)	133

[a] Cp(11) is the centroid of C11-C15; Cp(12) is the centroid of C16-C10; Cp(21) is the centroid of C21-C25; Cp(22) is the cent5roid of C26-C20.

placing their centroids at 1.91 and 1.95 Å from Ti(1) and Ti(2), respectively, further supporting the metallocene disposition.

Due to the bulkiness of the permethylated rings, the cyclopentadienyl rings of the bridging DMSCp$_2$ ligand are rotated around the Si–C(bridge-head) bond. In this way the titanium atoms are far enough from each other (7.33 Å) to prevent any interannular repulsions. In order to achieve the maximum distance between the two titanium atoms, the ligand loses its symmetry by rotating the rings in opposite directions around the Si–C(bridgehead) bond. Thus, the bridging ligand places the two titanium atoms on the same side of the plane defined by two bridgehead carbon atoms, C(11)–Si–(C(21), and the Si atom.

Following the proposal by Petersen[6b] to evaluate this rotation, we calculated the dihedral angle θ between the corresponding lines passing through each pair of proximal carbons of the linked five-membered rings. If the ligand were symmetric, this angle would be zero. The value found in the structure of **2** is 46.2°. The Cp* rings then remain in an external position with respect to the bridging ligand, showing an angle between planes of 95(1)°. Such distortion can also be evaluated by comparing the distances from the carbons adjacent to the bridge-head carbon to the plane defined by Si–C(31)–C(32). These distances, would be equal in a symmetric situation, but in our case are as follows: C(12), 1.65 Å; C(15), 2.74 Å; C(22), 2.17 Å; C(25), 1.75 Å.

The poor quality of the crystal prevented the acquisition of enough reflections to refine the carbon atoms anisotropically. Therefore, a detailed analysis of bond distances involving carbon atoms was not feasible.

An Ortep view of the molecular structure of compound **6** with the atomic labelling scheme is shown in Figure 3. Final atomic coordinates and equivalent isotropic thermal parameters are presented in Table III. Selected bond distances and angles are given in Table IV.

The molecular structure of **6** contains two CpTiCl fragments bound by a bridging oxygen atom and a bridging DMSCp$_2$ ligand. The coordination around each titanium atom is approximately tetrahedral, assuming that the ring centroids are in a unique coordination position.

The Ti(1)–O(1)–Ti(2) angle of 177.0(2)° shows a virtually linear disposition for the oxygen atom, for which Ti–O bond distances [Ti(1)–O(1) = 1.830(4) Å and Ti(2)–O(1) = 1.831(4) Å] indicate a multiple character commonly observed in this type of structure.[7]

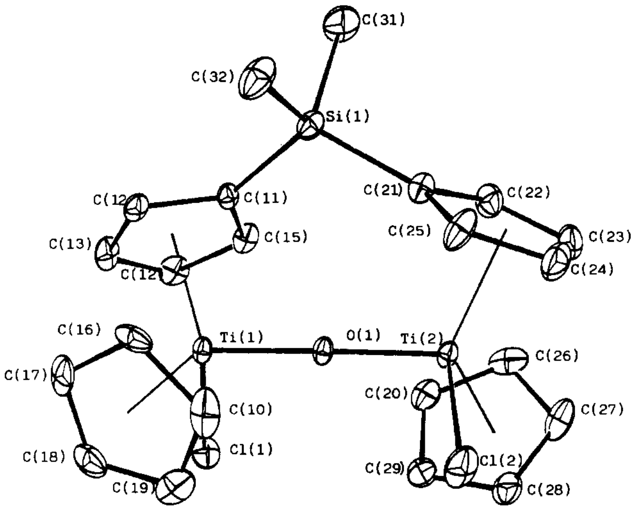

Figure 3. Ortep view of molecular structure of compound **6** with the atomic labeling scheme

Table III. Positional Parameters for Compound **6** and Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2
Tl(1)	0.0755(1)	0.11656(6)	0.65786(7)	2.18(2)
Tl(2)	−0.0142(1)	0.29650(6)	0.74638(7)	2.29(2)
Si(1)	−0.0801(3)	0.1178(1)	0.8761(1)	2.99(4)
Cl(1)	−0.0152(2)	0.1484(1)	0.5099(1)	3.87(4)
Cl(2)	0.2756(2)	0.3419(1)	0.7504(2)	4.80(5)
O(1)	0.0339(5)	0.2059(2)	0.7048(3)	2.28(8)
C(11)	−0.0973(7)	0.0750(3)	0.7659(4)	2.4(1)
C(12)	−0.0025(8)	0.0139(3)	0.7390(5)	3.1(1)
C(13)	−0.058(1)	−0.0028(4)	0.6530(6)	4.2(2)
C(14)	−0.1895(9)	0.0461(4)	0.6251(5)	4.0(2)
C(15)	−0.2125(8)	0.0939(4)	0.6922(5)	3.3(1)
C(16)	0.3431(8)	0.0840(4)	0.7363(5)	3.7(2)
C(17)	0.3287(9)	0.0404(4)	0.6591(6)	4.6(2)
C(18)	0.3306(9)	0.0852(5)	0.5892(6)	4.6(2)
C(19)	0.3501(9)	0.1569(5)	0.6186(7)	5.2(2)
C(10)	0.3609(8)	0.1566(4)	0.7094(6)	5.0(2)
C(21)	−0.0643(9)	0.2193(4)	0.8729(5)	3.0(1)
C(22)	−0.2011(9)	0.2698(4)	0.8545(5)	4.0(2)
C(23)	−0.135(1)	0.3417(4)	0.8711(5)	5.0(2)
C(24)	0.040(1)	0.3359(4)	0.8952(5)	4.8(2)
C(25)	0.085(1)	0.2622(4)	0.8946(5)	4.3(2)
C(26)	−0.2787(9)	0.3468(4)	0.6815(5)	4.7(2)
C(27)	−0.160(1)	0.4051(4)	0.6882(6)	5.3(2)
C(28)	−0.036(1)	0.3910(4)	0.6353(6)	4.6(2)
C(29)	−0.070(1)	0.3233(4)	0.5929(5)	4.1(2)
C(20)	−0.221(1)	0.2965(4)	0.6211(5)	3.9(2)
C(31)	−0.282(1)	0.0968(5)	0.9284(6)	5.5(2)
C(32)	0.111(1)	0.0805(4)	0.9441(5)	5.1(2)

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

The Ti(1)–Cl(1) and Ti(2)–Cl(2) distances are 2.387(2) and 2.412(2) Å, respectively, both atoms being positioned trans with respect to the Ti–O–Ti line, thus making the Cp rings trans with respect to the same line.

The structure of **6** also shows a nonsymmetric disposition for the bridging ligand. The lines defined by the carbon atoms adjacent to the bridgehead carbons in the Cp ring form a dihedral angle of 23° and their distances to the Si–C(31)–C(32) planes are as follows: C(12), 2.664 Å; C(15), 1.35 Å; C(22), 2.188 Å; C(25), 2.474 Å.

The centroids of both rings are equidistant to the plane defined by Ti–O–Cl in each half of the structure. However, the angle formed by the planes Ti(1)–O(1)–Cl(1) and Ti(2)–O(1)–Cl(2) is 83°, and this is considerably different than that found by Petersen for the analogous zirconium complex.[6b]

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for Compound **6**[a]

Ti(1)–Cl(1)	2.387(2)	Ti(2)–Cl(2)	2.412(2)
Ti(1)–O(1)	1.830(4)	Ti(2)–O(1)	1.831(4)
Ti(1)–C(11)	2.382(6)	Ti(2)–C(21)	2.473(6)
Ti(1)–C(12)	2.373(6)	Ti(2)–C(22)	2.386(8)
Ti(1)–C(13)	2.418(7)	Ti(2)–C(23)	2.379(8)
Ti(1)–C(14)	2.449(7)	Ti(2)–C(24)	2.398(8)
Ti(1)–C(15)	2.408(6)	Ti(2)–C(25)	2.415(7)
Ti(1)–C(16)	2.379(6)	Ti(2)–C(26)	2.385(7)
Ti(1)–C(17)	2.422(7)	Ti(2)–C(27)	2.416(7)
Ti(1)–C(18)	2.429(8)	Ti(2)–C(28)	2.425(8)
Ti(1)–C(19)	2.412(7)	Ti(2)–C(29)	2.409(7)
Ti(1)–C(10)	2.404(6)	Ti(2)–C(20)	2.380(7)
Ti(1)–Cp(11)	2.091	Ti(2)–CP(21)	2.091
Ti(1)–Cp(12)	2.097	Ti(2)–Cp(22)	2.088
Si(1)–C(11)	1.863(6)	Si(1)–C(21)	1.861(6)
Si(1)–C(31)	1.889(9)	Si(1)–C(32)	1.863(8)
Cl(1)–Ti(1)–O(1)	96.4(1)	O(1)–Ti(1)–Cp(11)	106.8
Cl(2)–Ti(2)–O(1)	95.2(1)	O(1)–Ti(1)–Cp(12)	107.4
Ti(1)–O(1)–Ti(2)	177.0(2)	O(1)–Ti(2)–Cp(21)	108.2
O(1)–Ti(2)–Cp(22)	106.8	Cp(11)–Ti(1)–Cp(12)	130.8
Cp(21)–Ti(2)–Cp(22)	131.1		

[a] Cp(11) is the centroid of C11–C15; Cp(12) is the centroid of C16–C10; Cp(21) is the centroid of C21–C25; Cp(22) is the centroid of C26–C20.

Experimental Section

All manipulations were carried out under an inert atmosphere (nitrogen or argon), using Schlenk techniques and a high vacuum line or a drybox Model HE-63-P. Solvents were purified by distillation with the appropriate deoxygenating, dehydrating agent. Hexane was distilled from Na/K amalgam, toluene from sodium, and dichloromethane from phosphorus pentoxide. $\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl_3}$,[15] $\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cl_3}$,[16] $\mathrm{LiCH_2PPh_2{\cdot}TMEDA}$,[17] and $\mathrm{Tl_2[Me_2Si(C_5H_4)_2]}$[7] were prepared by methods already published. LiMe (Aldrich), Na (Aldrich), and Hg (Aldrich) were used without further purification. NMR spectra were obtained with Varian FT-80A and Varian Unity FT-300 instruments ($\mathrm{SiMe_4}$ was used as internal reference for ^{1}H chemical shifts and $\mathrm{H_3PO_4}$ for ^{31}P). Mass spectra were obtained with a Hewlett-Packard 5890 spectrometer. Infrared spectra were obtained with a Perkin-Elmer Model 883 instrument between 4000 and 200 cm^{-1}. Elemental analyses for C and H were made with a Perkin-Elmer 204B microanalyzer.

Synthesis of $[\mathrm{TiCl_2}(\eta^5\text{-}\mathrm{C_5H_5})]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(\mathrm{C_5H_4})_2\mathrm{SiMe_2}]$ (1). A mixture of 1.69 g (7.70 mmol) of $\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl_3}$ and 2.36 g (3.97 mmol) of $\mathrm{Tl_2[Me_2Si(C_5H_4)_2]}$ in 100 mL of toluene was refluxed for 3 h. A deep red solution was formed. The reaction mixture was evaporated to dryness *in vacuo* and the resulting solid extracted with $\mathrm{CH_2Cl_2}$ in a Soxhlet apparatus. The solution was evaporated to dryness, the product washed with toluene and then with hexane, and dried under vacuum to obtain a reddish-brown powder. (1.33 g, 60% yield).

Anal. Calcd For $\mathrm{C_{22}H_{24}Cl_4SiTi_2}$ (found): C, 47.67 (46.62); H, 4.33 (4.34). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ 0.63 (s, 6H, $\mathrm{Me_2Si}$), 6.53 (s, 10H, $\mathrm{C_5H_5}$), 6.87 (t, $J = 2.44$ Hz, 4H, $\mathrm{C_5H_4}$), 6.62 (t, $J = 2.44$ Hz, 4H, $\mathrm{C_5H_4}$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C): δ −0.54 ($\mathrm{Me_2Si}$), 120.8 [$\mathrm{C_{3,4}(C_5H_4)}$], 129.2 [$\mathrm{C_{2,5}(C_5H_4)}$], 135.5 [$\mathrm{C_1(C_5H_4)}$].

Synthesis of $[\mathrm{TiCl_2}(\eta^5\text{-}\mathrm{C_5Me_5})]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(\mathrm{C_5H_4})_2\mathrm{SiMe_2}]$ (2). A mixture of 11.38 g (39.31 mmol) of $\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cl_3}$ and 11.69 g (19.65 mmol) of $\mathrm{Tl_2[Me_2Si(C_5H_4)_2]}$ in 200 mL of toluene was refluxed for 12 h. The reaction mixture was filtered while still warm and the residue washed with $\mathrm{CH_2Cl_2}$ (2 × 75 mL). The solutions were combined and concentrated *in vacuo* to 30 mL then stored overnight at −30 °C. Garnet-red crystals were obtained. These were washed with cold toluene and hexane to give a final product identified as **2**. A second crop was obtained by cooling the residual solution. (9.14 g; 67% yield).

Anal. Calcd for $\mathrm{C_{32}H_{44}Cl_4SiTi_2}$ (found): C, 55.35 (54.90); H, 6.34 (6.17). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 1.12 (s, 6H, $\mathrm{Me_2Si}$), 1.75 (s, 30H, $\mathrm{C_5Me_5}$), 5.71 (t, 4H, $\mathrm{C_5H_4}$), 6.62 (t, 4H, $\mathrm{C_5H_4}$). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ 0.65 (s, 6H, $\mathrm{SiMe_2}$), 2.01 (s, 30H, $\mathrm{C_5Me_5}$), 6.08

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(t, 4H, $\mathrm{C_5H_4}$), 6.42 (t, 4H, $\mathrm{C_5H_4}$). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 0.77 ($\mathrm{SiMe_2}$), 13.33 ($\mathrm{C_5}\mathit{Me}_5$), 129.10 ($\mathit{C}_5\mathrm{Me_5}$), 116.89, 130.06 [$\mathrm{C_{2,5}C_{3,4}}$-($\mathrm{C_5H_4}$)], 134.37 [$\mathrm{C_1(C_5H_4)}$]. ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C): δ −1.17 ($\mathrm{SiMe_2}$), 13.20 ($\mathrm{C_5}\mathit{Me}_5$), 128.90 ($\mathit{C}_5\mathrm{Me_5}$), 117.26, 129.41 [$\mathrm{C_{2,5}}$,$\mathrm{C_{3,4}}$-($\mathrm{C_5H_4}$)], 134.37 [$\mathrm{C_1(C_5H_4)}$].

Synthesis of $[\mathrm{TiMe_2}(\eta^5\text{-}\mathrm{C_5H_5})]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(\mathrm{C_5H_4})_2\mathrm{SiMe_2}]$ (3). A suspension of 0.50 g (0.90 mmol) of complex **1** in 20 mL of hexane at −78 °C was treated with 2.1 mL of 1.7 M LiMe (3.57 mmol). The cold bath was removed after 15 min, and the mixture was allowed to warm to room temperature and stirred until the solution became yellow. The reaction mixture was filtered and the solution concentrated *in vacuo* at 5 °C and then stored overnight at −15 °C to yield long orange needles. (0.36 g, 84% yield).

Anal. Calcd for $\mathrm{C_{26}H_{36}SiTi_2}$ (found): C, 66.11 (65.83); H, 7.68 (7.77). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 0.12 (s, 12H, Ti–Me), 0.16 (s, 6H, $\mathrm{Me_2Si}$), 5.97 (t, J = 2.5 Hz, 4H, $\mathrm{C_5H_4}$), 5.94 (t, J = 2.4 Hz, 4H, $\mathrm{C_5H_4}$), 5.76 (s, 10H, $\mathrm{C_5H_5}$). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, 25 °C): δ −0.8 ($\mathrm{Me_2Si}$), 47.00 (Ti–Me), 117.70 [$\mathrm{C_{2,5}}$ ($\mathrm{C_5H_4}$)], 120.20 [$\mathrm{C_{3,4}(C_5H_4)}$], 113.90 ($\mathrm{C_5H_5}$), $\mathrm{C_1}$ of $\mathrm{C_5H_4}$ not observed.

Synthesis of $[\mathrm{TiMe_2}(\eta^5\text{-}\mathrm{C_5Me_5})]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(\mathrm{C_5H_4})_2\mathrm{SiMe_2}]$ (4). A suspension of 1.50 g (0.90 mmol) of complex **2** in 30 mL of toluene at −78 °C was treated with 5.4 mL of 1.6 M LiMe (8.64 mmol). The cold bath was allowed to warm to room temperature, and the solution changed color from red to light-yellow. The reaction mixture was stirred at room temperature for 30 min and then filtered. The resulting solution was concentrated *in vacuo* to 10 mL and stored overnight at −30 °C to obtain fine yellow needles identified as **4**. The product was further purified by recrystallization from toluene/hexane. (1.30 g, 98% yield).

Anal. Calcd for $\mathrm{C_{36}H_{56}SiTi_2}$ (found): C, 70.60 (70.75); H, 9.15 (9.44). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ −0.15 (s, 12H, Ti–Me), 0.65 (s, 6H, $\mathrm{SiMe_2}$), 1.65 (s, 30H, $\mathrm{C_5Me_5}$), 5.47 (t, 4H, $\mathrm{C_5H_4}$), 6.29 (t, 4H, $\mathrm{C_5H_4}$). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 0.11 ($\mathrm{SiMe_2}$), 12.28 ($\mathrm{C_5}\mathit{Me}_5$), 47.13 (Ti–Me), 120.13 ($\mathit{C}_5\mathrm{Me_5}$), 115.59, 121.10 [$\mathrm{C_{2,5}}$,$\mathrm{C_{3,4}(C_5H_4)}$], 135.73 [$\mathrm{C_1(C_5H_4)}$].

Synthesis of $[\mathrm{Ti(CH_2PPh_2)_2}(\eta^5\text{-}\mathrm{C_5Me_5})]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(\mathrm{C_5H_4})_2]$ (5). A 1.00-g (1.44-mmol) sample of $[\mathrm{TiCl_2}(\eta^5\text{-}\mathrm{C_5Me_5})]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(\mathrm{C_5H_4})_2\mathrm{SiMe_2}]$ (**2**) in 50 mL of toluene was treated with 1.95 g (6.05 mmol) of $\mathrm{LiCH_2PPh_2{\cdot}TMEDA}$ at −78 °C. The reaction mixture was slowly warmed up to 0 °C in the absence of light and allowed to react for 6 h. The mixture was filtered and the solvent removed *in vacuo* to obtain a dark red oil. The product was washed with hexane (4 × 20 mL). Then, stirred for 1 h at −78 °C. The final product was a red solid identified as **5** (0.97 g, 50.0% yield).

Anal. Calcd for $\mathrm{C_{84}H_{92}SiP_4Ti_2}$ (found): C, 74.78 (76.09); H, 6.83 (7.13). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 0.58 (4H, Ti–$\mathrm{CH_2}$–P, $^2J_{\mathrm{HH}}$ = 9.8 Hz, $^2J_{\mathrm{HP}} < 2$ Hz), 1.44 (s, 6H, $\mathrm{SiMe_2}$), 1.45 (4H, Ti–$\mathrm{CH_2}$–P, $^2J_{\mathrm{HH}}$ = 9.8 Hz, $^2J_{\mathrm{HP}}$ = 4.3 Hz), 1.68 (s, 30H, $\mathrm{C_5Me_5}$), 6.13 (m, 4H, $\mathrm{C_5H_4}$), 6.67 (m, 4H, $\mathrm{C_5H_4}$), 6.88–7.22 (m, 24H, Ph), 7.38–7.47 (m, 8H, Ph), 7.64–7.72 (m, 8H, Ph). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 2.70 ($\mathrm{SiMe_2}$), 13.03 ($\mathrm{C_5}\mathit{Me}_5$), 58.14 (d, Ti–$\mathrm{CH_2}$–P, $^1J_{\mathrm{CP}}$ = 58.59 Hz), 117.92, 123.02 [$\mathrm{C_{2,5}}$, $\mathrm{C_{3,4}}$ ($\mathrm{C_5H_4}$)], $\mathrm{C_1}$ ($\mathrm{C_5H_4}$) not observed, 128.56–147.94 (Ph). ^{31}P NMR ($\mathrm{C_6D_6}$, 25 °C): δ 9.91.

Synthesis of $[\mathrm{TiCl}(\eta^5\text{-}\mathrm{C_5H_5})]_2(\mu\text{-O})[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(\mathrm{C_5H_4})_2\mathrm{SiMe_2}]$, (6). A 0.31-g (0.56-mmol) sample of **1** and 0.027 g (1.17 mmol) of 10% sodium amalgam in 50 mL of toluene was stirred for 17 h at room temperature. The resulting dark brown solution was exposed to air for several hours to obtain **6** in stoichiometric yields. A change to yellow-orange color was observed upon oxidation. After removal of the solvent *in vacuo*, an orange crystalline solid was obtained. Suitable crystals for X-ray analysis were obtained by slow evaporation of a saturated solution in $\mathrm{CH_2Cl_2}$.

Anal. Calcd for $\mathrm{C_{22}H_{22}Cl_2OSiTi_2}$ (found): C, 52.93 (53.23); H, 4.82 (4.83). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ 0.44 (s, 6H, $\mathrm{SiMe_2}$), 6.09 (m, 2H, $\mathrm{C_5H_4}$), 6.24 (m, 2H, $\mathrm{C_5H_4}$), 6.42 (s, 10H, $\mathrm{C_5H_5}$), 6.59 (m, 2H, $\mathrm{C_5H_4}$), 6.63 (m, 2H, $\mathrm{C_5H_4}$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C): δ −2.2 ($\mathrm{SiMe_2}$), 117.2 ($\mathrm{C_5H_5}$), 111.7, 114.2, 125.2, 129.2, 133.6 (5C, $\mathrm{C_5H_4}$). IR (Nujol, CsI): 725 cm^{-1} ($\nu_{\mathrm{Ti-O-Ti}}$).

Table V. Crystallographic Data for Compounds **2** and **6**

	2	**6**
chem formula	$\mathrm{Ti_2Cl_4SiC_{32}H_{44}}$	$\mathrm{Ti_2Cl_2SiOC_{22}H_{24}}$
a, Å	28.32(1)	7.835(2)
b, Å	14.023(6)	18.291(4)
c, Å	8.431(5)	15.415(2)
β, deg		96.22(1)
V, Å^3	3348(4)	2196(1)
Z	4	4
MW	694.4	449.2
symmetry, space group	orthorhombic $Pna2_1$	monoclinic $P2_1/n$
T, °C	22	22
λ, Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.37	1.5
μ, cm^{-1}	8.49	10.29
R^a	0.088	0.074
$R_w{}^b$	0.074^c	0.101^c

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum w[|F_o|/|F_c|]^2/\sum w|F_o|^2]^{1/2}$. ^{c} $w = 4F_o{}^2/[\sigma(F_o)^2]^2$.

Structural Data for $[\{\mathrm{TiCl_2}(\eta^5\text{-}\mathrm{C_5Me_5})\}_2\{\mu\text{-}\eta^5\text{-}\eta^5\text{-}(\mathrm{C_5H_4})_2\mathrm{SiMe_2}\}]$ (2) and $[\{\mathrm{TiCl}(\eta^5\text{-}\mathrm{C_5H_5})\}_2(\mu\text{-O})\{\mu\text{-}\eta^5\text{-}\eta^5\text{-}(\mathrm{C_5H_4})_2\mathrm{SiMe_2}\}]$ (6). Crystallographic and experimental details are given in Table V. Both sets of data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No extinction correction was made. Absorption correction was made for compound **6** with the DIFABS method.[18]

The structures were solved by a combination of direct methods and Fourier synthesis and refined (on F) by full-matrix least-squares calculations.

In compound **6**, all non-hydrogen atoms were refined anisotropically and in the last cycle of refinement the hydrogen atoms were included from geometrical positions and thermal parameters equivalent to the carbon to which they were attached.

In compound **2**, only the non-hydrogen non-carbon atoms were refined anisotropically due to the poor quality of the crystals. The carbon atoms were refined isotropically and the hydrogens were included from geometrical calculations and fixed.

Final values of $R = 0.074$ and $R_w = 0.101$ were obtained for compound **6** and $R = 0.088$ and $R_w = 0.074$ for compound **2** with $R_w = [\sum w[|F_o|/|F_c|]^2/\sum w|F_o|^2]^{1/2}$ and $w = 4F_o{}^2/[\sigma(F_o)^2]^2$.

Anomalous dispersion corrections and atomic scattering factors were taken from ref 19. Calculations were performed with the SDP Enraf-Nonius package,[20] Multan,[21] and Dirdif[22] on a MICROVAX II computer.

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Supplementary Material Available: Table of crystal data and refinement parameters hydrogen atom positional and isotropic thermal parameters, non-hydrogen atom anisotropic thermal parameters, and all bond distances and angles for **2** and **6** (18 pages). Ordering information is given on any current masthead page.

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