Synthesis, characterization, and solid-state structures of the 14-electron open metallocenes $M[1,5\text{-}(Me_3Si)_2C_5H_5]_2$ (M = Ti or Zr) ☆

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Abstract

Reactions of titanium(II) or zirconium(IV) chlorides with two or four equivalents of $K[1,5\text{-}(Me_3Si)_2C_5H_5]$, respectively, lead to the diamagnetic 14-electron $M[1,5\text{-}(Me_3Si)_2C_5H_5]_2$ complexes. Both have been characterized analytically, spectroscopically, and through single crystal X-ray diffraction studies.

Keywords: Titanium; Zirconium; Open metallocenes; X-ray crystal structure

1. Introduction

Pentadienyl ligands exhibit a number of interesting features in their transition metal complexes [1]. In addition to being sterically very demanding [2], they prefer binding to metals in low oxidation states [3] and generally seem to be better accepting ligands than C_5H_5 [4]. As an apparent result of the pentadienyl anion's lesser degree of resonance stabilization [5], there is greater mixing between metal and pentadienyl orbitals, and generally stronger M–dienyl bonding relative to $C_5H_5^-$, at least for the larger earlier transition metals [6]. For these metals, steric crowding is not so serious, and reasonable metal–dienyl orbital overlap can be achieved for the larger open dienyl ligands. The combination of these factors seems responsible for the stability of 14-electron open titanocenes such as $Ti(2,4\text{-}C_7H_{11})_2$, $Ti(2,3\text{-}C_7H_{11})_2$ (C_7H_{11} = dimethylpentadienyl), and $Ti[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]_2$ [7]. Thus, steric crowding inhibits coordination by additional ligands, while the greater backbonding ability of the pentadienyl groups probably contributes to the lack of formation of N_2 complexes, as well as the preference for bonding to metals in low oxidation states. Furthermore, the stronger metal–dienyl bonding (and perhaps, the splaying out of

the dienyl C-substituent bonds) are likely responsible for the relative lack of C–H bond activation reactions, which are so common in various "titanocenes" [8]. To date, a structural study on an open titanocene has not been published, in part due to the fact that $Ti(2,4\text{-}C_7H_{11})_2$ is a liquid. Herein we report on the synthesis and characterization of $Ti[1,5\text{-}(Me_3Si)_2C_5H_5]_2$, a solid open titanocene for which single crystal structural data could be obtained. Furthermore, we also demonstrate that it is even possible to prepare the corresponding open zirconocene complex, for which structural data have also been obtained.

2. Experimental details

All operations were carried out under dinitrogen. Solvents were distilled from benzophenone ketyl to ensure complete removal of oxygen and water. Spectroscopic data were obtained as previously described [9]. The numbers of carbon atoms are given for the ^{13}C NMR spectra in accord with their assignments, but the spectra were not precisely integrated.

2.1. Potassium 1,5-di(trimethylsilyl)pentadienide, $K[1,5\text{-}(Me_3Si)_2C_5H_5]$

This could be prepared from 1,5-di(trimethylsilyl)-1,3-pentadiene and either potassium sand or LiR/KOR

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mixtures. The latter method may be carried out as follows. To a stirred slurry of 7.15 g (0.0638 mol) of pulverized $KOC(CH_3)_3$ in 75 ml of hexane at 0 °C was added by syringe 13.55 g (0.0638 mol) of degassed (E,E)-1,5-$(Me_3Si)_2C_5H_6$ [10]. To this was added dropwise 27 ml of 2.6 M (0.070 mol) of Bu^nLi in hexane. The slurry was warmed to room temperature and stirred 18 h which resulted in a bright yellow precipitate. The product was filtered and washed with two 25 ml portions of hexane. The bright yellow pyrophoric powder was dried in vacuo yielding 7.38 g (ca. 46%).

2.2. Bis[η⁵-1,5-di(trimethylsilyl)pentadienyl]titanium, $Ti(\eta^5$-1,5-$(Me_3Si)_2C_5H_5)_2$

To a frozen mixture of 30 ml of THF and 0.0266 g (1.09 mmol) of 70–80 mesh Mg metal was added 0.10 ml (0.91 mmol) of $TiCl_4$. The frozen mixture was warmed to room temperature slowly and heated under reflux for 1 h to give a black slurry of "$TiCl_2$". The slurry was then cooled to −78 °C and a solution of 0.48 g (1.9 mmol) of $K[1,5-(Me_3Si)_2C_5H_5]$ in 40 ml of THF was added dropwise with stirring. The solution was warmed to room temperature slowly and stirred overnight, producing a dark green solution. The solvent was removed in vacuo and the dark green residue extracted into three 25 ml portions of hexane which were then filtered. The volume was reduced in vacuo to approximately 20 ml and dark green crystals were isolated by cooling to −86 °C, yielding 0.41 g (ca. 95%). The moderately air-sensitive product (m.p. = 165–167 °C) was purified by recrystallization from hexane or sublimation in vacuo (ca. 110 °C). Anal. Calc. for $C_{22}H_{46}Si_4Ti$: C, 56.12; H, 9.85. Found: C, 56.22; H, 10.24%.

2.2.1. Spectral data

¹H NMR data (benzene-d_6, ambient): δ 7.96 (d of d of d, 1H, $J = 17, 10, 2$ Hz, H(2,4)), 6.33 (t, 1H, $J = 10$ Hz, H(3)), 5.40 (d of d of d, 1H, $J = 16, 10, 2$ Hz, H(2,4)′), 2.27 (d, 1H, $J = 17$ Hz, H(1,5)), 0.25 (s, 9H, Si($CH_3)_3$), −0.31 (s, 9H, Si($CH_3)_3$), −1.83 (d, 1H, $J = 16$ Hz, H(1,5)′).

¹³C NMR data (benzene-d_6, ambient): δ 117.5 (d of d of d, $J = 161, 10, 2$ Hz, C(2,4), 115.8 (d of d, $J = 159, 10$ Hz, C(2,4)′), 113.8 (d of t, $J = 160, 5$ Hz, C(3)), 89.8 (d, $J = 128$ Hz, C(1,5)), 78.8 (d, $J = 136$ Hz, C(1,5)′), 1.8 (q, $J = 118$ Hz, Si($CH_3)_3$), 0.13 (q, $J = 118$ Hz, Si($CH_3)_3$).

Complete IR data (Nujol mull): 3041sh, 1447vs, 1420ms, 1400m, 1291ms, 1250vs, 1242sh, 1237sh, 1209m, 1162s, 1088ms, 1015vw, 995vw, 970ms, 933m, 910vw, 875sh, 848vs, 835vs, 790s, 775m, 758ms, 743s, 720m, 685ms, 669mw, 660w, 611ms cm^{-1}.

Mass spectrum (EI, 17 eV): m/e (relative intensity),

184 (100), 240 (10), 256 (36), 322 (32), 394 (35), 470 (41), 471 (10).

2.3. Bis(η⁵-1,5-di(trimethylsilyl)pentadienyl)zirconium, $Zr[\eta^5$-1,5-$(Me_3Si)_2C_5H_5]_2$

To a solution of 0.56 g (1.5 mmol) of $ZrCl_4(THF)_2$ in 30 ml of THF at −78 °C was added dropwise with stirring a solution of 1.50 g (5.99 mmol) of $K[1,5-(Me_3Si)_2C_5H_5]$ in 40 ml of THF. The solution was warmed to room temperature slowly and stirred overnight, producing a dark orange solution. The solvent was removed in vacuo and the residue extracted with three 25 ml portions of pentane. The dark red extracts were filtered under dinitrogen and all the solvent was removed in vacuo. The red oil was cooled to −86 °C producing extremely air-sensitive dark red crystals. To remove the oily impurities, the product was recrystallized from pentane three times, yielding 0.31 g (ca. 40%). The product (m.p. = 163–166 °C) was further purified by recrystallization from pentane or sublimation in vacuo (ca. 125 °C). Anal. Calc. for $C_{22}H_{46}Si_4Zr$: C, 51.39; H, 9.02%. Found: C, 50.60; H, 9.50%.

Table 1
Crystallographic data for $M[1,5-(Me_3Si)_2C_5H_5]_2$ complexes

Crystal parameters	Ti	Zr
Formula	$TiC_{22}H_{46}Si_4$	$ZrC_{22}H_{46}Si_4$
Formula weight	470.8	514.2
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
a (Å)	22.122(12)	22.173(11)
b (Å)	10.024(4)	10.044(3)
c (Å)	13.611(8)	13.931(9)
β (°)	105.23(5)	105.22(5)
V (Å³)	2912.4	2993.6
Z	4	4
D_{calc} (g cm⁻³)	1.074	1.114
T (K)	293	291
Color	green	red
Data collection		
Diffractometer	Enraf-Nonius CAD-4	Nicolet-Siemens $P\bar{1}$
Radiation	Mo-Kα	Mo-Kα
λ (Å)	0.71073	0.71073
2θ range (°)	3–46	4–50
μ (Mo-Kα) (cm⁻¹)	4.57	5.24
Independent reflections	2281	2843
Independent observed reflections	897	1760
Refinement		
R (F)	0.073	0.057
R_w (F)	0.076	0.064
N_0/N_v	7.4	14.3
ρ (e Å⁻³)	0.34	0.36

Table 2
Positional parameters for the nonhydrogen atoms of Ti[1,5-(Me$_3$Si)$_2$C$_5$H$_5$]$_2$

Atom	x	y	z
Ti	0.5000(0)	0.2331(3)	0.2500(0)
Si(1)	0.6564(2)	0.0949(4)	0.2248(3)
Si(2)	0.4156(2)	0.5412(4)	0.1168(3)
C(1)	0.5779(5)	0.174(1)	0.179(1)
C(2)	0.5235(5)	0.092(1)	0.135(1)
C(3)	0.4629(5)	0.139(1)	0.094(1)
C(4)	0.4370(5)	0.269(1)	0.0934(9)
C(5)	0.4654(5)	0.391(1)	0.1240(9)
C(6)	0.7115(7)	0.210(2)	0.311(2)
C(7)	0.6858(7)	0.069(2)	0.115(1)
C(8)	0.6508(8)	−0.066(2)	0.289(2)
C(9)	0.3823(6)	0.554(1)	0.228(1)
C(10)	0.3497(7)	0.531(2)	0.001(1)
C(11)	0.4624(6)	0.697(1)	0.106(1)

Table 4
Positional parameters for the nonhydrogen atoms of Zr[1,5-(Me$_3$Si)$_2$C$_5$H$_5$]$_2$

Atom	x	y	z
Zr	0.0000(0)	0.7680(1)	0.2500(0)
Si(1)	−0.15585(9)	0.9139(2)	0.2836(2)
Si(2)	0.08518(9)	0.4589(2)	0.3895(2)
C(1)	−0.0777(3)	0.8314(7)	0.3272(5)
C(2)	−0.0240(3)	0.9080(8)	0.3743(5)
C(3)	0.0391(3)	0.8625(8)	0.4145(5)
C(4)	0.0645(3)	0.7330(8)	0.4158(5)
C(5)	0.0359(3)	0.6090(7)	0.3825(5)
C(6)	−0.2116(4)	0.802(1)	0.1974(9)
C(7)	−0.1879(4)	0.948(1)	0.3923(7)
C(8)	−0.1488(5)	1.072(1)	0.221(1)
C(9)	0.1203(3)	0.4514(9)	0.2799(6)
C(10)	0.1514(4)	0.466(1)	0.5069(7)
C(11)	0.0382(4)	0.3066(8)	0.3941(6)

2.3.1. Spectral data

^{1}H NMR data (benzene-d$_6$, ambient): δ 7.42 (d of d of d, 1H, $J = 16, 10, 2$ Hz, H(2,4)), 6.05 (t, 1H, $J = 10$ Hz, H(3)), 5.44 (d of d of d, 1H, $J = 16, 10, 2$ Hz, H(2,4)′), 1.51 (d, 1H, $J = 16$ Hz, H(1,5)), 0.28 (s, 9H, Si(CH_3)$_3$), −0.20 (s, 9H, Si(CH_3)$_3$), −1.36 (d, 1H, $J = 16$ Hz, H(1,5)′).

^{13}C NMR data (benzene-d$_6$, ambient): δ 111.9 (d of d of d, $J = 161, 10, 2$ Hz, C(2,4)), 111.6 (d of d, $J = 158, 10$ Hz, C(2,4)′), 110.1 (d of t, $J = 160, 5$ Hz, C(3)), 80.0 (d, $J = 127$ Hz, C(1,5)), 69.5 (d, $J = 136$ Hz, C(1,5)′), 1.8 (q, $J = 118$ Hz, Si(CH_3)$_3$), 0.4 (q, $J = 118$ Hz, Si(CH_3)$_3$).

Complete IR data (Nujol mull): 3034m, 1633w, 1411s, 1287m, 1257sh, 1247vs, 1227s, 1196m, 1156s, 1079m, 995mw, 955m, 921m, 903mw, 848vs, 833vs, 722m, 740s, 687m, 676sh, 611w cm^{-1}.

Mass spectrum (EI, 17 ev): m/e (relative intensity), 73 (85), 108 (13), 109 (45), 123 (12), 124 (14), 196 (12), 268 (48), 269 (12), 282 (20), 283 (11), 284 (16), 286 (15), 350 (13), 436 (10), 438 (10), 439 (12), 440 (10), 510 (11), 512 (100), 513 (50), 514 (42), 516 (13).
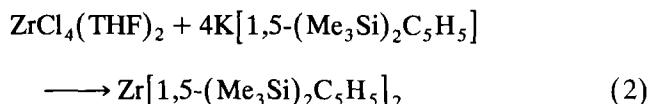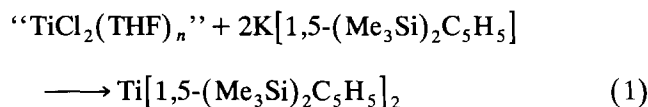
2.4. X-ray diffraction studies

Single crystals of the compounds were grown by slow vacuum sublimation, and thereafter mounted in glass capillaries under dinitrogen. After being transferred to their respective diffractometers, unit cell determinations and data collection were carried out. Direct methods were used for initial structure solutions, after which difference Fourier maps were used to locate the remaining atoms. In the titanium structure, most hydrogen atoms could be located and their positions were subsequently idealized. Pertinent unit cell, data collection, and refinement information are presented in Table 1, while atomic coordinates are listed in Tables 2 and 4, and bond distances and angles are given in Tables 3 and 5. Additional bonding parameters and structure factor tables may be obtained from the authors.

Table 3
Selected bond distances (Å) and angles (deg) for Ti[1,5-(Me$_3$Si)$_2$C$_5$H$_5$]$_2$

| Bond distances					
Ti–C(1)	2.264(5)	Si(1)–C(6)	1.857(7)	Si(2)–C(11)	1.902(6)
Ti–C(2)	2.268(5)	Si(1)–C(7)	1.801(7)	C(1)–C(2)	1.450(7)
Ti–C(3)	2.278(6)	Si(1)–C(8)	1.855(7)	C(2)–C(3)	1.391(7)
Ti–C(4)	2.248(5)	Si(2)–C(5)	1.849(5)	C(3)–C(4)	1.423(8)
Ti–C(5)	2.315(5)	Si(2)–C(9)	1.849(6)	C(4)–C(5)	1.396(7)
Si(1)–C(1)	1.865(5)	Si(2)–C(10)	1.846(7)		
Bond angles					
C(1)–C(2)–C(3)	125.9(5)	C(1)–Si(1)–C(6)	110.2(3)	C(5)–Si(2)–C(9)	111.8(3)
C(2)–C(3)–C(4)	130.6(5)	C(1)–Si(1)–C(7)	106.9(3)	C(5)–Si(2)–C(10)	109.0(3)
C(3)–C(4)–C(5)	131.1(5)	C(1)–Si(1)–C(8)	111.0(3)	C(5)–Si(2)–C(11)	110.2(2)
C(2)–C(1)–Si(1)	119.7(4)	C(6)–Si(1)–C(7)	107.3(4)	C(9)–Si(2)–C(10)	107.6(3)
C(4)–C(5)–Si(2)	119.1(4)	C(6)–Si(1)–C(8)	110.9(4)	C(9)–Si(2)–C(11)	110.3(3)
		C(7)–Si(1)–C(8)	110.4(4)	C(10)–Si(2)–C(11)	107.8(3)

3. Results and discussion

The $M[1,5\text{-}(Me_3Si)_2C_5H_5]_2$ complexes for titanium and zirconium were prepared by the reactions of appropriate metal halides with $K[1,5\text{-}(Me_3Si)_2C_5H_5]$ in THF (Eqs. (1) and (2)).

$$\text{``}TiCl_2(THF)_n\text{''} + 2K[1,5\text{-}(Me_3Si)_2C_5H_5]$$

$$\longrightarrow Ti[1,5\text{-}(Me_3Si)_2C_5H_5]_2 \qquad (1)$$

$$ZrCl_4(THF)_2 + 4K[1,5\text{-}(Me_3Si)_2C_5H_5]$$

$$\longrightarrow Zr[1,5\text{-}(Me_3Si)_2C_5H_5]_2 \qquad (2)$$

The vanadium and chromium analogs may be prepared similarly [11]. The facile reduction of Zr(IV) to Zr(II) is notable, and underscores the favorability of pentadienyl ligands for bonding to transition metals in low oxidation states. The titanium and zirconium complexes were isolated as green and red crystalline solids that are thermally quite stable, being isolable by sublimation at 125 °C. The titanium complex, while slightly to somewhat air-sensitive, differed greatly from the nearly pyrophoric $Ti(2,4\text{-}C_7H_{11})_2$ [7], a clear result of steric shielding by the Me_3Si groups. Replacement of titanium by the larger zirconium center renders the complex extremely air-sensitive.

The ^1H and ^{13}C NMR spectra for these complexes are quite similar, and each contains seven resonances (see Section 2), indicating equivalent ligands in unsymmetric environments. This would be consistent with the expected species having a conformation angle of ca. 90 ° (I), as observed for $V(2,4\text{-}C_7H_{11})_2$ [12], but does not eliminate other conformations save the more symmetric syn-eclipsed (C_{2v}, II) and anti-eclipsed (C_{2h}, III) forms. Similar behavior was exhibited by $Ti(2,4\text{-}C_7H_{11})_2$, although its resonances were noticeably

broadened at room temperature, whereas the NMR resonances for the

(I)

(II)   **(III)**
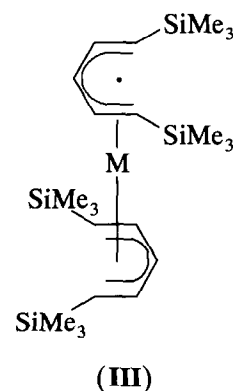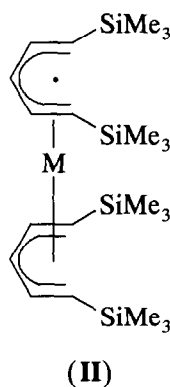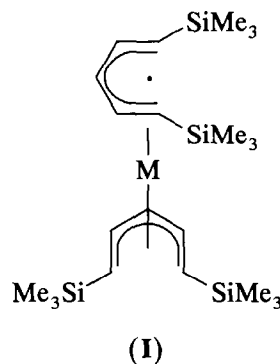
silyl-substituted complexes were quite sharp, and remained so even at 120 °C. This indicates that the barriers to ligand oscillation for the $M[1,5\text{-}(Me_3Si)_2C_5H_5]_2$ complexes are significantly greater than the 15.3 ± 0.2 kcal mol^{-1} found for $Ti(2,4\text{-}C_7H_{11})_2$, or the 15.5 ± 0.2 kcal mol^{-1} found for $Ti[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]_2$ [7]. Whether this reflects a steric or electronic effect is not clear. Regarding the steric possibility, exo substituents (such as the Me_3Si groups) on the terminal (1,5) carbon atoms tilt down toward the other dienyl ligand more than do substituents in the 2, 3 or 4 positions [1], and

Table 5
Selected bond distances (Å) and angles (deg) for $Zr[1,5\text{-}(Me_3Si)_2C_5H_5]_2$

| Bond distances					
Zr–C(1)	2.346(8)	Si(1)–C(6)	1.860(10)	Si(2)–C(11)	1.861(9)
Zr–C(2)	2.397(8)	Si(1)–C(7)	1.865(11)	C(1)–C(2)	1.425(9)
Zr–C(3)	2.421(7)	Si(1)–C(8)	1.842(12)	C(2)–C(3)	1.438(9)
Zr–C(4)	2.403(6)	Si(2)–C(5)	1.850(8)	C(3)–C(4)	1.415(12)
Zr–C(5)	2.412(7)	Si(2)–C(9)	1.889(9)	C(4)–C(5)	1.421(11)
Si(1)–C(1)	1.872(7)	Si(2)–C(10)	1.890(8)		
Bond angles					
C(1)–C(2)–C(3)	128.1(7)	C(1)–Si(1)–C(6)	110.1(4)	C(5)–Si(2)–C(9)	110.7(4)
C(2)–C(3)–C(4)	129.9(7)	C(1)–Si(1)–C(7)	109.6(4)	C(5)–Si(2)–C(10)	109.2(4)
C(3)–C(4)–C(5)	131.2(6)	C(1)–Si(1)–C(8)	110.5(4)	C(5)–Si(2)–C(11)	110.1(4)
C(2)–C(1)–Si(1)	120.1(5)	C(6)–Si(1)–C(7)	107.8(5)	C(9)–Si(2)–C(10)	108.0(4)
C(4)–C(5)–Si(2)	119.3(5)	C(6)–Si(1)–C(8)	110.1(5)	C(9)–Si(2)–C(11)	110.4(4)
		C(7)–Si(1)–C(8)	108.8(6)	C(10)–Si(2)–C(11)	108.5(4)
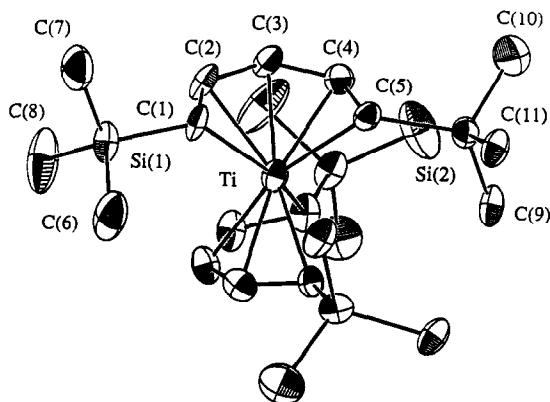
Fig. 1. Perspective view and numbering scheme for Ti[1,5-$(Me_3Si)_2C_5H_5]_2$.

hence could more easily prevent dienyl oscillation, especially given the fact that C–Si bonds are significantly longer than C–C ones. That the Me_3Si groups have significant electronic effects is also well known [13], and in the case at hand reflected by the $J(^{13}C-H)$ coupling constants for the dienyl terminal carbon atoms, which range from 127 to 136 Hz for these silylated complexes. These values are much closer to those expected for sp^3, rather than sp^2, hybridization.

The solid state structure of Ti[1,5-$(Me_3Si)_2C_5H_5]_2$ is presented in Fig. 1, while pertinent bonding parameters are given in Table 1. The molecule is situated on a crystallographic C_2 axis, relating one ligand to the other. The molecule has a conformation angle of 82.5°, as defined by the two Ti–C(3)–1/2(C(1) + C(5)) planes. A value close to 90° had been expected, based on the value of 89.8° for V(2,4-$C_7H_{11})_2$ [12] (cf., 59.7° for Fe(2,4-$Cd_7H_{11})_2$ [14] and 82.3° for Cr(2,4-$C_7H_{11})_2$) [15]. In this case, the deviation from 90° may be attributed to interactions between the symmetry related $Me_3Si(2)$ groups.

Some evidence for the $Me_3Si \cdots Me_3Si$ interaction may be gathered from the Ti–C bond lengths. For the (1,5), (2,4), and 3 positions one observes average values of 2.29, 2.258(4), and 2.278(6) Å (average 2.275(3) Å), the bonds involving C(1) and C(5) being longest, and significantly different from each other, at 2.264(5) vs. 2.315(5) Å, respectively. The longer value for C(5) is likely a reflection of the $Me_3Si \cdots Me_3Si$ interaction; furthermore, the average Ti–C(1,5) length is longest of all three types, perhaps due to the $Me_3Si \cdots Me_3Si$ and $Me_3Si \cdots$ dienyl steric interactions. In contrast, for V(2,4-$C_7H_{11})_2$, the V–C(1,5) distances were shortest of all [12]. It is also possible that the larger angles about C(3) and C(4) relative to C(2) come about as an attempt to separate the Me_3Si groups attached to the C(5) positions.

The dienyl carbon framework does not exhibit the usual short–long–long–short alternation expected from

a contribution of resonance form IV [1]. Instead, a long–short–long–short pattern is evident, apparently reflecting a

(IV)   (V)
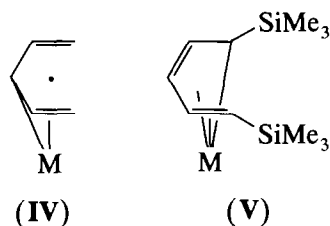
contribution from form V. It is possible that as the $Me_3Si \cdots Me_3Si$ interactions lead to a weakening of the Ti–C(5) bond, the contribution involving an enhanced Ti–C(1) interaction (V) becomes more important, leading to the alternation. However, it might also be that the apparent enhanced Ti–C(1) interaction arises from the positioning of C(1) nearly opposite to the open edge of the other dienyl ligand (a *trans* influence). In fact, while one generally observes significant tilting toward the metal center by "*exo*" substituents on pentadienyl terminal carbon atoms [1], that of Si(1) actually occurs in the opposite direction (-0.011 Å, cf., 0.149 Å by Si(2)), suggesting perhaps greater steric problems for Si(1), which is not located near the open edge of the other dienyl ligand. This is supported by the observation that the hydrogen substituent on C(3) is also tilted in the wrong direction (away from the metal), by 0.129 Å. To overcome these steric problems, an electronic effect favoring Ti–C(1), as opposed to Ti–C(5) bonding, seems necessary.

A perspective view for the isostructural Zr[1,5-$(Me_3Si)_2C_5H_5]_2$ may be seen in Fig. 2, while bonding parameters are given in Table 4. In general, these data reinforce the notion that steric interactions greatly affected the bonding parameters in the smaller titanium species. Thus, the respective average Zr–C bond lengths for the C(1,5), C(2,4), and C(3) positions are 2.38, 2.400(5), and 2.421(7) Å, revealing that like V(2,4-$C_7H_{11})_2$ [12] (and presumably Ti(2,4-$C_7H_{11})_2$), the
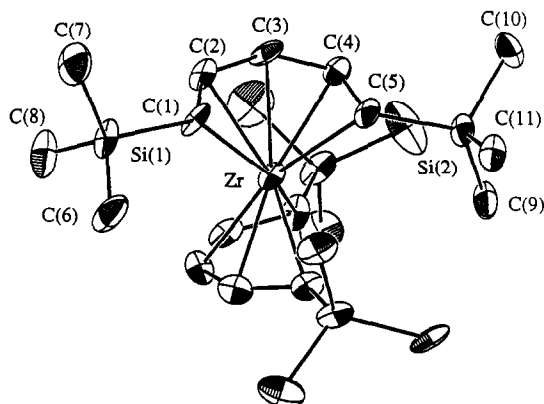

Fig. 2. Perspective view and numbering scheme for Zr[1,5-$(Me_3Si)_2C_5H_5]_2$.

M–C(1,5) bond lengths are shortest. In addition, the C–C–C bond angles about C(2), C(3), and C(4) are now more comparable. While one might also expect to see even greater tilting of the Me_3Si substituents toward the zirconium center, there is little difference relative to the titanium complex (here, -0.028 and 0.135 Å). This can readily be ascribed to the enhancement of the Zr–C(1,5) bonds in the zirconium complex, which thus works to keep the silyl groups involved in the various steric interactions described before for the titanium complex. Similar considerations may also be responsible for the failure of the conformation angle (82.2 °) to approach 90 °. However, the Zr–C(5) bond length of 2.412(7) Å is still notably longer than that for C(1), 2.346(8) Å, suggesting that the shorter Ti–C(1) and Zr–C(1) bond lengths actually derive from an electronic effect (vide supra). The overall average Zr–C bond length is 2.396(4) Å, 0.12 Å larger than that for the titanium complex.

Acknowledgments

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