In conclusion, we have prepared several interesting neutral and cationic derivatives of (EBTHI)ZrCl₂ and (EBTHI)HfCl₂. These compounds are potentially useful for the asymmetric synthesis of organic compounds.

Group 4 *ansa*-Metallocenes in Oxidation State III: Synthesis, Characterization, and Chemical Behavior. Crystal Structure of {[η⁵:η⁵-(C₅H₄)₂Si(CH₃)₂]TiCl(PMe₂Ph)}

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Two new dimeric titanium(III) and zirconium(III) *ansa*-metallocenes {[(Me₂SiCp₂)MCl]₂} (M = Ti (**2a**), Zr (**2b**)) were synthesized by reducing the dichlorometallocenes with Na/Hg. The same reduction of the titanium derivative in the presence of PMe₂Ph led to the monomeric titanium(III) complex [(Me₂SiCp₂)TiCl(PMe₂Ph)] (**3**), which was also obtained by addition of PMe₂Ph to **2a**. Alkylation of **3** led to the titanium(III) alkyls [(Me₂SiCp₂)TiR(PMe₂Ph)] (R = Me (**4**), CH₂SiMe₃ (**5**)). **4** was also obtained by reduction of [(Me₂SiCp₂)TiClMe] (**6**) with Na/Hg in the presence of PMe₂Ph. All the titanium(III) complexes were paramagnetic, and their EPR behavior was studied, whereas the diamagnetic zirconium(III) derivative was characterized by NMR spectroscopy. All of them are easily oxidized by oxygen, and the intermediate dimeric {(μ-O)[(Me₂SiCp₂)ZrCl]₂} (**7**) was spectroscopically identified in solution. The structure of **3** has been determined by X-ray diffraction methods. Crystals are triclinic, space group P1̄ with Z = 4 in a unit cell of dimensions a = 7.130 (3) Å, b = 15.201 (6) Å, c = 20.261 (6) Å, α = 105.42 (2)°, β = 96.20 (2)°, and γ = 92.46 (2)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 4449 observed reflections to R and R_w values of 0.0517 and 0.0696, respectively. The structure of **3** is very similar to that of comparable Ti(IV) compound [(Me₂SiCp₂)TiCl₂], except for the much longer Ti–Cl bond (2.463 (2) against 2.356 (1) and 2.379 (2) Å), whereas no significant modifications are induced into the dimethylsilyl bridge.

Introduction

The synthesis and structural characterization of dichloro *ansa*-metallocenes of group 4 metals in oxidation state IV ([X(C₅H₄)₂MCl₂], X = CH₂, C₂H₄, C₃H₆, R₂Si (R = Me, Et, *n*-Pr); M = Ti, Zr) have been extensively studied.[1]

A few alkyltitanium and -zirconium derivatives[2] with both cyclopentadienyl rings bridged by –CH₂CH₂– or Me₂Si groups as well some hydrido complexes[3] have also been reported.

In contrast, the chemistry of the *ansa*-metallocenes of the group 4 metals in low oxidation states has been scarcely studied in spite of the expected stabilization of low-valent titanium and zirconium complexes produced by using two cyclopentadienyl rings bridged by an interannular group which hinders the participation of the cyclopentadienyl ligands in reactions involving rings C–H activation processes.

Some studies on electrochemical reduction have been published,[1f,p,3a,4] but to the best of our knowledge, only one

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Scheme I

1a-b
M= Ti(a), Zr(b)   2a-b

Scheme II

Scheme III
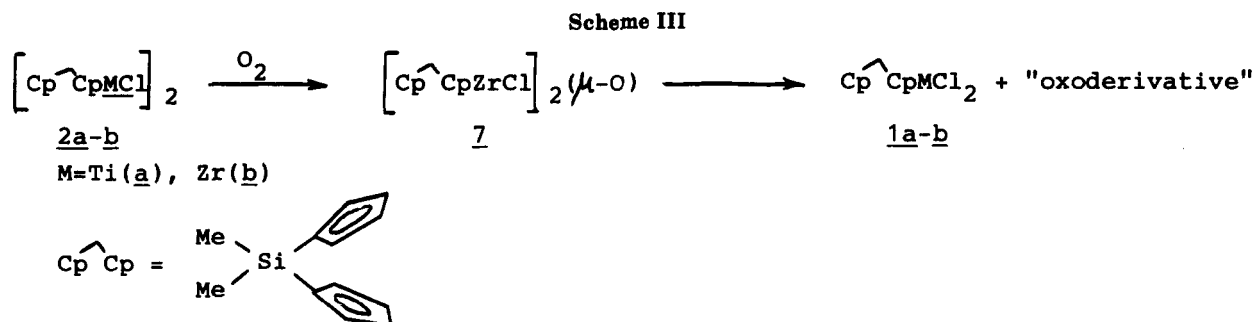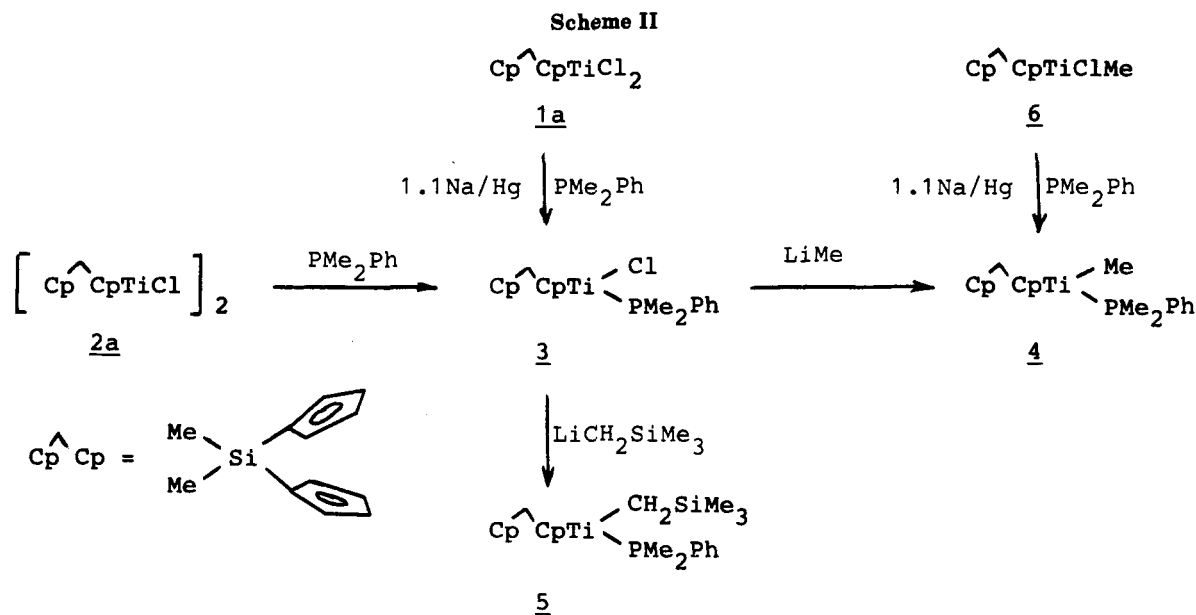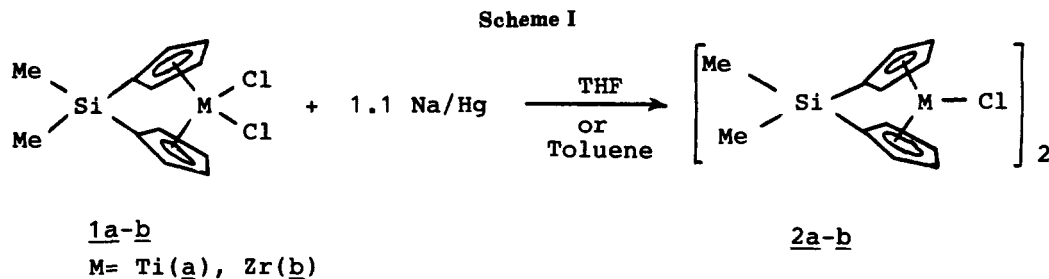
ansa-zirconocene(III) and other dicarbonyl *ansa*-titanocene(III) compounds have been characterized by NMR spectroscopy.[1e,3b]

We describe here the synthesis and characterization of new titanium(III) and zirconium(III) derivatives with the ligand $[\eta^5:\eta^5-(C_5H_4)_2Si(CH_3)_2]^{2-}$, some aspects of their chemical behavior, and the crystal structure of $\{[\eta^5:\eta^5-(C_5H_4)_2Si(CH_3)_2]TiCl(PMe_2Ph)\}$ (3).

Results and Discussion

The titanium and zirconium(III) chloro derivatives $\{[Me_2SiCp_2)MCl]_2\}$ (2a,b) were synthesized in 65-75% yield by reduction of the metal(IV) dichloro derivatives $[(Me_2SiCp_2)MCl_2]$ (1a,b) with 1 equiv of Na/Hg.

Compound 2a was obtained as a dark brown solid scarcely soluble in THF (see Experimental Section), whereas the red-violet compound 2b is much more soluble in THF and toluene.

Treatment of a suspension of 2a with PMe_2Ph in THF yielded $[(Me_2SiCp_2)TiCl(PMe_2Ph)]$ (3), as a green compound soluble in the usual solvents. The reaction of 3 with equivalent amounts of LiR (R = Me, CH_2SiMe_3) permits

the isolation of $[(Me_2SiCp_2)TiMe(PMe_2Ph)]$ (4) and $[(Me_2SiCp_2)Ti(CH_2SiMe_3)(PMe_2Ph)]$ (5) in yields near 50%. The same compounds 3 and 4 were also obtained in similar yields starting respectively from 1a and $[(Me_2SiCp_2)TiClMe]$ (6) by reduction with Na/Hg in the presence of PMe_2Ph.

All the titanium(III) and zirconium(III) derivatives described are oxygen and moisture sensitive, but they can be stored unchanged under nitrogen or argon for months. Complexes 2a,b react with chlorinated solvents such as CH_2Cl_2 or $CHCl_3$ to give 1a,b. More interesting is the reaction of 2a,b with oxygen. The red-violet 2b reacted immediately in solution, with oxygen giving a yellow solution, in which the presence of the oxozirconium(IV) complex 7 was spectroscopically identified by ^1H NMR analysis. However, this complex is immediately transformed into 1b and other unidentified products, probably some oxozirconium(IV) species. A similar behavior is also shown by 2a, but now the oxotitanium complex similar to 7 was not spectroscopically observed, and the reaction goes finally to the formation of 1a and some unidentified oxotitanium(IV) species.
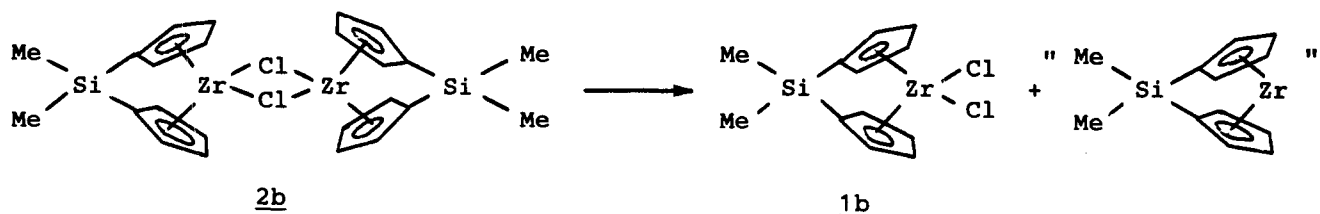
Scheme IV

2b ⟶ **1b**

Table I. EPR Data for Titanium(III) Complexes

compd	g	A, G	width, G
{[[Me$_2$Si(C$_5$H$_4$)$_2$]TiCl]$_2$}	1.9809	11.6	8.5
{[Me$_2$Si(C$_5$H$_4$)$_2$]TiCl(PMe$_2$Ph)}	1.9877	a	25
{[Me$_2$Si(C$_5$H$_4$)$_2$]TiMe(PMe$_2$Ph)}	1.9735	a	50
{[Me$_2$Si(C$_5$H$_4$)$_2$]Ti(CH$_2$SiMe$_3$)(PMe$_2$Ph)}	1.9756	a	75

^{a} Not observed.

2b is a diamagnetic compound. The ^{1}H NMR spectrum shows the dimethylsilylene protons as a singlet at δ 0.36 and the cyclopentadienyl ring protons as two pseudotriplets at δ 5.40 and 5.11, as expected for a typical AA'BB' system.

Recent studies[5] make clear that III is an unstable oxidation state for zirconium, which decomposes rapidly in solution, with disproportionation into zirconium(IV) and -(II). However, this process depends on the nature of the substituents[5e,6] and in some cases stable zirconium(III) derivatives can be isolated. A clear example is the synthesis of the fulvalene zirconium(III) complex {(μ-C$_{10}$H$_8$)[(η^5-C$_5$H$_5$)ZrCl]$_2$},[5a,f] which does not disproportionate either in the solid or in solution, whereas similar alkyl and aryl fulvalene derivatives cannot be isolated, as they are very easily disproportionated.[6]

In this way, the presence of two cyclopentadienyl rings bridged by an interannular group (Me$_2$Si in our complex) seems to be a reasonable strategy to stabilize the chloro zirconium(III) derivative. Nevertheless the ^{1}H NMR spectrum of complex **2b** in benzene-d_6 shows the presence of small amounts of **1b**, which must be formed by disproportionation of **2b**. This process is therefore more favorable for the ansa-metallocenes than for corresponding fulvalene derivatives but much less than for cyclopentadienyl compounds.

The structure of **7** must be similar to that found for [(μ-O)[(C$_5$H$_5$)$_2$ZrCl]$_2$].[7] However, the presence of two different substituents, Cl and μ-O, makes both methyl groups of the bridging Me$_2$Si fragment unequivalent and also transforms the AA'BB' rings into an ABCD system. The methyl protons for the SiMe$_2$ unit appear as two singlets at δ 0.30 and 0.41, and the cyclopentadienyl rings protons show four multiplets at δ 5.66, 5.89, 6.76, and 6.87. After $^1/_2$ h these signals disappear and new signals for **1b** are observed together with a yellow insoluble solid in the NMR tube. This is in agreement with the decomposition process shown in Scheme 3.

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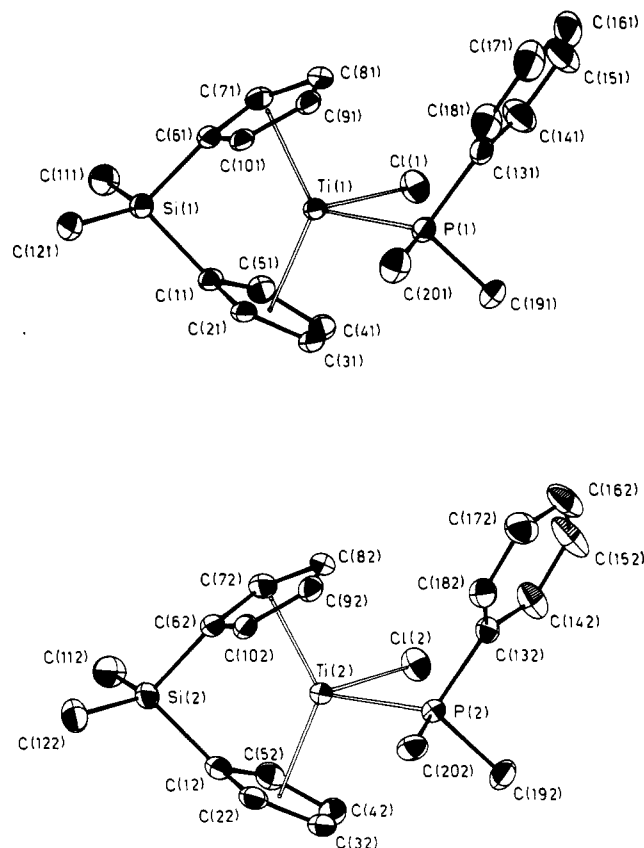
Figure 1. Perspective views of the molecular structure of the two independent complexes {[η^5:η^5-(C$_5$H$_4$)$_2$Si(CH$_3$)$_2$]TiCl(PMe$_2$Ph)} (3) with the atomic labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

The titanium(III) derivatives were characterized by EPR spectroscopy, and the structure of **3** was determined by X-ray diffraction methods (vide infra). The EPR spectra were recorded at room temperature in THF solution (ca. 10^{-3} M). Relevant data are summarized in Table I and are comparable to those reported for other titanium(III) derivatives.[1f,8]

The average g values found, in any case, are indicative of a considerable spin–orbit coupling corresponding to the location of the unpaired electron in the LUMO orbital, basically a metal-based orbital,[9] this contribution being more important for the alkyl derivatives.

Only for compound **2a** are satellites due to coupling with nonzero nuclear spin isotopes ^{47}Ti (I = $^5/_2$, natural abundance 7.28%) and ^{49}Ti (I = $^7/_2$, natural abundance 5.51%) observed, with a hyperfine structure containing eight lines (by the superposition of six and eight equidistant lines as implied by the same coupling constants A(^{47}Ti) and A-(^{49}Ti)). A broader signal with no hyperfine structure is observed for complexes **3–5**. The EPR spectra observed

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for our complexes do not show the Ti–P and Ti–H coupling, observed for some alkyl phosphine titanium(III) derivatives,[10] but not observed for complexes with PMe_2Ph.[11] The width of the signals depends strongly on the nature of the ligands and varied from 9.5 G for 2a to 75 G for 5.

Description of the X-ray Structure of {[Me₂Si-(C₅H₄)₂]TiCl(PMe₂Ph)} (3). The unit cell of 3 contains two crystallographically independent but essentially identical molecules. The structure of one of them is depicted in Figure 1 together with the atomic numbering scheme; the most important bond distances and angles are given in Table II. If the ring centroids are considered as coordination sites, the coordination geometry around titanium is a distorted tetrahedron, the other two coordination sites being occupied by the chlorine atom and by the phosphorus atoms from the PMe_2Ph ligand. This geometry is very similar to that observed for titanocene derivatives of this type.[1f] The examination of the structural parameters involving the cyclopentadienyl rings indicates that the Ti–C bonds are not quite equal, the ones with C(3) and C(4) and with C(8) and C(9) are slightly longer than those with C(1), C(2), and C(5) and with C(6), C(7), and C(10), suggesting that the ring carbon atoms interact with the metal in a slightly asymmetric η^5-fashion (probably determined by the dimethylsilyl bridge). The distances between the metal and the centroids of the cyclopentadienyl rings are 2.067 (5) and 2.066 (5) Å [2.066 (6) and 2.054 (6) Å, hereafter the values in brackets refer to the second independent molecule]. The cyclopentadienyl rings are planar, with the Si atom deviating from the mean plane through them by 0.626 (2) and 0.656 (3) Å [0.659 (2) and 0.647 (3) Å], because of the strain due to the interannular bridge, which induces also slightly pyramidal configurations at the C(1) and C(6) atoms (the bond angles at them being 354.5 and 353.8° [353.7 and 354.1°]). The C–C distances within the two cyclopentadienyl rings range from 1.391 (9) to 1.433 (7) Å [1.376 (9) to 1.433 (8) Å] with the two C–C bonds to the bridgehead carbons, C(1) and C(6), longer than the other three. The ring centroid–Ti ring centroid angle, 132.2 (3)° [131.5 (3)°], and the dihedral angle between the mean planes of the rings, 53.4 (2)° [52.5 (2)°], are related to the degree of canting of the rings. As a consequence of the rather narrow bite of the dimethylsilyl bridge, the bridgehead carbons are the two carbons of closest approach, 2.711 (6) Å [2.702 (7) Å].

The values of the Ti–Cl and Ti–P bond distances are 2.463 (2) and 2.612 (2) Å [2.464 (2) and 2.604 (2) Å] with a very narrow Cl–Ti–P angle, 82.0 (1)° [82.4 (1)°], probably caused by the steric demand of the PMe_2Ph ligand with respect to the carbon atoms of the cyclopentadienyl rings, as shown by the rather short contacts between the P atom and C(3) and C(9) atoms, 3.202 (6) and 3.154 (6) Å [3.177 (6) and 3.179 (7) Å]. The value of the Ti–P bond distance is a little longer than those found in the other Ti(III) compound $Ti(BH_4)_3(PMe_3)_2$, 2.571 (3) and 2.539 (3) Å, even if in this compound the titanium atom displays a trigonal-bipyramidal geometry.[12]

It is noteworthy to compare the structural parameters of 3 with those of {[η⁵:η⁵-(C₅H₄)₂Si(CH₃)₂]TiCl₂},[1f] from which 3 can be derived by replacing a chlorine atom with the PMe_2Ph ligand, in order to evaluate the effect of the

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Table II. Important Interatomic Distances (Å) and Angles (deg) for 3[a]

	molecule 1	molecule 2
Bond Distances		
Ti–Cl	2.463 (2)	2.464 (2)
Ti–P	2.612 (2)	2.604 (2)
Ti–C(1)	2.346 (5)	2.364 (5)
Ti–C(2)	2.375 (5)	2.385 (6)
Ti–C(3)	2.443 (5)	2.443 (6)
Ti–C(4)	2.427 (5)	2.413 (7)
Ti–C(5)	2.353 (5)	2.345 (6)
Ti–C(6)	2.357 (5)	2.351 (6)
Ti–C(7)	2.359 (6)	2.326 (6)
Ti–C(8)	2.426 (5)	2.384 (5)
Ti–C(9)	2.437 (5)	2.441 (6)
Ti–C(10)	2.371 (5)	2.387 (6)
Ti–CE(1)	2.067 (5)	2.066 (6)
Ti–CE(2)	2.066 (5)	2.054 (6)
Si–C(1)	1.859 (6)	1.862 (6)
Si–C(6)	1.868 (5)	1.855 (5)
C(1)–C(2)	1.427 (8)	1.430 (9)
C(2)–C(3)	1.400 (8)	1.400 (11)
C(3)–C(4)	1.391 (9)	1.398 (12)
C(4)–C(5)	1.395 (9)	1.406 (11)
C(5)–C(1)	1.421 (8)	1.428 (9)
C(6)–C(7)	1.433 (7)	1.433 (8)
C(7)–C(8)	1.413 (9)	1.427 (9)
C(8)–C(9)	1.400 (9)	1.376 (9)
C(9)–C(10)	1.393 (7)	1.385 (8)
C(10)–C(6)	1.428 (8)	1.430 (8)
Si–C(11)	1.849 (8)	1.853 (8)
Si–C(12)	1.846 (7)	1.865 (8)
P–C(13)	1.844 (5)	1.821 (5)
P–C(19)	1.832 (7)	1.846 (7)
P–C(20)	1.826 (7)	1.820 (6)
Bond Angles		
Cl–Ti–P	82.0 (1)	82.4 (1)
Cl–Ti–CE(1)	107.8 (2)	109.0 (2)
Cl–Ti–CE(2)	109.2 (2)	108.4 (2)
P–Ti–CE(1)	107.7 (2)	107.3 (2)
P–Ti–CE(2)	106.5 (2)	107.2 (2)
CE(1)–Ti–CE(2)	132.2 (3)	131.5 (3)
C(1)–Si–C(6)	93.3 (3)	93.3 (3)
C(1)–Si–C(11)	113.3 (3)	113.2 (3)
C(1)–Si–C(12)	112.3 (3)	112.8 (3)
C(6)–Si–C(11)	110.6 (3)	111.5 (3)
C(6)–Si–C(12)	113.2 (3)	112.2 (3)
C(11)–Si–C(12)	112.7 (3)	112.5 (3)
Ti–P–C(13)	117.9 (2)	116.7 (2)
Ti–P–C(19)	114.6 (3)	114.7 (2)
Ti–P–C(20)	112.9 (3)	114.7 (2)
C(13)–P–C(19)	101.3 (3)	102.3 (3)
C(13)–P–C(20)	104.0 (3)	104.0 (3)
C(19)–P–C(20)	104.6 (4)	102.7 (3)
Si–C(1)–C(2)	123.2 (4)	123.5 (5)
Si–C(1)–C(5)	125.7 (4)	124.8 (5)
C(2)–C(1)–C(5)	105.6 (5)	105.4 (6)
Si–C(6)–C(7)	125.0 (4)	125.2 (5)
Si–C(6)–C(10)	123.0 (4)	123.5 (4)
C(7)–C(6)–C(10)	105.8 (5)	105.4 (5)

[a] Estimated standard deviations are given in parentheses. CE(1) and CE(2) are the centroids of the C(1)···C(5) and C(6)···C(10) rings, respectively.

change of the oxidation state of titanium. The main difference concerns the Ti–Cl bond, 2.356 (1) and 2.379 (2) Å, much shorter than in 3 and comparable to those of about 2.35 Å found in similar bridge dichloride compounds {[CH₂)ₙ(C₅H₄)₂]TiCl₂} (n = 1–3).[1f] A comparable lengthening of the Ti–Cl bond has been observed when a chlorine atom is substitued by the pyridine ligand in the compounds [Ti(salen)Cl₂]·THF[13] and [Ti(salen)Cl(py)]·THF[14]

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(salen = *N,N′*-ethylenebis(salicylidenaminato), 2.418 (4) against 2.346 (2) Å. On the contrary, no significant modifications can be noted in the bonding of the metal with the bridging ligand. In fact the Ti–C distances in $\{[\eta^5:\eta^5-(C_5H_4)_2Si(CH_3)_2]TiCl_2\}^{1f}$ are practically equal and have the same trend as in 3; i.e. the ones involving C(3) and C(4), 2.436 (2) and 2.432 (2) Å, are longer than those involving the others, 2.379 (2), 2.366 (2), and 2.356 (2) Å, the distance between titanium and the centroid of the ring is 2.075 (5), and the degree of canting of the cyclopentadienyl rings is not influenced, the ring centroid–Ti ring centroid angle being only slightly narrower, 128.7 (1)° and the dihedral angle between the mean planes of the rings 51.2° being only slightly narrower. The substitution of one chloride by a PMe$_2$Ph ligand influences also the angle at the two terminal ligands, so the Cl–Ti–Cl angle, 95.7 (1)°, is much larger than the P–Ti–Cl one in 3.

Experimental Section

All operations were performed under dry nitrogen by use of Schlenk techniques. Solvents were distilled under nitrogen, dried by standard methods, and degassed before use. EPR spectra were obtained on a Bruker E.R.200TT spectrometer equipped with EIP frequency meter, Bruker NMR gauss meter, and Oxford cryostat accessories with THF used as solvent. ^{1}H and ^{13}C NMR spectra were recorded on Varian FT-80 A and Varian UNITY 300 instruments. IR spectra were obtained as Nujol mulls in a 883 Perkin-Elmer spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240B microanalyzer.

The starting complexes $\{[Me_2Si(C_5H_4)_2]MCl_2\}$ (M = Ti, Zr) were synthesized as described elsewhere.^{1f} Na, Mg (Ventron), PMe$_2$Ph (Strem Chemicals), and LiMe (Aldrich) were obtained commercially and LiCH$_2$SiMe$_3$ was prepared by literature methods.^{15}

Synthesis of $\{[[Me_2Si(C_5H_4)_2]TiCl]_2\}$ (2a). A mixture of 0.5 g (1.64 mmol) of $\{[Me_2Si(C_5H_4)_2]TiCl_2\}$ and 0.042 g (1.80 mmol) of 10% sodium amalgam in 40 mL of THF was stirred for 0.5 h. A pink brownish precipitate was formed, and the brown solution was filtered. The precipitate was extracted several times with fresh THF. All fractions were collected together and evaporated to give 0.287 g (yield 65%) of complex 1 as a pink brownish microcrystalline solid. Anal. Calcd for C$_{24}$H$_{28}$Cl$_2$Si$_2$Ti$_2$: C, 53.45; H, 5.23. Found: C, 52.85; H, 5.17.

Synthesis of $\{[[Me_2Si(C_5H_4)_2]ZrCl]_2\}$ (2b). A mixture of 0.5 g (1.43 mmol) of $\{[Me_2Si(C_5H_4)_2]ZrCl_2\}$ and 0.036 g (1.57 mmol) of sodium amalgam in 50 mL of toluene was stirred for 12 h. After this, a deep red solution was formed, which was filtered and evaporated in vacuo, resulting 0.322 g (75%) of complex 2 as a red violet crystalline solid. ^{1}H NMR spectrum (80 MHz, C$_6$D$_6$, 28 °C): δ 0.36 (s, 6 H, SiMe$_2$), 5.11 (t, *J* = 2.48 Hz, 4 H$_\alpha$, C$_5$H$_4$), 5.40 (t, *J* = 2.48 Hz, 4 H$_\beta$, C$_5$H$_4$). Anal. Calcd for C$_{24}$H$_{28}$Cl$_2$Si$_2$Zr$_2$: C, 46.05; H, 4.51. Found: C, 43.83; H, 4.47.

Synthesis of $\{[Me_2Si(C_5H_4)_2]TiCl(PMe_2Ph)\}$ (3). Method a. A 0.092-mL (0.649 mmol) aliquot of PMe$_2$Ph was added at room temperature to a suspension of 0.350 g (0.649 mmol) of $\{[[Me_2Si(C_5H_4)_2]TiCl]_2\}$ in 50 mL of dry toluene. The mixture changed immediatly to green. After filtration the solvent was removed in vacuo to give 0.227 g (yield 86%) of complex 3 as pale green crystals.

Method b. A mixture of 0.5 g (1.64 mmol) of $\{[Me_2Si(C_5H_4)_2]TiCl_2\}$, 0.042 g (1.80 mmol) of 10% sodium amalgam, and 0.25 mL (1.80 mmol) of PMe$_2$Ph in 60 mL of toluene was stirred at room temperature until the solution became pale green. The solution was filtered, concentrated in vacuo, and cooled to –20 °C to give complex 3 as pale green crystals. Yield: 0.453 g (67.8%). Anal. Calcd for C$_{20}$H$_{25}$ClPSiTi: C, 58.90; H, 6.18. Found: C, 58.84; H, 6.40.

Synthesis of $\{[Me_2Si(C_5H_4)_2]TiMe(PMe_2Ph)\}$ (4). Method a. A 0.5-mL (0.8 mmol) aliquot of a 1.6 M solution of methyllithium in diethylether was added to a solution of 0.320 g (0.785 mmol) of $\{[Me_2Si(C_5H_4)_2]TiCl(PMe_2Ph)\}$ in 50 mL of dry toluene

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Table III. Summary of Crystallographic Data for 3

formula	C$_{20}$H$_{25}$ClPSiTi	Z	4
mol wt	407.83	D_{calcd}, g cm^{-3}	1.291
cryst syst	triclinic	$F(000)$	852
space group	P$\bar{1}$	cryst size, mm	0.15 × 022 × 028
λ(Ni-filtered Cu Kα radiation), Å	1.541 838	μ(Cu Kα), cm^{-1}	59.56
		2θ range, deg	6–140
		reflns measd	h,±k,±l
a, Å	7.130 (3)	no. of unique total data	7988
b, Å	15.201 (6)		
c, Å	20.261 (6)	no. of unique obsd data	4449
α, deg	105.42 (2)		
β, deg	96.20 (2)	$[I > 2\sigma(I)]$	
γ, deg	92.46 (2)	R	0.0517
V, Å^{-3}	2099 (1)	R_w	0.0696

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) with Esd's in Parentheses for the Non-Hydrogen Atoms of 3

	x/a	y/b	z/c	U^a
		Molecule 1		
Ti(1)	4185 (1)	3069 (1)	7035 (1)	40.7 (3)
Cl(1)	7589 (2)	2888 (1)	7270 (1)	72.5 (6)
P(1)	4030 (2)	2331 (1)	8056 (1)	51.1 (5)
Si(1)	1901 (2)	3886 (1)	5917 (1)	51.8 (5)
C(11)	2510 (7)	2711 (3)	5924 (3)	47.4 (18)
C(21)	1578 (8)	2180 (3)	6294 (3)	49.3 (18)
C(31)	2788 (8)	1532 (4)	6431 (3)	56.6 (20)
C(41)	4473 (9)	1650 (4)	6166 (3)	64.4 (23)
C(51)	4324 (8)	2368 (4)	5859 (3)	59.0 (23)
C(61)	2897 (7)	4392 (3)	6839 (3)	46.1 (20)
C(71)	4867 (8)	4618 (3)	7082 (3)	55.3 (21)
C(81)	5182 (9)	4589 (4)	7776 (3)	62.3 (24)
C(91)	3445 (9)	4342 (3)	7965 (3)	57.3 (22)
C(101)	2058 (8)	4206 (3)	7401 (3)	49.0 (18)
C(111)	3231 (10)	4368 (4)	5343 (3)	80.5 (30)
C(121)	–674 (9)	3968 (4)	5757 (3)	73.2 (25)
C(131)	5119 (10)	2999 (4)	8922 (3)	63.0 (24)
C(141)	7040 (12)	3241 (6)	9021 (4)	97.4 (36)
C(151)	7893 (14)	3752 (6)	9663 (4)	117.0 (44)
C(161)	6903 (17)	4032 (6)	10195 (4)	122.1 (49)
C(171)	5009 (17)	3834 (7)	10105 (4)	120.2 (44)
C(181)	4101 (13)	3303 (5)	9471 (4)	94.1 (37)
C(191)	5209 (10)	1264 (4)	7958 (4)	76.6 (28)
C(201)	1612 (9)	2032 (5)	8182 (4)	83.2 (33)
		Molecule 2		
Ti(2)	387 (1)	1839 (1)	2702 (1)	46.3 (3)
Cl(2)	3023 (2)	1606 (1)	1996 (1)	73.6 (7)
P(2)	–914 (2)	2669 (1)	1797 (1)	50.0 (5)
Si(2)	–128 (2)	1184 (1)	4052 (1)	56.1 (6)
C(12)	818 (8)	2278 (4)	3921 (3)	56.5 (21)
C(22)	–352 (10)	2920 (4)	3712 (3)	66.9 (24)
C(32)	695 (13)	3438 (4)	3382 (3)	83.0 (32)
C(42)	2509 (12)	3124 (5)	3365 (4)	87.8 (34)
C(52)	2598 (10)	2410 (4)	3686 (3)	71.1 (28)
C(62)	–934 (8)	680 (3)	3120 (3)	50.4 (18)
C(72)	256 (9)	279 (4)	2611 (3)	61.9 (22)
C(82)	–615 (10)	354 (4)	1962 (3)	67.3 (26)
C(92)	–2266 (9)	782 (4)	2056 (3)	60.2 (22)
C(102)	–2471 (8)	995 (4)	2752 (3)	55.7 (21)
C(112)	1732 (10)	530 (5)	4370 (4)	81.1 (29)
C(122)	–2137 (10)	1335 (5)	4580 (3)	81.9 (31)
C(132)	–1524 (8)	1964 (4)	913 (3)	54.0 (22)
C(142)	–84 (11)	1643 (5)	516 (3)	86.0 (30)
C(152)	–525 (14)	1069 (6)	–136 (4)	114.1 (45)
C(162)	–2354 (14)	791 (6)	–417 (4)	105.3 (40)
C(172)	–3786 (12)	1094 (5)	–38 (4)	89.7 (33)
C(182)	–3354 (10)	1685 (4)	625 (3)	70.8 (28)
C(192)	727 (9)	3580 (4)	1691 (4)	75.2 (26)
C(202)	–3036 (8)	3261 (4)	1991 (3)	68.5 (28)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U$_{ij}$ tensor.

at –78 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The resulting dark red solution was filtered to eliminate the insoluble LiCl, and the solvent was removed in vacuo to give 0.128 g (42.3% yield) of complex 4 as a dark red microcrystalline solid.

Method b. A mixture of 0.410 g (1.44 mmol) of {[Me₂Si-(C₅H₄)₂]TiClMe}, 0.036 g (1.58 mmol) of 10% sodium amalgam, and 0.22 mL (1.58 mmol) of PMe₂Ph in 60 mL of toluene was stirred at –78 °C, allowed to warm to room temperature, and stirred for 12 h more. The resulting dark red solution was filtered and the solvent removed in vacuo, yielding 0.325 g (58.5%) of **4** as a dark red crystalline solid (being air sensitive, no elemental analysis was performed).

Synthesis of {[Me₂Si(C₅H₄)₂]Ti(CH₂SiMe₃)(PMe₂Ph)} (5). A 0.094-g (1 mmol) sample of LiCH₂SiMe₃ in toluene was added to a solution of 0.370 g (0.90 mmol) of {[Me₂Si(C₅H₄)₂]TiCl-(PMe₂Ph)} in toluene at –78 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The dark red solution was filtered and evaporated in vacuo, to give 0.193 g (46.6% yield) of complex **5** as a dark red crystalline solid (being air sensitive, no elemental analysis was performed).

X-ray Data Collection, Structure Determination, and Refinement for {[Me₂Si(C₅H₄)₂]TiCl(PMe₂Ph)} (3). A single crystal of **3** was sealed in Lindemann glass capillary under dry nitrogen and used for data collection. The crystallographic data are summarized in Table III. Unit cell parameters were determined from the θ values of 30 carefully centered reflections, having $25 < \theta < 40°$. Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the nickel-filtered Cu Kα radiation and the $\theta/2\theta$ scan type. The reflections were collected with a variable scan speed of 3–12° min⁻¹ and a scan width from $(\theta - 0.6)°$ to $(\theta + 0.6 + 0.142 \tan \theta)°$. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following Lehmann and Larsen.[16] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.2623 and 0.7750).[17] Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic thermal

parameters and then with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed at their geometrically calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 437 variables; after the last cycles, no parameters shifted by more than 0.32 esd. The biggest remaining peak in the final difference maps was equivalent to about 0.42 e/ų. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used; at convergence the K and g values were 0.3643 and 0.0068, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 18. All calculations were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the GOULD POWER-NODE 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[19] The final atomic coordinates for the non-hydrogen atoms are given in Table IV. The atomic coordinates of the hydrogen atoms and the thermal parameters are given in the supplementary material.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, principal axes of the thermal ellipsoids, bond distances and angles, least-squares planes, and interatomic contacts (33 pages); a listing of observed and calculated structure factors from the final cycle of least-squares refinement (27 pages). Ordering information is given on any current masthead page.

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Reactivity of Dianionic Hexacoordinate Germanium Complexes toward Organometallic Reagents. A New Route to Organogermanes[†]

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Lithium and potassium tris(benzene-1,2-diolato)germanates (**2a** and **2b**, respectively) and potassium tris(butane-2,3-diolato)germanate (**3**) are easily prepared from GeO₂ in quantitative yields. They are very reactive toward organometallic reagents, the reactivity depending on the ligands on the germanium. Complexes **2** react with an excess of Grignard reagent to give the corresponding tetraorganogermanes R₄Ge while the less reactive complex **3** leads to the functional triorganogermanes R₃GeX. Tetraorganogermanes can also be prepared from complex **2b** by reaction with organic bromides in the presence of Mg (Barbier reaction). The influence of Cp₂TiCl₂ and MgBr₂ on the reactivity of Grignard reagents with these complexes was also investigated: in both cases formation of triorganogermanes was favored.

Introduction

We have shown recently that the hypervalent silicon complexes **1**, though negatively charged, react with organometallic reagents to give organosilanes[2] (Scheme I).

The reactivity of these complexes depends on the cation, the lithium complex being much less reactive than the sodium or potassium complexes.[3]

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[†]For a preliminary communication, see ref 1.