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Dicyclopentadienyl titanium and zirconium complexes with the double bridged bis(dimethylsilanodiyl) dicyclopentadienyl $[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]^{2-}$ ligand: X-ray molecular structure of $[Ti\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me_2]$ [1]

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Abstract

The reaction of the doubly bridged bis(1,1′,2,2′-dimethylsilanodiyl)-η^5-dicyclopentadienyl titanium and zirconium complexes $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me_2]$ (M = Ti (**3**), Zr (**4**)) with water gave the μ-oxo derivatives $[\{M[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}O)]$ (M = Ti (**5**), Zr (**6**)). Addition of one equivalent of M′R (M′ = MgCl, R = CH_3, CH_2SiMe_3; M′ = Li, R = CH_2CMe_2Ph) to toluene or diethyl ether solutions of $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl_2]$ (M = Ti(**1**), Zr (**2**)) afforded the chloro alkyl derivatives $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}ClR]$ (M = Ti, R = CH_2SiMe_3 (**8**); M = Zr, R = Me (**7**), CH_2CMe_2Ph (**9**)). Compounds **3** and **4** reacted with $[CPh_3][B(C_6F_5)_4]$ at −78 °C in CD_2Cl_2 leading to the cationic species $[\{M[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}Me)]^+$ (M = Ti (**10**), Zr (**11**)) as demonstrated by NMR spectroscopy. The titanium(III) and zirconium(III) derivatives $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}(\mu\text{-}Cl)]_2$ (M = Ti (**12**), Zr (**13**)) were obtained by reduction of **1** and **2** with one equivalent of sodium amalgam. The X-ray molecular structure of $[Ti\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me_2]$ (**3**) has been determined by diffraction methods.

Keywords: Titanium; Zirconium; Cationic metallocenes; Alkyl group 4 metals

1. Introduction

Ansa-metallocene complexes of the early transition metals have received considerable attention in recent years [1]. The presence of a bridging group restricts the mobility of the cyclopentadienyl rings, providing a more rigid system that renders the activation of their C–H bonds more difficult.

The bis(dimethylsilanodiyl)dicyclopentadienyl anion $[SiMe_2(C_5H_4)_2]^{2-}$ can be coordinated to metal centers as a chelating or as a bridging group. This ligand has been successfully used to stabilize Group 4 metal complexes in both high and low oxidation states. The chemistry of mononuclear compounds with symmetric and asymmetric rings bridged by an SiR_2 fragment, and their potential applications as catalysts in stereo- and enantioselective hydrogenation and polymerization of olefins, has been extensively studied. Chiral *ansa*-metallocenes containing a C_2 symmetrical arrangement of ring substituents have also proved to be effective precursors for generating Ziegler–Natta catalysts, which induce isotacticity in the polymerization of propylene and other α-olefins [2,3]. Recently, the syntheses of similar halo- and alkyl-titanium(IV) derivatives [4], as well as new titanium(III) and (II) metallocene complexes [5] containing this ligand as a chelating system have been reported, including some aspects of their chemical behavior.

Dinuclear compounds are also well represented [6], although they are less well-known for Group 4 metals [7] and not many dinuclear derivatives of these metals are known in low oxidation states.

We were interested in isolating and studying the reactivity of cyclopentadienyl Group 4 metal complexes by using the bis(dimethylsilanodiyl)dicyclopentadienyl dianion $[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]^{2-}$ as a ligand to increase the stereorigidity of the complex. Different mono- and oligo-nuclear transition metal derivatives containing this

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[1] Dedicated to Professor Rafael Usón on the occasion of his 70th birthday.

[2] X-ray diffraction studies.

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ligand have been reported [8], but few Group 4 metal complexes are known [9,10]. Here we report the synthesis and structural characterization of the bis(1,1',2,2'-dimethylsilanodiyl)-η^5-dicyclopentadienyl titanium(IV) and zirconium(IV) oxoderivatives $[\{M[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}O)]$ (M = Ti (**5**), Zr (**6**)), the chloroalkyl complexes $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}ClR]$ (M = Ti, R = CH_2SiMe_3 (**8**); M = Zr, R = Me (**7**), CH_2CMe_2Ph (**9**)) and the characterization of the previously reported [10] complex **3** by X-ray diffraction methods. The spectroscopic characterization of the cationic species $[\{M[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}Me)]^+$ (M = Ti (**10**), Zr (**11**)) is also reported.

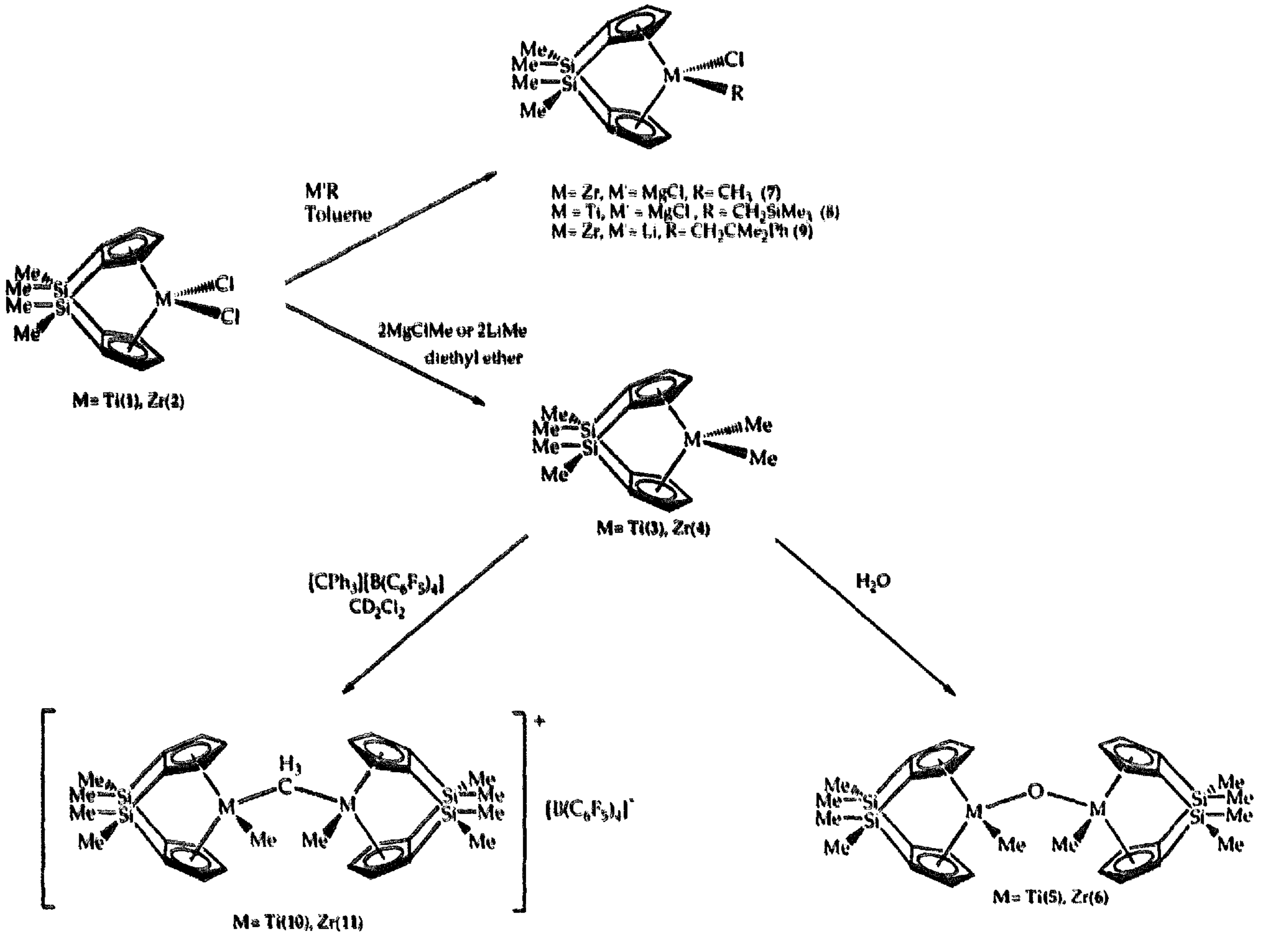
2. Results and Discussion

The reaction of a diethyl ether solution of $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl_2]$ (M = Ti (**1**), Zr (**2**)) at −78 °C with two equivalents of the appropriate alkylating agent (LiMe or MgClMe) led to the dimethyl derivatives $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me_2]$ (M = Ti (**3**), Zr (**4**)) as previously described [10]. Complexes **3** and **4** are air- and moisture-sensitive, both in solution and in the solid state. They can, however, be stored unaltered for weeks if strictly anaerobic conditions are maintained. In the presence of a stoichiometric amount of water, hydrolysis takes place and the μ-oxo dinuclear derivatives $[\{M[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}O)]$ (M = Ti (**5**), Zr (**6**)) are isolated in 40–50% yield (Scheme 1).

When **2** reacts with one equivalent of MgClMe the chloro methyl compound $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}ClMe]$ (**7**) is obtained. Analogous chloro alkyl complexes $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}ClR]$ (M = Ti, R = CH_2SiMe_3 (**8**); M = Zr, R = CH_2CMe_2Ph (**9**)) are the only products obtained from the reaction of **1** or **2** with $MgCl(CH_2SiMe_3)$ or $LiCH_2CMe_2Ph$, whatever the molar ratio may be.

All of the new isolated compounds are soluble in chlorinated solvents (chloroform, dichloromethane) as well as in aromatic hydrocarbons (benzene, toluene) and slightly soluble in hexane and pentane. Their solubilities range in the order **7,8,9** > **3,4**, > **5,6** > **1,2**.

The IR spectra of all of these complexes show the characteristic absorptions reported [11] for ν_{as}(Si–C)

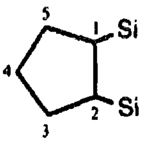


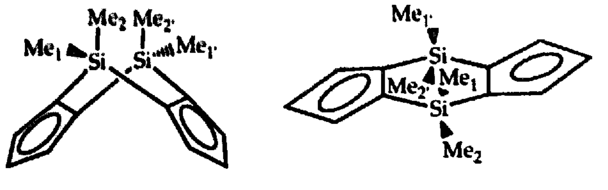
Scheme 1.

Table 1
NMR data (δ) for complexes **5**–**9**

Compound	^{1}H NMR		^{13}C NMR [a]
	C_6D_6	$CDCl_3$	C_6D_6
5	−0.19 (s, 6H, Me–Ti)	—	
	0.15 (s, 6H, Me–Si)	—	
	0.33 (s, 6H, Me–Si)	—	
	0.40 (s, 6H, Me–Si)	—	
	0.90 (s, 6H, Me–Si)	—	
	6.64 (m, 4H, C_5H_3)	—	
	6.74 (m, 4H, C_5H_3)	—	
	6.79 (m, 4H, C_5H_3)	—	
6	0.23 (s, 6H, Me–Zr)	0.10 (s, 6H, Me–Zr)	
	0.25 (s, 6H, Me–Si)	0.35 (s, 6H, Me–Si)	
	0.50 (s, 6H, Me–Si)	0.63 (s, 6H, Me–Si)	
	0.58 (s, 6H, Me–Si)	0.67 (s, 6H, Me–Si)	
	0.74 (s, 6H, Me–Si)	0.84 (s, 6H, Me–Si)	
	6.05 (m, 4H, C_5H_3)	5.93 (m, 4H, C_5H_3)	
	6.51 (m, 4H, C_5H_3)	6.35 (m, 4H, C_5H_3)	
	6.82 (m, 4H, C_5H_3)	6.79 (m, 4H, C_5H_3)	
7	0.05 (s, 3H, Me–Zr)		
	0.32 (s, 3H, Me–Si)		
	0.42 (s, 3H, Me–Si)		
	0.46 (s, 3H, Me–Si)		
	0.48 (s, 3H, Me–Si)		
	6.19 (m, 2H, C_5H_3)		
	6.68 (m, 2H, C_5H_3)		
	6.70 (m, 2H, C_5H_3)		
8	−0.14 (s, 3H, Me–Si)	−0.02 (s, 9H, Me_3–Si)	−5.5 (Me–Si)
	0.17 (s, 3H, Me–Si)	0.22 (s, 3H, Me–Si)	−4.92 (Me–Si)
	0.31 (s, 9H, Me_3–Si)	0.36 (s, 3H, Me–Si)	1.39 (Me–Si)
	0.37 (s, 3H, Me–Si)	0.71 (s, 3H, Me–Si)	1.8 (Me–Si)
	0.42 (s, 3H, Me–Si)	0.75 (s, 3H, Me–Si)	2.96 (Me_3–Si)
	1.13 (s, 2H, –CH_2–)	1.03 (s, 2H, –CH_2–)	56.41 (–CH_2–)
	6.75 (m, 2H, C_5H_3)	6.77 (m, 2H, C_5H_3)	110.39 (C_1 (C_5H_3))
	6.79 (m, 2H, C_5H_3)	6.87 (m, 2H, C_5H_3)	115.00 (C_5 (C_5H_3))
	6.81 (m, 2H, C_5H_3)	6.98 (m, 2H, C_5H_3)	119.84 (C_3 (C_5H_3))
			137.08 (C_2 or C_4 (C_5H_3))
			140.33 (C_2 or C_4 (C_5H_3))
9	0.019 (s, 6H, Me–Si)	—	−5.148 (Me–Si)
	0.33 (s, 6H, Me–Si)	—	−4.66 (Me–Si)
	0.38 (s, 6H, Me–Si)	—	0.70 (Me–Si)
	0.46 (s, 6H, Me–Si)	—	1.55 (Me–Si)
	1.478 (s, 12H, Me_2C)	—	34.48 (C–Me_2)
	1.59 (s, 4H, –CH_2–)	—	40.06 (C–Me_2)
	5.97 (m, 4H, C_5H_3)	—	69.37 (CH_2)
	6.15 (m, 4H, C_5H_3)	—	110.75 (Ph)
	6.68 (m, 4H, C_5H_3)	—	113.62 (C_5H_3)
	7.4–7.2 (m, 10H, Ph)	—	114.66 (Ph)
			124.76 (C_5H_3)
			125.76 (C_5H_3)
			131.66 (C_5H_3)
			134.89 (C_5H_3)
			135.18 (Ph)

[a] Key:





"Chelating ligand" "Bridging ligand"

(A) (B)

Fig. 1. Chelating (A) and bridging (B) dispositions for the bis(1,1',2,2'-dimethylsilanodiyl-η^5-dicyclopentadienyl) ligand.

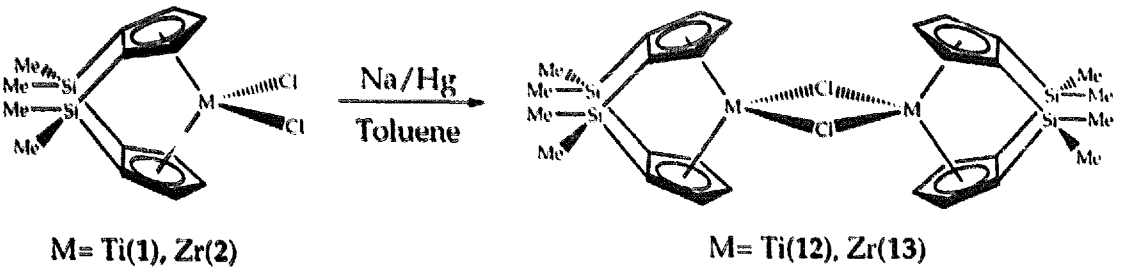
and ν_s(Si–C) vibrations between 700 and 600 cm^{-1} and broad signals near 800 cm^{-1} for ν(M–O–M) vibrations.

^{1}H and ^{13}C NMR spectra for complexes **5**–**9** in C_6D_6 and $CDCl_3$ are summarized in Table 1. These spectra show three multiplets for the non-equivalent cyclopentadienyl protons (H_3–H_5) and four singlets for the methyl protons bonded to silicon in the bridging group, indicating loss of the plane of symmetry observed for compounds $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}X_2]$ with two equivalent substituents in the reflection plane. Similar features are observed in the ^{13}C NMR spectra in which five signals for the C_1–C_5 atoms and four signals for the Me–Si groups are present. All these data are in agreement with the chelating disposition (A) (Fig. 1) of the bis(1,1',2,2'-dimethylsilanodiyl-η^5-dicyclopentadienyl) ligand in metallocene-type derivatives, and with the presence of two different ligands occupying the other pseudotetrahedral positions around the metal center.

The reaction of the dimethyl complexes **3** and **4** with half an equivalent of $[CPh_3][B(C_6F_5)_4]$ at −78 °C in CD_2Cl_2 led to the quantitative formation of dinuclear methyl-bridged cationic complexes $[\{M[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}Me)]^+$ M = Ti, **10** (red) and M = Zr, **11** (yellow) (Scheme 1), as evidenced by ^{1}H NMR spectroscopy. When the same reactions are carried out in a 1:1 molar ratio no identifiable species are observed. Complexes **10** and **11** have been identified by ^{1}H NMR at low temperature, decomposing above −40 °C. They could not be isolated as solids at room temperature. The μ-CH_3 ligands are identified in the ^{1}H NMR spectrum by a singlet at δ −1.22 for the titanium and δ −0.83 for the zirconium compound, and by a signal in the ^{13}C NMR spectra at δ 29.8 and δ 30.1 respectively, whereas the terminal methyl groups appear at δ 0.05 for **10** (^{13}C NMR: δ 51.1) and δ −0.19 for **11** (^{13}C NMR: δ 51.9). These $[\{M[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}Me)]^+$ complexes can be considered as containing one cationic 14-electron fragment $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me]^+$ stabilized by adduct formation with the neutral dimethyl metallocene complexes $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me_2]$ as ligands [3]. With this disposition the three protons of the cyclopentadienyl rings and the methyl groups bonded to silicon are not equivalent, and three multiplets (δ 6.20, 6.97 and 7.11 for **10** and δ 6.33, 6.59 and 6.98 for **11**) and four singlets (δ 0.15, 0.44, 0.67 and 0.73 for **10** and δ 0.28, 0.29, 0.80 and 0.85 for **11**) are observed in the ^{1}H NMR at −78 °C. The same features are observed in the ^{13}C NMR spectra (**10**: δ −8.0, −5.8, −4.1, 0.9 (Si–Me); 125.9, 127.8, 128.2, 128.4, 129.1 (C_5H_3); **11**: δ 1.4, 1.8, 3.6, 4.9 (Si–Me); 117.1, 125.8, 127.7, 128.5, 148.6 (C_5H_3)).

Reduction of a toluene solution of the titanium(IV) and zirconium(IV) derivatives **1** and **2** with sodium amalgam (10%) in a 1:1 molar ratio gave the μ-chloro-titanium(III) and zirconium(III) complexes $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}(\mu\text{-}Cl)]_2$ (M = Ti, **12**; Zr, **13**) as red and red-brown solids respectively, in 75–80% yield (Scheme 2).

Complexes **12** and **13** are scarcely soluble in THF or toluene and insoluble in hexane. They react in chloroform or dichloromethane, being immediately transformed into the corresponding chloro-metal(IV) derivatives **1** and **2**. Complex **13** is diamagnetic, and the ^{1}H NMR spectrum in C_6D_6 shows two signals at δ 0.62 and 0.74 for the methylsilyl protons of the bridging ligand and two signals at δ 5.02 (pseudotriplet) and 5.93 (pseudodoublet) for the cyclopentadienyl protons of an AA'B spin system (ratio 3:3:1:2). Complex **12** is paramagnetic, and the ^{1}H NMR shows broad signals at δ 17, 3 and 0.0 and the spin-lattice relaxation times [12] confirm the paramagnetic nature of the compound (see Table 2).



Scheme 2.

Table 2
Spin-lattice relaxation time $\{T_1\}$ (deg) for compound **12**

Compound	$\delta(C_6D_6)$	T_1 (deg)
12	17.5	0.0010
	3.84	0.0017
	2.89	0.0051
	0.10	0.0792
	0.0087	0.0163

2.1. *Description of the crystal structure of Ti[μ-(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]Me$_2$ (3)*

The crystal and molecular structure of **3** was determined by X-ray diffraction methods. There are two independent molecules in the asymmetric unit of the unit cell. Since the structures of the two molecules are similar, only one is described in detail; data for the second are given in parentheses.

Fig. 2 shows the molecular structure and atom numbering scheme of molecule 1. Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 3. Selected bond distances and angles are given in Table 4.

The molecular structure of **3** is typical of a bis ligand metallocene system, with the two Cp moieties linked by two SiMe$_2$ bridges, similar to [M(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$)Cl$_2$] (M = Ti,Zr) [10].

Owing to the rigidity imposed by the double bridge, the Cp rings are eclipsed, and the two silicon and single titanium atoms define a plane in which the two methyl groups bonded to each titanium and silicon atom are located.

The two Cp rings are planar and the dihedral angle between them is 63.5(2)° (64.1(2)°), similar to that found in the aforementioned [Ti{(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$)Cl$_2$] [10].

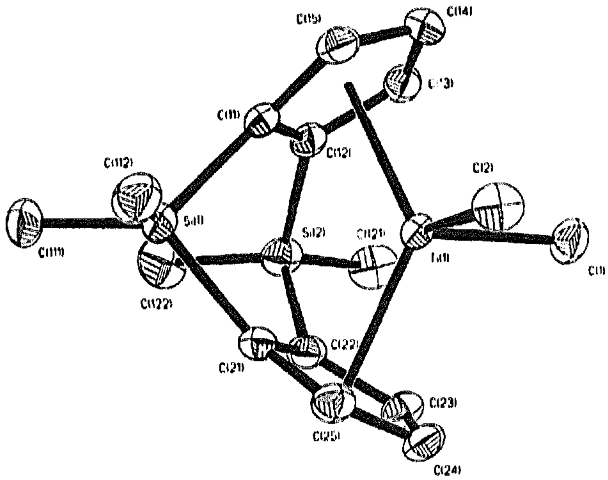


Fig. 2. ORTEP view of molecular structure of compound **3** with the atomic labeling scheme.

Table 3
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for compound **3**

	x	y	z	U_{eq}
Ti(1)	8175(1)	1941(1)	3855(1)	45(1)
C(1)	9210(4)	1796(4)	3100(4)	68(2)
C(2)	8434(4)	3198(4)	4018(4)	72(2)
Ti(2)	7472(1)	1328(1)	9086(1)	46(1)
C(3)	6582(4)	1816(4)	9855(4)	76(2)
C(4)	8492(4)	2320(4)	9431(4)	72(2)
C(11)	6495(3)	1735(3)	3609(3)	51(1)
C(12)	6857(3)	1079(3)	3182(3)	53(1)
C(13)	7069(3)	1410(4)	2410(3)	59(2)
C(14)	6861(3)	2219(4)	2354(3)	63(2)
C(15)	6505(3)	2423(4)	3074(3)	58(1)
Si(1)	6596(1)	1742(1)	4861(1)	60(1)
C(111)	5730(3)	1054(4)	5178(3)	85(2)
C(112)	6438(3)	2767(3)	5248(3)	77(2)
Si(2)	7487(1)	178(1)	3830(1)	67(1)
C(121)	8207(4)	− 353(3)	3174(4)	93(2)
C(122)	6689(5)	− 567(4)	4162(4)	111(2)
C(21)	7946(3)	1461(3)	5200(3)	53(1)
C(22)	8320(3)	810(3)	4777(3)	56(1)
C(23)	9318(3)	1015(4)	4868(3)	61(2)
C(24)	9562(3)	1736(4)	5311(3)	60(2)
C(25)	8734(3)	2006(4)	5531(3)	56(1)
C(31)	8408(3)	189(3)	9090(3)	51(1)
C(32)	7509(3)	− 43(3)	9277(3)	50(1)
C(33)	7597(3)	237(3)	10169(3)	59(1)
C(34)	8491(3)	649(3)	10528(3)	63(1)
C(35)	8991(3)	609(3)	9876(3)	62(1)
C(41)	7305(3)	969(4)	7576(3)	46(1)
C(42)	6402(3)	720(3)	7764(2)	45(1)
C(43)	5898(3)	1437(3)	7838(3)	53(1)
C(44)	6437(4)	2091(4)	7716(3)	58(2)
C(45)	7296(3)	1795(4)	7550(3)	56(1)
Si(3)	8453(1)	340(1)	7888(1)	57(1)
C(131)	8406(4)	− 561(3)	7170(4)	92(2)
C(132)	9562(3)	935(3)	7904(4)	80(2)
Si(4)	6295(1)	− 234(1)	8341(1)	53(1)
C(141)	5239(3)	− 207(3)	8808(3)	78(2)
C(142)	6183(4)	− 1151(3)	7630(3)	74(2)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Related to it the angle Cp(1)–Ti(1)–Cp(2) is 126.8° (126.7°). The Ti–C distances range from 2.313(5) to 2.487(4) Å, but this does not imply a deviation from planarity in the rings, nor a significant variation in the C–C distances. The Ti-centroid distances are 2.07 Å, and all these values correspond to a 5° mean deviation of the metal centroid line from the normal between titanium and the ring plane, comparable with the reference complex [10]. The Ti–methyl distances are in the range from 2.138(7) to 2.158(5) Å, normal for these systems.

3. Experimental section

All manipulations were performed under an inert atmosphere (argon) using Schlenk and high vacuum line

Table 4
Selected bond lengths (Å) and angles (deg) for compound **3**

Ti(1)–C(1)	2.158(5)	Ti(2)–C(3)	2.149(6)
Ti(1)–C(2)	2.138(7)	Ti(2)–C(4)	2.157(6)
Ti(1)–C(11)	2.320(4)	Ti(2)–C(31)	2.324(4)
Ti(1)–C(12)	2.325(4)	Ti(2)–C(32)	2.313(5)
Ti(1)–C(13)	2.425(4)	Ti(2)–C(33)	2.433(5)
Ti(1)–C(14)	2.487(4)	Ti(2)–C(34)	2.485(4)
Ti(1)–C(15)	2.424(4)	Ti(2)–C(35)	2.424(4)
Ti(1)–C(21)	2.327(4)	Ti(2)–C(41)	2.321(4)
Ti(1)–C(22)	2.330(5)	Ti(2)–C(42)	2.332(4)
Ti(1)–C(23)	2.411(5)	Ti(2)–C(43)	2.431(4)
Ti(1)–C(24)	2.471(4)	Ti(2)–C(44)	2.487(5)
Ti(1)–C(25)	2.425(4)	Ti(2)–C(45)	2.410(5)
Si(1)–C(111)	1.861(5)	Si(3)–C(131)	1.855(5)
Si(1)–C(112)	1.854(5)	Si(3)–C(132)	1.859(5)
Si(1)–C(11)	1.872(4)	Si(3)–C(41)	1.871(5)
Si(1)–C(21)	1.878(4)	Si(3)–C(31)	1.876(4)
Si(2)–C(121)	1.873(6)	Si(4)–C(141)	1.860(4)
Si(2)–C(122)	1.865(6)	Si(4)–C(142)	1.859(5)
Si(2)–C(12)	1.867(5)	Si(4)–C(32)	1.878(4)
Si(2)–C(22)	1.871(5)	Si(4)–C(42)	1.855(5)
C(11)–C(15)	1.415(6)	C(31)–C(35)	1.406(6)
C(11)–C(12)	1.455(6)	C(31)–C(32)	1.450(5)
C(12)–C(13)	1.421(6)	C(32)–C(33)	1.409(6)
C(13)–C(14)	1.383(7)	C(33)–C(34)	1.393(6)
C(14)–C(15)	1.395(6)	C(34)–C(35)	1.402(6)
C(21)–C(25)	1.405(6)	C(41)–C(45)	1.386(7)
C(21)–C(22)	1.456(6)	C(41)–C(42)	1.464(5)
C(22)–C(23)	1.422(6)	C(42)–C(43)	1.422(6)
C(23)–C(24)	1.374(7)	C(43)–C(44)	1.384(7)
C(24)–C(25)	1.400(6)	C(44)–C(45)	1.415(7)
Ti(1)–Cp1	2.073	Ti(2)–Cp3	2.074
Ti(1)–Cp2	2.138	Ti(2)–Cp4	2.073
C(2)–Ti(1)–C(1)	93.0(2)	C(3)–Ti(2)–C(4)	92.4(3)
Cp1–Ti(1)–Cp2	126.8	Cp3–Ti(2)–Cp4	126.7
C(2)–Ti(1)–Cp2	108.7	C(4)–Ti(2)–Cp4	107.9
C(2)–Ti(1)–Cp1	107.8	C(4)–Ti(2)–Cp3	108.3
C(1)–Ti(1)–Cp2	108.3	C(3)–Ti(2)–Cp4	108.3
C(1)–Ti(1)–Cp1	107.4	C(3)–Ti(2)–Cp3	107.9

Cp1 is the centroid of C(11), C(12), C(13), C(14) and C(15).
Cp2 is the centroid of C(21), C(22), C(23), C(24) and C(25).
Cp3 is the centroid of C(31), C(32), C(33), C(34) and C(35).
Cp4 is the centroid of C(41), C(42), C(43), C(44) and C(45).

techniques or a VAC Model HE 63P glovebox. Solvents were purified by distillation from an appropriate drying–deoxygenating agent (sodium–benzophenone for diethyl ether, sodium for toluene, and sodium–potassium alloy for hexane).

4,4,8,8-Tetramethyltetrahydro-4,8-disila-s-indacene [13], the metallocenes $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl_2]$ (M = Ti, Zr) [10], $[M\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me_2]$ (M = Ti, Zr) [10], and $LiCH_2CMe_2Ph$ [14] were prepared according to literature procedures.

LiMe (1.6 M solution in diethyl ether), MgClMe (1 M solution in THF), $MgCl(CH_2SiMe_3)$ (3 M solution in THF), $TiCl_4$, $ZrCl_4$, Na, Hg (Aldrich) were obtained commercially.

NMR spectra were recorded either on Varian Unity 300 and Varian Unity 500 Plus instruments (^1H and ^{13}C chemical shifts were referenced to external Me_4Si, δ = 0 ppm). IR spectra were performed (Nujol mulls) on a Perkin–Elmer 883 spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5890 spectrometer. Elemental C and H analysis were carried out on a Perkin–Elmer 240B microanalyzer.

3.1. *Synthesis of* $[\{Ti[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}O)]$ *(5)*

A solution of $[Ti\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me_2]$ **3** (0.5 g, 1.56 mmol) in toluene (50 ml) was treated with H_2O (28.1 μl, 1.56 mmol). The reaction mixture was stirred for 12 h. The solvent was completely removed in vacuo to give an orange solid. Recrystallization from toluene–hexane at −20 °C gave a microcrystalline solid characterized as **5** (0.24 g, 50% yield). Anal. Found: C, 57.3; H, 6.70. $C_{30}H_{42}OSi_4Ti_2$. Calc.: C, 57.49; H, 6.75%. Mass spectrum *m*/*z*: $M^+-[\{Ti[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]\}_2(\mu\text{-}O)]$ 15.7%; $M^+-[Ti\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}]$ (2.90%).

3.2. *Synthesis of* $[\{Zr[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}O)]$ *(6)*

A solution of $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Me_2]$ **4** (0.5 g, 1.37 mmol) in toluene (50 ml) was treated with H_2O (24.7 μl, 1.37 mmol). The reaction mixture was stirred for 12 h. The solvent was evaporated in vacuo to a volume of 10 ml and cooled at −20 °C to obtain a yellow solid which was recrystallized from toluene–hexane and characterized as **6**. (0.21 g, 43% yield). Anal. Found: C, 51.32; H, 5.71. $C_{30}H_{42}OSi_4Zr_2$. Calc.: C, 50.91; H, 5.93%. Mass spectrum *m*/*z*: $M^+-[\{Zr[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]\}_2(\mu\text{-}O)]$ (15.7%).

3.3. *Synthesis of* $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}ClMe]$ *(7)*

MgClMe (1.81 ml of a 1 M THF solution, 1.81 mmol) was added dropwise to a stirring solution of $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl_2]$ **2** (0.5 g, 1.24 mmol) in toluene (50 ml) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. After filtration, the solution was concentrated under vacuum to yield a white product, which was recrystallized from diethyl ether to yield a crystalline solid characterized as **7** (0.21 g, 45% yield). Anal. Found: C, 47.2; H, 5.63. $C_{15}H_{21}ClSi_2Zr$. Calc.: C, 46.9; H, 5.93%. Mass spectrum *m*/*z*: $[M]^+$ (7.08%).

3.4. *Synthesis of* $[Ti\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl(CH_2SiMe_3)]$ *(8)*

$MgCl(CH_2SiMe_3)$ (1.38 ml of a 1 M THF solution, 1.38 mmol) was added dropwise to a stirring solution of

$[Ti\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl_2]$ **1** (0.5 g, 1.38 mmol) in diethyl ether (50 ml) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. After filtration, the solution was evaporated to dryness and the resultant solid extracted into hexane. The white precipitate which formed was allowed to settle and was removed by filtration. The resulting solution was evaporated to yield an orange solid which was recrystallized from hexane at −30 °C and characterized as **8**. (0.37 g, 65% yield). Anal. Found. C, 51.90; H, 7.32; Cl, 7.98. $C_{18}H_{29}ClSi_3Ti$. Calc.: C, 52.35; H, 7.08; Cl, 8.58%. Mass spectrum m/z: $[M]^+-(CH_2SiMe_3)$ (14.10%).

3.5. *Synthesis of* $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl(CH_2CMe_2Ph)]$ *(9)*

A solution of $Li(CH_2CMe_2Ph)$ (0.19 g, 1.48 mmol) in diethyl ether (20 ml) was added dropwise to a stirring solution of $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl_2]$ **2** (0.3 g, 0.74 mmol) in diethyl ether (40 ml) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. After filtration, the solvent was completely removed in vacuo and the solid obtained extracted into hexane. The white precipitate which formed was allowed to settle and was removed by filtration. The resulting solution was evaporated to yield an orange solid which was recrystallized from hexane at −30 °C and characterized as **9**. (0.26 g, 63% yield). Anal. Found: C, 51.49; H, 5.23. $C_{24}H_{31}ClSi_2Zr$. Calc.: C, 51.43; H, 5.93%. Mass spectrum m/z: $[M^+]$ (12.1%).

3.6. *Synthesis of* $[\{Ti[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}Me)]^+$ *(10)*

A solution of $[CPh_3][B(C_6F_5)_4]$ (0.028 g, 0.0312 mmol) in CD_2Cl_2 (1.5 ml) at −78 °C was added to a solution of **3** (0.020 g, 0.062 mmol) in CD_2Cl_2 (2 ml) in an NMR tube at ca. −78 °C. The tube was sealed under vacuum at −78 °C and the reaction was studied by NMR spectroscopy.

3.7. *Synthesis of* $[\{Zr[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]Me\}_2(\mu\text{-}Me)]^+$ *(11)*

A solution of $[CPh_3][B(C_6F_5)_4]$ (0.025 g, 0.0275 mmol) in CD_2Cl_2 (1.5 ml) at −78 °C was added to a solution of **4** (0.020 g, 0.05 mmol) in CD_2Cl_2 (2 ml) in an NMR tube at ca. −78 °C. The tube was sealed under vacuum at −78 °C and the reaction was studied by NMR spectroscopy.

3.8. *Synthesis of* $[Ti\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}(\mu\text{-}Cl)]_2$ *(12)*

Toluene (60 ml) was added to a mixture of $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl_2]$ **2** (0.5 g, 1.38 mmol) and 10% sodium-amalgam (0.035 g, 1.52 mmol) at room temperature and then stirred for 12 h. An amber solution was formed. After filtration and complete removal of solvent in vacuo, a red-brown solid was obtained. Recrystallization from toluene–hexane at −35 °C gave a microcrystalline solid characterized as **12**. (0.33 g, 75% yield). Anal. Found: C, 51.23.; H, 5.96. $C_{14}H_{18}ClSi_2Ti$. Calc.: C, 51.60.; H, 5.58%.

3.9. *Synthesis of* $[Zr\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}(\mu\text{-}Cl)]_2$ *(13)*

Toluene (60 ml) was added to a mixture of $[Ti\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Cl_2]$ **1** (0.5 g, 1.24 mmol) and 10% sodium-amalgam (0.043 g, 1.9 mmol) at room temperature. The mixture was then stirred for 12 h. A purple solution was formed. After filtration and complete removal of solvent in vacuo, a red-brown solid was obtained. Recrystallization from toluene–hexane at −35 °C gave a microcrystalline solid characterized as **13**. (0.32 g, 70% yield). Anal. Found: C, 45.31; H, 5.28. $C_{14}H_{18}ClSi_2Zr$. Calc.: C, 45.55; H, 4.91%.

Table 5
Crystal data and structure refinement for **3**

Compound	**3**
Empirical formula	$TiSi_2C_{16}H_{24}$
Crystal size (mm^3)	0.2 × 0.2 × 0.3
Color	Red
Crystal habit	Prismatic
Formula weight	320.43
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	14.221(7)
b (Å)	16.755(1)
c (Å)	15.282(7)
β (deg)	108.96(2)
Volume (Å^3)	3443(2)
Z	8
Density(calc) (g cm^{-3})	1.236
Absorption coefficient (cm^{-1})	6.22
$F(000)$	1360
θ range for data collection (deg)	2.09 to 26.91
Index ranges	$-18 < h < 18, 0 < k < 11, 0 < l < 19$
Reflections collected	5632
Independent reflections	5275 ($R_{int} = 0.0492$)
Refl. observed with $I > 2\sigma(I)$	3369
Absorption correction	N/A
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5265/0/421
Goodness-of-fit on F^2	1.151
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0421$, $wR2 = 0.0980$
R indices(all data)	$R1 = 0.1247$, $wR2 = = 0.1766$
Largest diff. peak and hole (e Å^{-3})	0.283 and −0.239

Weighting scheme calc.: $w = 1/[\sigma^2(F_o^2)+(0.0499P)^2+2.1915P]$ where $P = (F_o^2+2F_c^2)/3$.

3.10. Crystal and structural data for 3

A suitable crystal of **3** was sealed in a Lindemann tube under an atmosphere of argon and mounted on an Enraf–Nonius CAD-4 automatic four-circle diffractometer with bisecting geometry and using a graphite-oriented monochromator, with Mo Kα radiation $\lambda = 0.71096$ Å. Crystallographic and experimental details are summarized in Table 5.

Data were collected at room temperature. Two check reflections were monitored every 120 min and showed no significant variation. Intensities were corrected for Lorentz and polarization effects in the usual manner. No extinction correction was made, and it was not necessary to apply an absorption correction.

The structure was solved by a combination of direct methods (SHELXS 90) [15] and Fourier synthesis and refined (on F^2) (SHELXL 93) [16] by full matrix least squares calculations.

All the non-hydrogen atoms were refined anisotropically. Most of the hydrogen atoms were found in the Fourier synthesis map and refined, with the exception of the silicon-bonded methyl hydrogens which were located using geometric calculations and refined using a riding model with a thermal parameter equivalent to that of the C atom to which they were attached. Calculations were performed on an Alpha AXP Digital workstation.

4. Supplementary material

The supplementary material includes a complete list of bond distances and angles, anisotropic thermal factors, the calculated fractional coordinates of the hydrogen atoms, and a list of observed and calculated structure factors.

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