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Double-Dimethylsilyl-Bridged Dicyclopentadienyl Group 4 Metal Complexes. X-ray Molecular Structures of $M[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]Cl_2$ (M = Ti, Zr) and $(TiCl_3)_2\{\mu\text{-}[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]\}$

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The synthesis of the dithallium salt of the double-dimethylsilyl-bridged dicyclopentadienyl ligand $Tl_2[(Me_2Si)_2(C_5H_3)_2]$ (1) is described. The reaction of 1 with 1 equiv of MCl_4 (M = Ti, Zr, Hf) by refluxing their toluene solutions leads to the metallocene-type species $M[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]Cl_2$ (M = Ti (2), Zr (3), Hf (4)) in 65–70% yields. Complexes 2–4 are methylated by MeLi or MeMgCl leading to the dimethylmetallocenes $M[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]Me_2$ (M = Ti (5), Zr (6), Hf (7)) in 70% yields. When the same reaction of 1 with $TiCl_4$ is carried out in a 1:2 molar ratio at room temperature, the monocyclopentadienyl-type species $(TiCl_3)_2\{\mu\text{-}[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]\}$ (8) is obtained. The ^1H and ^{13}C NMR data are discussed in terms of establishing useful criteria to distinguish between species containing chelated and bridging cyclopentadienyl ligands and comparing electronic effects due to the double-silyl-bridged system. The X-ray crystal structures of complexes 2, 3, and 8 are described. Complexes 2 and 3 are metallocene-type compounds: 2 crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.483(2)$ Å, $b = 11.558(6)$ Å, $c = 14.892(5)$ Å, $\beta = 91.92(1)°$, $V = 1631(1)$ Å^3, and $Z = 4$. 3 crystallizes in the same space group with $a = 9.392(3)$ Å, $b = 13.863(4)$ Å, $c = 13.376(4)$ Å, $\beta = 101.82(1)°$, $V = 1704(1)$ Å^3, and $Z = 4$. Compound 8 is a dinuclear complex with the metals in trans position relative to the ligand plane. 8 crystallizes with a toluene molecule in the monoclinic space group $P2_1/c$ with $a = 11.339(2)$ Å, $b = 11.292(3)$ Å, $c = 14.006(3)$ Å, $\beta = 105.08(1)°$, $V = 1732(1)$ Å^3, and $Z = 4$.

Introduction

ansa-Metallocene complexes of the early transition metals have received a 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. This feature helps to stabilize lower oxidation states, as it has already been reported for several titanium and zirconium(III) compounds.[2] Chiral *ansa*-metallocenes containing a C_2 symmetrical arrangement of ring substituents have also proven to be effective precursors for generating Ziegler–Natta catalysts to induce isotacticity in the polymerization of propylene and other α-olefines.[3]

We were interested in isolating and studying the reactivity of cyclopentadienyl group 4 metal complexes by using the bis(dimethylsilyl)dicyclopentadienyl dianion, $[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]^{2-}$, as a ligand to increase the stereorigidity of the complex. Different mono- and oligonuclear transition metal derivatives containing this ligand have been reported,[4] but few group 4 metal complexes are known. Recently, Brintzinger[5] has described the synthesis and crystal structure of double-dimethylsilyl-bridged chiral zirconocene complexes by using vicinal disubstituted cyclopentadienyl rings.

Here we report the synthesis of the dithallium salt of the doubly bridged bis(dimethylsilyl)dicyclopentadienyl ligand and the preparation and structural characterization of $M[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]X_2$ (M = Ti, Zr, Hf; X = Cl, Me) and $(TiCl_3)_2\{\mu\text{-}[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]\}$.

Results and Discussion

Synthetic and NMR Studies. Deprotonation of 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene[6] can give either the cyclopentadienylcyclopentadiene monoanion or the dicyclopentadienyl dianion depending on the choice of deprotonating agents. When the mixture of the

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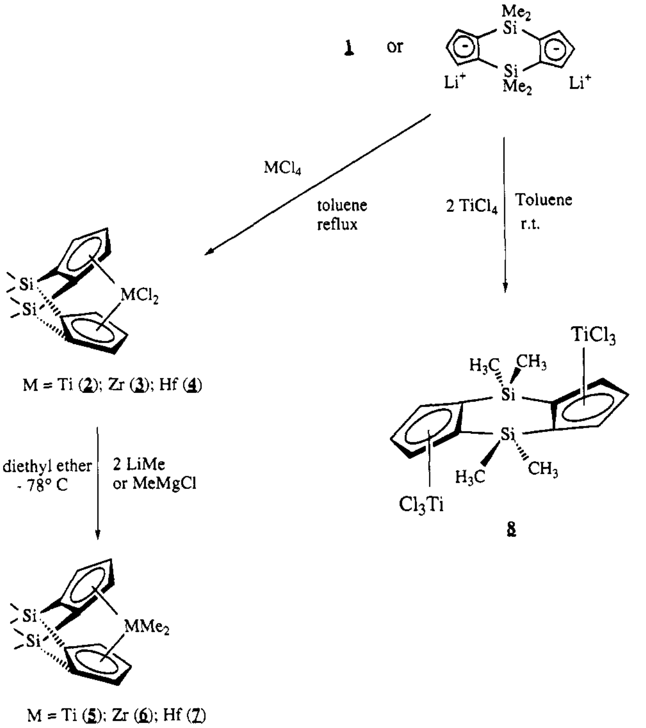
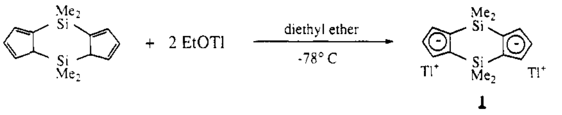
Scheme 1



cis and *trans* isomers of 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene is reacted with 2 equiv of thallium ethoxide in diethyl ether, a white precipitate of the insoluble dithallium salt 1 is obtained in 95% yield (reaction 1).



(1)

Heating under reflux a toluene solution of the metal tetrachlorides MCl_4 (M = Ti, Zr, Hf) treated with stoichiometric amounts of 1 leads to the isolation of the mononuclear metallocene derivatives $M[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]Cl_2$ (M = Ti (**2**), Zr (**3**), Hf (**4**)) in 65–70% yields. Complexes **2**–**4** react in diethyl ether with 2 equiv of MeLi or MeMgCl to give the dimethyl derivatives $M[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]Me_2$ (M = Ti (**5**), Zr (**6**), Hf (**7**)) in 70% yields. However, when **1** is added to a toluene solution of $TiCl_4$ in a Tl/Ti molar ratio 1/2 at room temperature, the dinuclear complex $(TiCl_3)_2[\mu\text{-}\{(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2\}]$ (**8**) results as a dark red solid in 75% yield (Scheme 1).

The chloro complexes **2**–**4** are soluble in aromatic hydrocarbons (benzene, toluene), dichloromethane, chloroform, and THF, scarcely soluble in diethyl ether, and insoluble in alkanes (hexane). They are air-stable compounds in the solid and slowly hydrolyzed in solution. The dinuclear complex **8** shows a similar solubility, but it is much more air sensitive. The dimethyl complexes **5**–**7** are more soluble, dissolving even in diethyl ether, and are air sensitive in solution and in the solid, although they can be stored unaltered for weeks under dry argon.

^1H and ^{13}C NMR spectra of complexes **2**–**8** in $CDCl_3$ and C_6D_6 are summarized in Table 1, assignments being referred to the labeling shown in it.

All the mononuclear complexes show a pseudo-doublet for the equivalent H_1 and a pseudo-triplet for H_2 protons (J_{H-H} = 2.7–2.9 Hz for Ti and Zr; J_{H-H} = 1.3–1.4 Hz for Hf), indicating the existence of a plane of symmetry. The pseudo-doublet (H_1) is observed at lower fields than the pseudo-triplet (H_2) for all the mono and dinuclear complexes **2**–**4** and **6**–**8**, whereas the reverse behavior is shown by the dimethyltitanium compound **5**. In contrast, the ^{13}C resonance of C_1 appears consistently downfield ($\sim\delta$ 130–145) from those due to the C_2 and C_3 for all the mononuclear compounds. The ^{13}C resonance of the *ipso*-carbon, C_3, appears downfield from that of C_2 for the mononuclear chloro complexes **2**–**4**, with the reverse relationship observed for the methyl derivatives **5**–**7**. $\Delta(\delta(C_3)-\delta(C_2))$ is higher for titanium (9–13 ppm) than for zirconium and hafnium derivatives (1–2 ppm). All these results are the consequence of the different electron donor capacity of the metal substituents and the electron charge distribution on the rings imposed by the presence of two dimethylsilyl groups bound to vicinal ring carbon atoms.

For the dinuclear complex **8**, the ^{13}C resonance of the *ipso*-carbon atom C_3 (δ 141.9) is located downfield from those corresponding to C_1 (δ 132.7) and C_2 (δ 129.7). This behavior is the reverse to that observed for all the mononuclear complexes. This difference cannot be used, however, as a criterion[4d,f] to distinguish between chelating and bridging disposition of the rings in complexes with the bis(dimethylsilyl)dicyclopentadienyl ligand. The same criterion has been suggested[7] to predict the chelating or bridging dispositions of both cyclopentadienyl rings of mono-*ansa*-(dimethylsilyl)dicyclopentadienyl, $[Me_2Si(\eta^5\text{-}C_5H_4)_2]$, metal compounds, but we have also recently found[8] exceptions to this general rule. For these mono-*ansa* compounds, another criterion also used[7] to make such a type of prediction is based on the comparative values of $\Delta\delta = \delta_d - \delta_p$ (δ_d and δ_p being the chemical shifts of the distal and proximal protons with respect to the bridging head carbon atom). When a similar parameter $\Delta\delta = \delta_1 - \delta_2$ (δ_1 and δ_2 being the chemical shifts of the H_1 and H_2 proton resonances, respectively) is used for complexes containing the double-*ansa*-dicyclopentadienyl ligand, the chelated mononuclear complex **2** shows a value (0.22) lower than that for the bridged dinuclear complex **8** (0.44), which is the reverse behavior observed for compounds containing the mono-*ansa* ligand. The mononuclear zirconium and hafnium complexes **3**, **4** and **6**, **7** show higher $\Delta\delta$ values than the titanium derivatives, as it is also observed for complexes containing the mono-*ansa* ligand.

When the bis(dimethylsilyl)dicyclopentadienyl ligand adopts the disposition which favors the chelated metallocene structure of all the mononuclear complexes, two ^1H resonances due to methyl groups bound to silicon are observed. This indicates that the two methyl groups bound to each silicon are not equivalent, because they are located in *exo* (Me_1 and Me_1') and *endo* (Me_2 and Me_2') positions, as shown in Figure 1A. The two equivalent *endo* methyl groups undergo a better shielding by the field induced by the π-conjugated ring systems and therefore give the higher field signal.[9]

However when both cyclopentadienyl rings swing around the Si–C bond axis, the ligand adopts the conformation represented in Figure 1B, which avoids the chelation and favors the bridging disposition by bonding two different

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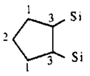
Table 1. NMR Data (δ) for the Bis(dimethylsilyl)-Bridged Complexes[a]

	^{1}H NMR		^{13}C NMR	
compd	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
2	0.42 (s, 6H, Me–Si)	0.10 (s, 6H, Me–Si)	–5.34 (Me–Si)	
	0.92 (s, 6H, Me–Si)	0.39 (s, 6H, Me–Si)	1.84 (Me–Si)	
	6.74 (t, 2H, C_5H_3)	6.60 (t, 2H, C_5H_3)	122.5 [$C_2(C_5H_3)$]	
	6.96 (d, 4H, C_5H_3)	6.84 (d, 4H, C_5H_3)	135.5 [$C_3(C_5H_3)$]	
			145.3 [$C_1(C_5H_3)$]	
3	0.54 (s, 6H, Me–Si)	0.23 (s, 6H, Me–Si)	–4.86 (Me–Si)	
	0.92 (s, 6H, Me–Si)	0.45 (s, 6H, Me–Si)	1.83 (Me–Si)	
	6.45 (t, 2H, C_5H_3)	6.21 (t, 2H, C_5H_3)	114.4 [$C_2(C_5H_3)$]	
	6.94 (d, 4H, C_5H_3)	6.78 (d, 4H, C_5H_3)	115.6 [$C_3(C_5H_3)$]	
			139.3 [$C_1(C_5H_3)$]	
4	0.56 (s, 6H, Me–Si)	0.22 (s, 6H, Me–Si)	–4.46 (Me–Si)	
	0.91 (s, 6H, Me–Si)	0.48 (s, 6H, Me–Si)	2.21 (Me–Si)	
	6.36 (t, 2H, C_5H_3)	6.16 (t, 2H, C_5H_3)	113.0 [$C_2(C_5H_3)$]	
	6.85 (d, 4H, C_5H_3)	6.72 (d, 4H, C_5H_3)	115.1 [$C_3(C_5H_3)$]	
			138.1 [$C_1(C_5H_3)$]	
5		–0.11 (s, 6H, Me–Ti)		–4.55 (Me–Si)
		0.14 (s, 6H, Me–Si)		2.5 (Me–Si)
		0.37 (s, 6H, Me–Si)		42.0 (Me–Ti)
		6.67 (d, 4H, C_5H_3)		111.6 [$C_3(C_5H_3)$]
		6.90 (t, 2H, C_5H_3)		120.5 [$C_2(C_5H_3)$]
				133.8 [$C_1(C_5H_3)$]
6		–0.11 (s, 6H, Me–Zr)		–4.3 (Me–Si)
		0.09 (s, 6H, Me–Si)		2.5 (Me–Si)
		0.44 (s, 6H, Me–Si)		27.31 (Me–Zr)
		6.23 (t, 2H, C_5H_3)		111.2 [$C_3(C_5H_3)$]
		6.62 (d, 4H, C_5H_3)		113.5 [$C_2(C_5H_3)$]
				129.9 [$C_1(C_5H_3)$]
7		–0.24 (s, 6H, Me–Hf)		–4.31 (Me–Si)
		0.12 (s, 6H, Me–Si)		2.52 (Me–Si)
		0.48 (s, 6H, Me–Si)		33.1 (Me–Hf)
		6.20 (t, 2H, C_5H_3)		111.5 [$C_3(C_5H_3)$]
		6.57 (d, 4H, C_5H_3)		112.4 [$C_2(C_5H_3)$]
				129.9 [$C_1(C_5H_3)$]
8	0.65 (s, 12H, Me–Si)		1.4 (Me–Si)	
	7.13 (t, 2H, C_5H_3)		129.7 [$C_2(C_5H_3)$]	
	7.57 (d, 4H, C_5H_3)		132.7 [$C_1(C_5H_3)$]	
			141.9 [$C_3(C_5H_3)$]	

[a] Key:



metal fragments in a mutually *trans* configuration. All the methyl groups bound to silicon are equivalent for this diposition, so a unique ^{1}H resonance is observed for the dinuclear complex 8 and the same effect is also observed in the ^{13}C NMR spectrum. Similar *trans* dinuclear complexes have been reported[4d,f] for different transition metals, and also some examples of dinuclear compounds exhibiting a *cis* configuration A are known,[4d,f] according to their NMR spectral behavior. Therefore, NMR measurements can be used to differentiate between chelated mononuclear or bridging dinuclear *cis* or *trans* configurations.

X-ray Crystal Structures. The molecular structures of the chlorotitanium 2 and -zirconium 3 complexes are very close, although we provide different views of the molecules as shown in Figures 2 and 3, respectively, together with the atomic labeling scheme. Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are displayed in Tables 2 and 3. Selected bond distances and angles are given in Table 4.

Both molecular structures are typical dichlorometallocene systems, as reported previously for species containing free[10] or single-dimethylsilyl-bridged[2a] cyclopentadienyl rings. Both bridging silicon atoms and the carbon atoms of their methyl groups are exactly located on the plane defined by the metal and the chlorine atoms. Therefore, both cyclopentadienyl rings are necessarily in an eclipsed configuration. The dihedral angle between the cyclopentadienyl ring planes is smaller for titanium [64.35(6)°] than for zirconium [69.6(1)°] and smaller than that found (72–73°) for similar chiral zirconocene complexes recently reported.[5] These dihedral angles are ca. 13° more than the corresponding values of 51.2 and 56.8° reported[2a] for $[Me_2Si(C_5H_4)_2]TiCl_2$ and $[Me_2Si(C_5H_4)_2]ZrCl_2$, respectively, and thereby indicate that the introduction of the second bridging $SiMe_2$ group further increases the opening of the metallocene wedge. The Cp1(centroid)–M–Cp2(centroid) angle is correspondingly more open for titanium (126.0°) than for zirconium (120.6°),

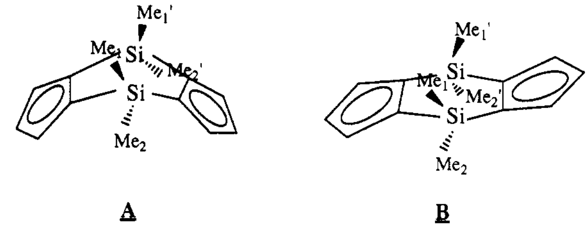


Figure 1. Chelating (A) and bridging (B) dispositions of the bis(dimethylsilyl)dicyclopentadienyl ligand.

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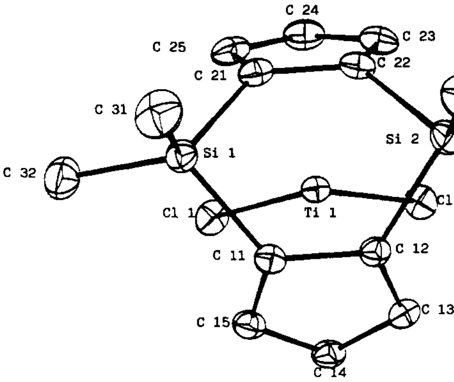

Figure 2. ORTEP view of molecular structure of compound **2** with the atomic labeling scheme.

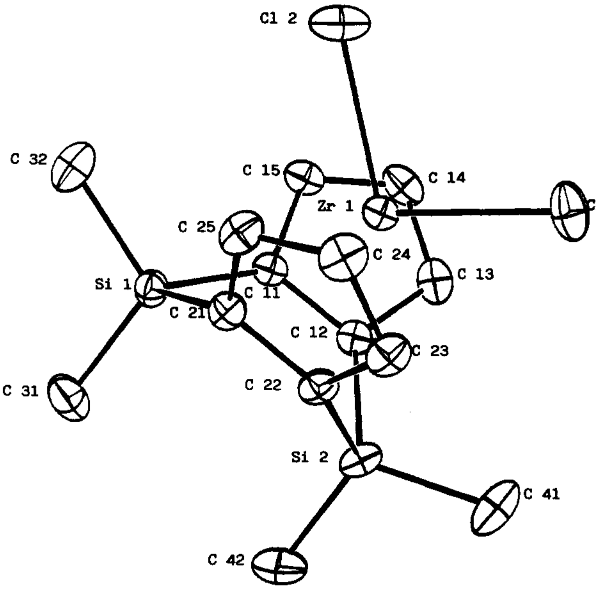

Figure 3. ORTEP view of molecular structure of compound **3** with the atomic labeling scheme.

Table 2. Positional Parameters and *B* Values and Their Estimated Standard Deviations for the Non-Hydrogen Atoms for Compound 2

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ti1	0.48760(4)	0.13334(3)	0.22207(3)	2.205(6)
Si2	0.78624(6)	0.14057(5)	0.13633(4)	2.51(1)
Cl1	0.29835(6)	0.12526(5)	0.31923(4)	3.82(1)
Cl2	0.35140(6)	0.14074(5)	0.08798(4)	3.66(1)
Si1	0.73356(7)	0.12646(5)	0.36912(4)	2.57(1)
C11	0.6627(2)	0.0167(2)	0.2866(1)	2.35(3)
C12	0.6839(2)	0.0227(2)	0.1906(1)	2.28(3)
C13	0.5713(2)	−0.0394(2)	0.1480(1)	2.62(4)
C14	0.4808(2)	−0.0807(2)	0.2133(2)	2.87(4)
C15	0.5379(2)	−0.04181(2)	0.2977(1)	2.76(4)
C21	0.6604(2)	0.2448(2)	0.2954(2)	2.67(4)
C22	0.6825(2)	0.2504(2)	0.1998(1)	2.63(4)
C23	0.5687(3)	0.3153(2)	0.1609(2)	3.32(4)
C24	0.4769(3)	0.3476(2)	0.2282(2)	3.75(5)
C25	0.5334(2)	0.3065(2)	0.3106(2)	3.42(4)
C31	0.9268(3)	0.1291(2)	0.3947(2)	3.82(5)
C32	0.6397(3)	0.1171(2)	0.4753(2)	4.42(6)
C33	0.7413(3)	0.1510(2)	0.0140(2)	4.25(6)
C34	0.9804(3)	0.1377(2)	0.1544(2)	3.92(5)

[a] *B* 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 3. Positional Parameters and *B* Values and Their Estimated Standard Deviations for the Non-Hydrogen Atoms for Compound 3

atom	*x*	*y*	*z*	*B*,[a] Å^2
Zr1	0.32838(3)	0.15060(2)	0.72697(2)	2.441(5)
Si1	0.52417(9)	0.23542(6)	0.57450(6)	2.86(2)
Si2	0.64229(9)	0.04872(6)	0.74638(7)	3.16(2)
Cl1	0.2438(1)	0.05466(7)	0.85502(7)	4.80(2)
Cl2	0.11819(9)	0.25436(7)	0.67380(9)	4.98(2)
C11	0.5405(3)	0.2489(2)	0.7163(2)	2.48(5)
C12	0.5891(3)	0.1712(2)	0.7877(2)	2.63(5)
C13	0.5325(3)	0.1913(3)	0.8761(2)	3.38(6)
C14	0.4516(3)	0.2772(2)	0.8606(2)	3.56(6)
C15	0.4573(3)	0.3128(2)	0.7637(2)	3.00(6)
C21	0.4209(3)	0.1189(2)	0.5736(2)	2.80(6)
C22	0.4709(3)	0.0406(2)	0.6447(2)	2.75(6)
C23	0.3479(4)	−0.0154(2)	0.6510(2)	3.22(6)
C24	0.2240(4)	0.0251(2)	0.5888(3)	3.54(7)
C25	0.2690(4)	0.1059(2)	0.5401(2)	3.33(6)
C41	0.6394(5)	−0.0424(3)	0.8475(3)	5.4(1)
C42	0.8187(4)	0.0418(3)	0.7055(3)	5.24(9)
C31	0.6944(4)	0.2255(3)	0.5257(3)	4.47(8)
C32	0.4106(5)	0.3333(3)	0.5060(3)	5.04(9)

[a] *B* 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 4. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 2 and 3[a]

	2 (M = Ti)	**3** (M = Zr)
M–Cl1	2.3447(7)	2.427(1)
M–Cl2	2.3430(7)	2.428(1)
M–Cp1	2.068	2.205
M–Cp2	2.072	2.192
M–C11	2.322(2)	2.442(2)
M–C12	2.319(2)	2.433(2)
M–C13	2.427(2)	2.531(2)
M–C14	2.478(2)	2.601(3)
M–C15	2.420(2)	2.553(3)
M–C21	2.327(2)	2.426(3)
M–C22	2.323(2)	2.435(3)
M–C23	2.427(2)	2.537(3)
M–C24	2.481(2)	2.582(3)
M–C25	2.427(2)	2.525(3)
C11–C12	1.452(3)	1.450(4)
C11–C15	1.414(3)	1.413(4)
C12–C13	1.418(3)	1.420(4)
C13–C14	1.402(3)	1.405(5)
C14–C15	1.403(3)	1.398(5)
C21–C22	1.447(3)	1.456(4)
C21–C25	1.424(3)	1.416(4)
C22–C23	1.421(3)	1.409(4)
C23–C24	1.401(4)	1.402(4)
C24–C25	1.405(4)	1.405(5)
Cl1–M–Cl2	96.66(2)	99.64(4)
Cl1–M–Cp1	107.5	109.6
Cl1–M–Cp2	107.8	107.8
Cl2–M–Cp1	107.6	108.6
Cl2–M–Cp2	107.5	108.6
Cp1–M–Cp2	126.0	120.6

[a] Cp1 is the centroid of C11–C12–C13–C14–C15. Cp2 is the centroid of C21–C22–C23–C24–C25.

and both are also smaller than those found[2a] for mono-*ansa*-titanium (128.7°) and -zirconium (125.4°) compounds. This inclination corresponds to a deviation of the metal-centroid line from the normal on the respective ring plane by ca. 5°. This inclination also results in metal–bridgehead ring carbon (C11, C12, C21, C22) distances 0.15 Å shorter than the metal–external ring carbon (C14, C24) distances. This asymmetry is also observed with respect to the ring carbon–carbon distances, the internal C11–C12 and C21–C22 distances (average 1.450 Å) being significantly larger than those formed with the external C14 and C24 atoms (average 1.400 Å). Nevertheless this asymmetry does not imply a significant deviation from the planarity of the ring as would be expected for an ene–

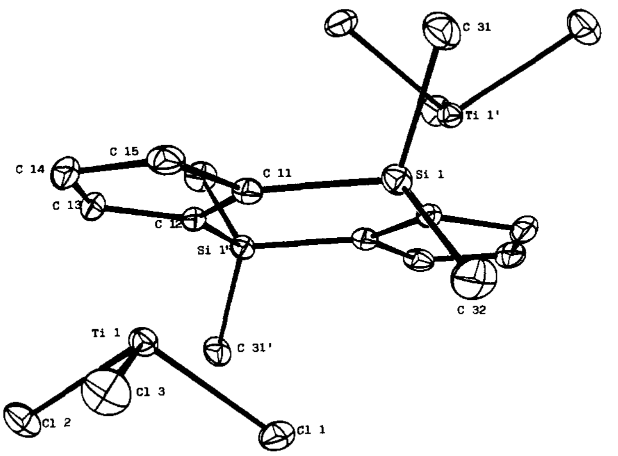

Figure 4. ORTEP view of molecular structure of compound 8 with the atomic labeling scheme.

Table 5. Positional Parameters and *B* Values and Their Estimated Standard Deviations for the Non-Hydrogen Atoms of 8

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ti1	0.9478(1)	0.2306(1)	0.05570(8)	3.39(2)
Si1	0.8478(1)	0.5055(2)	−0.0934(1)	3.27(3)
Cl1	0.8748(2)	0.3622(1)	0.1446(1)	5.09(4)
Cl2	1.0667(2)	0.1189(2)	0.1722(1)	5.62(4)
Cl3	0.7896(2)	0.1100(2)	−0.0036(2)	5.73(4)
C11	0.9548(5)	0.3778(5)	−0.0613(4)	3.2(1)
C12	1.0734(5)	0.3733(5)	0.0111(4)	3.1(1)
C13	1.1244(6)	0.2598(6)	0.00001(5)	4.3(1)
C14	1.0411(7)	0.1918(6)	−0.0731(5)	4.7(2)
C15	0.9385(7)	0.2657(6)	−0.1108(4)	4.3(1)
C31	0.8209(7)	0.5364(7)	−0.2272(5)	5.1(2)
C32	0.6957(6)	0.4815(8)	−0.0709(6)	5.6(2)
C21[b]	1.1276(7)	0.1928(8)	0.2742(6)	6.2(2)
C22[b]	1.5120(9)	0.2787(9)	0.2824(8)	7.4(3)
C23[b]	1.5727(9)	0.295(1)	0.2077(9)	9.1(3)
C24[b]	1.5527(9)	0.225(1)	0.1298(8)	9.0(3)
C25[b]	1.466(1)	0.132(1)	0.1204(8)	8.1(3)
C26[b]	1.4051(8)	0.1196(9)	0.1932(8)	7.0(2)
C27[b]	1.368(1)	0.173(1)	0.3548(8)	9.7(4)

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

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for Compound 8

Ti1–Cl1	2.231(2)	C11–C12	1.459(7)
Ti1–Cl2	2.219(2)	C11–C15	1.432(8)
Ti1–Cl3	2.233(2)	C12–C13	1.431(8)
Ti1–Cp1	2.004	C13–C14	1.424(8)
Ti1–C11	2.349(6)	C14–C15	1.418(9)
Ti1–C12	2.341(6)	Si1–C11	1.863(6)
Ti1–C13	2.353(7)	Si1–C31	1.852(7)
Ti1–C14	2.357(8)	Si1–C32	1.851(8)
Ti1–C15	2.341(6)		
Cl1–Ti1–Cl2	102.2(1)	Cl1–Ti1–Cp1	117.7
Cl1–Ti1–Cl3	103.6(1)	Cl2–Ti1–Cp1	115.4
Cl2–Ti1–Cl3	101.7(1)	Cl3–Ti1–Cp1	114.3

allyl-type distorsion, observed in singly Me$_2$Si bridged titanocene and zirconocene complexes.[2a] The metal–chloro bond distances are in the same range of those measured in the already mentioned species.

The X-ray crystal structure of the dinuclear titanium complex 8 is shown in Figure 4 with the atomic labeling scheme for the independent atoms. One molecule of toluene, not shown in the figure for clarity, is present in the asymmetric unit of the unit cell. Final atomic parameters for non-hydrogen atoms are displayed in Table 5. Selected bond distances and bond angles are given in Table 6.

The molecular structure consists of two crystallographic equivalent fragments bonded and related by a center of symmetry. The dihedral angle formed by the cyclopentadienyl ring plane and that defined by both silicon and the C11 and C12 atoms is only 4(2)°, so that the bridging ligand is almost exactly planar and the two metal centers are located in mutually trans positions with respect to this plane. A similar disposition has been found[6] for Li$_2$(tmeda)$_2$[μ-{(Me$_2$Si)$_2$(η^5-C$_5$H$_3$)$_2$}]. The plane defined by the three chlorine atoms is parallel to the cyclopentadienyl ring of the ligand, and the average value of the Cl–Ti–Cl angles is ca. 102°. One of the chlorine atoms of each fragment is directed toward the central region between the two methyl groups, belonging each to a silicon atom, in such a way that a weak chlorine–hydrogen interaction corresponding to a short distance (2.77 Å) is observed. Nevertheless neither agostic Ti–H nor Ti–C (4.03 Å) interactions are present. The Ti–C(ring) distances are fairly uniform, ranging between 2.341(6) and 2.357(8) Å, as corresponds to an η^5-coordination, in contrast to the situation described for the mononuclear complexes 2 and 3. Both Cp(centroid)–Ti distances (2.004 Å) are slightly shorter. The C–C ring distances show very small differences, and only the C11–C12 distance [1.459(7) Å] between carbons directly bound to silicon is slightly larger than the others. The two silicon and the methyl carbon atoms define a plane which divides the molecule into two equivalent fragments.

Experimental Section

All manipulations were performed under an inert atmosphere (dinitrogen or argon) using Schlenk and high vacuum line 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[6] and Li$_2$[(Me$_2$Si)$_2$(η^5–C$_5$H$_3$)$_2$][6] were prepared according to literature procedures. TlOEt, MeLi (1.6 M solution in diethyl ether), MeMgCl, TiCl$_4$, ZrCl$_4$, and HfCl$_4$ (Aldrich) were obtained commercially. NMR spectra were recorded on Varian FT-80 and Varian Unity FT-300 instruments (^{1}H and ^{13}C chemical shifts were referenced to Me$_4$Si, 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 analyses were carried out on a Perkin-Elmer 240B microanalyzer.

Synthesis of Tl$_2$[(Me$_2$Si)$_2$(C$_5$H$_3$)$_2$] (1). A solution of 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene (5 g, 20.5 mmol) in 30 mL of diethyl ether was cooled at −78 °C and treated with 2.9 mL of TlOEt, and the reaction mixture was stirred for 12 h. A white precipitate was formed. The solution was filtered, and the precipitate was washed twice with diethyl ether and characterized as compound 1 (12.7 g, 19.51 mmol, 95% yield). Anal. Calcd for C$_{14}$H$_{18}$Si$_2$Tl$_2$: C, 25.81; H, 2.76. Found: C, 25.76; H, 2.71.

Synthesis of Ti[(Me$_2$Si)$_2$(η^5-C$_5$H$_3$)$_2$]Cl$_2$ (2). A suspension of 12.7 g (19.45 mmol) of 1 in 50 mL of toluene was treated with a solution of 2.14 mL of TiCl$_4$ (19.45 mmol), in 20 mL of toluene, at room temperature. After being stirred for 12 h, the reaction mixture was heated under reflux for 3 h. The TlCl formed was filtered off, and the solution obtained was concentrated, under vacuum, to a final volume of 20 mL. The solution was then cooled at −20 °C to give a red-brown solid, which was recrystallized from toluene/hexane to yield a crystalline solid. This solid was washed with hexane and was characterized as 2 (8.2 g, 22.8 mmol,

Table 7. Crystal Data, Experimental Data, and Structure Refinement Procedures for Mononuclear 2 and 3 and Dinuclear 8 Compounds

formula	$C_{14}H_{18}Cl_2Si_2Ti$	$C_{14}H_{18}Cl_2Si_2Zr$	$TiCl_3SiC_7H_9{\cdot}C_7H_8$
cryst habit	prismatic	prismatic	prismatic
color	red	pale-yellow	red
cryst size	0.30 × 0.15 × 0.15	0.20 × 0.15 × 0.15	0.35 × 0.20 × 0.15
symmetry	monoclinic $P2_1/n$	monoclinic $P2_1/n$	monoclinic $P2_1/c$
unit cell determination	least-squares fit from 25 reflns	least-squares fit from 25 reflns	least-squares fit from 25 reflns
unit cell dimens			
a, b, c, Å	9.483(2), 11.558(6), 14.892(5)	9.392(3), 13.863(4), 13.376(4)	11.339(2), 11.292(3), 14.006(3)
β, deg	91.92(1)	101.82(1)	105.08(1)
V, Å^3	1631(1)	1704(1)	1732(1)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.47	1.57	1.41
M_r	361.59	404.59	367.63
$F(000)$	744	816	752
μ, cm^{-1}	9.78	10.74	10.09
scan mode	$\omega/2\theta$ scans; $\theta_{max} = 27°$	$\omega/2\theta$ scans; $\theta_{max} = 27°$	$\omega/2\theta$ scans; $\theta_{max} = 25°$
no. of reflns			
measd	3856	4239	4270
indpdt	3578	4104	3578
obsd	2984 ($I > 2\sigma(I)$ criterion)	2841 ($I > 2\sigma(I)$ criterion)	2578 ($I > 3\sigma(I)$ criterion)
range of hkl	$h/-12$ to 12; $k/0$ to 14; $l/0$ to 19	$h/0$ to 12; $k/0$ to 17; $l/-17$ to 17	$h/-13$ to 13; $k/0$ to 13; $l/0$ to 16
std reflns	3 reflns every 120 min, no variation		
R	0.04	0.032	0.07
R_w	0.056	0.040	0.11
goodness of fit indicator	2.149	1.353	3.791
largest param shift/error	0.01	0.02	0.2
max peak in final diff map, e/Å^3	1.0	0.732	0.853
min peak in final diff map, e/Å^3	0.33	0.46	0.685

65% yield). Anal. Calcd for $C_{14}H_{18}Cl_2Si_2Ti$: C, 46.52; H, 4.98. Found: C, 46.35; H, 4.43. Mass spectrum: m/z = 361 ([M]$^+$, 50%).

Synthesis of Zr[(Me$_2$Si)$_2$(η^5-C$_5$H$_3$)$_2$]Cl$_2$ (3). A suspension of 10 g (39.04 mmol) of $Li_2[(Me_2Si)_2(C_5H_3)_2]$ in 50 mL of toluene was treated with a suspension of 9.1 g (39.04 mmol) of $ZrCl_4$ in 20 mL of toluene. The reaction mixture was heated under reflux for 12 h. After being cooled at room temperature, the solution was filtered, and the filtrate was evaporated to dryness giving a white crystalline solid. Recrystallization form toluene/hexane at -20 °C gave white single crystals used for X-ray studies, which were washed with hexane and characterized as compound 3 (10.2 g, 24.8 mmol, 64% yield). Anal. Calcd for $C_{14}H_{18}Cl_2Si_2Zr$: C, 40.93; H, 4.38. Found: C, 40.88; H, 4.29. Mass spectrum: m/z = 410 ([M]$^+$, 8%).

Synthesis of Hf[(Me$_2$Si)$_2$(η^5-C$_5$H$_3$)$_2$]Cl$_2$ (4). Solid $Li_2[(Me_2Si)_2(C_5H_3)_2]$ (2.80 g, 10.90 mmol) was added at ca. 20 °C to a stirred solution of $HfCl_4$ (3.5 g, 10.90 mmol) in toluene (ca. 200 mL), and the reaction mixture was heated to 90 °C for 70 h. The white precipitate formed was allowed to settle, and the supernatant liquid was filtered through Celite. Volatiles were removed from the filtrate under vacuum to yield a white crystalline solid of compound 4 (3.8 g, 7.84 mmol, 72% yield). Anal. Calcd for $C_{14}H_{18}Cl_2Si_2Hf$: C, 34.18; H, 3.66. Found: C, 34.35; H, 3.93. Mass spectrum: m/z = 491 ([M]$^+$, 11%).

Synthesis of Ti[(Me$_2$Si)$_2$(η^5-C$_5$H$_3$)$_2$]Me$_2$ (5). LiMe (3.46 mL of a 1.6 M diethyl ether solution, 5.54 mmol) in 15 mL of diethyl ether was dropwise added at -78 °C to 30 mL of a diethyl ether solution containing 1 g (2.77 mmol) of 2. The reaction mixture was warmed to room temperature and stirred for 2 h. After filtration, the solution was concentrated under vacuum to 10 mL and then cooled at -20 °C to give a microcrystalline yellow-orange solid, which was washed with hexane and recrystallized from toluene/hexane to give 5 (0.63 g, 1.98 mmol, 72% yield). Anal. Calcd for $C_{16}H_{24}Si_2Ti$: C, 59.96, H, 7.49. Found: C, 59.18; H, 7.13. Mass spectrum: m/z = 320 ([M]$^+$, 6%).

Synthesis of Zr[(Me$_2$Si)$_2$(η^5-C$_5$H$_3$)$_2$]Me$_2$ (6). LiMe (3.04 mL of a 1.6 M diethyl ether solution, 4.87 mmol) in 20 mL of diethyl ether was added dropwise at -78 °C to 30 mL of a diethyl ether solution containing 1 g (2.43 mmol) of 3. The reaction mixture was warmed to room temperature and stirred for 2 h. After filtration, the solution was concentrated under vacuum until reaching a volume of 10 mL. The solution was cooled at -20 °C to give a microcrystalline white solid, which was washed with hexane and recrystallized from toluene/hexane to give 6 (0.67 g, 1.81 mmol, 70% yield). Anal. Calcd for $C_{16}H_{24}Si_2Zr$: C, 46.78; H, 5.84. Found: C, 47.04; H, 5.90.

Synthesis of Hf[(Me$_2$Si)$_2$(η^5-C$_5$H$_3$)$_2$]Me$_2$ (7). A solution of MeMgCl (0.77 mL, 2.32 mmol) in diethyl ether (ca. 30 mL) was added dropwise to a stirred solution of 4 (0.57 g, 1.16 mmol) in diethyl ether (ca. 100 mL) at ca. -78 °C. The reaction mixture immediately turned cloudy due to the precipitation of $MgCl_2$ and was stirred upon the addition of MeMgCl for 8 h at ca. 20 °C to ensure completion of the reaction. The white precipitate which formed was allowed to settle and removed from the filtrate under vacuum to yield a white crystalline solid of the title compound 7 (0.22 g, 0.48 mmol, 42% yield). Anal. Calcd for $C_{16}H_{24}Si_2Hf$: C, 42.62; H, 5.29. Found: C, 42.75; H, 5.33.

Synthesis of (TiCl$_3$)$_2${μ-[(Me$_2$Si)$_2$(η^5-C$_5$H$_3$)$_2$]} (8). A solution of $TiCl_4$ (3.37 mL, 30.63 mmol), in 25 mL of toluene, was added dropwise to a suspension of 10 g (15.32 mmol) of 1 in 50 mL of toluene. The reaction mixture was stirred for 12 h. After filtration, the resulting solution was evaporated to dryness to give a yellow solid. Recrystallization from toluene/hexane at -40 °C gave yellow crystals, which were washed with hexane and characterized as 8 (2.5 g, 4.53 mmol, 30% yield). Anal. Calcd for $C_{14}H_{18}Si_2Ti_2Cl_6$: C, 30.48; H, 3.26. (8·2(toluene) loses variable amounts of toluene under vacuum but could never be obtained free of toluene and, therefore, satisfactory analytical data could not be obtained). Mass spectrum: m/z = 480 ([M - 2Cl]$^+$, 15%).

Crystal Structures of M[(Me$_2$Si)$_2$(η^5-C$_5$H$_3$)$_2$]Cl$_2$ (M = Ti (2), Zr (3)). Suitable crystals of 2 and 3 were sealed in Lindeman glass capillaries under an argon atmosphere and mounted on an Enraf-Nonius CAD-4 automatic four-circle diffractometer with bisecting geometric and using a graphite-oriented monochromator with Mo Kα radiation (λ(Mo Kα) = 0.710 73 Å). Crystallographic and experimental details for both crystals are summarized in Table 7. Data were collected at room temperature. No absorption or extinction corrections were made. The structures were solved by a combination of heavy atoms, direct methods, and Fourier syntheses. The structures were refined (based on F) by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found in the Fourier map and refined for one cycle isotropically. The hydrogens of the methyl groups of the zirconium compound were regularized. Final $R = 0.04$ and $R_w = 0.056$ for the Ti compound and $R = 0.032$ and $R_w = 0.040$ for the zirconium compound 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 11. Calculations were performed with the SDP Enraf-Nonius[12] package, MULTAN,[13] and DIRDIF[14] on a Microvax II computer.

Crystal Structure of $(TiCl_3)_2\{\mu\text{-}[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2]\}$ (8). The single crystal of 8 suitable for X-ray structural determination was obtained by crystallization from toluene at −30 °C. The crystal was sealed in a Lindemann tube with solvent atmosphere after checking that some decomposition took place after 1 day under argon. Crystallographic and experimental details are given in Table 7. The X-ray technique used for data collection and for solving the structure was similar to that for the other structure described, except that in this case an empirical absorption correction was made with the DIFABS[15] method and the hydrogen atoms were introduced from geometrical calculation with thermal parameters equivalent to the ones of the carbons to which they are attached and refined only one cycle isotropically.

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Supplementary Material Available: Tables of anisotropic temperature factors, positional parameters for hydrogen atoms, and bond lengths and bond angles for compounds **2**, **3**, and **8** (16 pages). Ordering information is given on any current masthead page.

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