Journal of Organometallic Chemistry, 382 (1990) 103–108
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20498

Stereorigid titanocene and zirconocene derivatives. Synthesis and crystal structure of the dialkyl complex $[\eta^5$-η^5-$(C_5H_4)_2Si(CH_3)_2]Ti[CH_2Si(CH_3)_3]_2$ *

Rafael Gómez, Tomás Cuenca, Pascual Royo *

Departamento de Química Inorgánica, Universidad de Alcalá de Henares, Campus Universitario, 28871 Alcalá de Henares, Madrid (Spain)

W.A. Herrmann and E. Herdtweck

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, D-8046 Garching (F.R.G.)

(Received May 24th, 1989)

Abstract

Reaction of $M'_2[(\eta^5$-$C_5H_4)_2Si(CH_3)_2]$ (M′ = Li, Na, K) with MCl_4 produced the known complexes $[(\eta^5$-$C_5H_4)_2Si(CH_3)_2]MCl_2$ (M = Ti (**1**) and Zr (**2**). Along with the predominant product in each case a new titanium and zirconium compound is isolated. Treatment of the complexes **1** and **2** with $LiCH_2Si(CH_3)_3$ gives the novel derivatives $[(\eta^5$-$C_5H_4)_2Si(CH_3)_2]M[CH_2Si(CH_3)_3]_2$ (M = Ti (**4**) and Zr (**5**)) which have been characterized by NMR and mass spectrometry and in the case of **4** by an X-ray structural determination.

Introduction

A large variety of substituted cyclopentadienyl rings have been used to synthesize electron-deficient complexes of so-called early transition metals. Chelating dicyclopentadienyl ligands with interannular bridges, particularly with ethylene or dialkylsilylene bridges, have been reported recently [1,2]. This type of compound reacts in a quite different way from complexes containing independent cyclopentadienyl rings, and this is of particular interest in relation to reduction [2a] and C–H bond activation at these ring ligands. We describe here the isolation and crystallographic characterization of the first titanocene and zirconocene alkyl complexes containing cyclopentadienyl rings bridged by a dimethylsilylene $[Si(CH_3)_2]$ group.

---

* Dedicated to Professor Günther Wilke on the occasion of his 65th birthday.

0022-328X/90/$03.50

Results and discussion

The precursors **1** and **2** (Scheme 1) were prepared as previously described [2], although we were not able to obtain yields as high as those reported (ca. 70% for Ti and 48% for Zr). We examined the use of the sodium and potassium in place of the lithium salts $M_2[(C_5H_4)_2Si(CH_3)_2]$ (M = Li, Na, K), but the yields never exceeded 40%. When **1** was prepared by isolating each of the intermediate compounds shown in the Scheme 1 and using stoichiometric amounts of reagents, a new compound **3** was found to be formed also as the predominant product. Compounds **1** and **3** have the same analytical composition, but **3** gives a ^1H NMR spectrum consisting of two multiplets a δ 6.86 and 6.70 ppm (C_5H_4 protons) and a broad signal at δ 0.50 ppm due to the protons of the dimethylsilylene group. Similar behaviour was also observed in the preparation of **2**. Complete characterization of **3**, whose formation is responsible for the low yields of **1** and **2**, is being carried out.

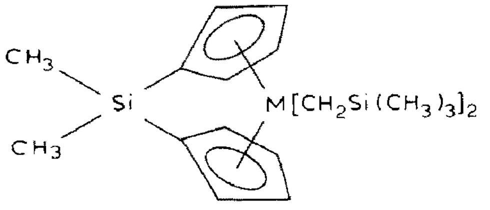
$$\begin{tikzcd}
2NaC_5H_5 + Si(CH_3)_2Cl_2 \arrow[r, "i"] & Si(CH_3)_2(C_5H_5)_2 \arrow[d, "ii"] \\
{[(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2]MCl_2} & {Li_2[(C_5H_4)_2Si(CH_3)_2]} \arrow[l, "iii"']
\end{tikzcd}$$

(M = Ti (**1**); Zr (**2**))

Scheme 1. Reagents and conditions: (i) n-hexane, −60 °C, −2NaCl, yield 60%; (ii) $+Li\text{-}n\text{-}C_4H_9$, n-hexane, −78 °C, $-n\text{-}C_4H_{10}$, yield 70%; (iii) $+MCl_4$, tetrahydrofuran (THF).

Treatment of **1** and **2** with 2.1 equivalents of (trimethylsilylmethyl)lithium $Li[CH_2Si(CH_3)_3]$ in 40 ml of diethyl eter with rigorous exclusion of air, gave the novel alkyl derivatives **4** and **5** in yields of ca. 70 and 50%, respectively, based on the amounts of titanium and zirconium complexes initially taken.

$$\left[(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\right]MCl_2 + 2.1\ LiCH_2Si(CH_3)_3 \longrightarrow$$



(M = Ti (**4**); Zr (**5**))

The compounds were identified from their elemental analyses, and EI-mass spectra and ^1H and ^{13}C NMR spectra.

In the ^{13}C NMR spectra of **4** and **5** the resonance due to the ring C(1) atom, directly bonded to Si, is displaced by 5–10 ppm to higher field (δ 102.4 ppm for **4**; δ 99.70 ppm for **5**) with respect to that for the corresponding chloro precursor compounds **1** and **2**, as expected in view of the presence of the less electronegative alkyl substituents. This displacement is even more pronounced when compared with compounds containing unsubstituted rings, e.g. $(\eta^5\text{-}C_5H_5)_2MCl_2$ (δ 120.4 ppm for M = Ti; δ 115.7 ppm for M = Zr). However, the opposite is observed [3] for $[\eta^5\text{-}C_5H_4Si(CH_3)_3]_2ZrCl_2$, in which C(1) is deshielded (δ 124.0 ppm) with respect

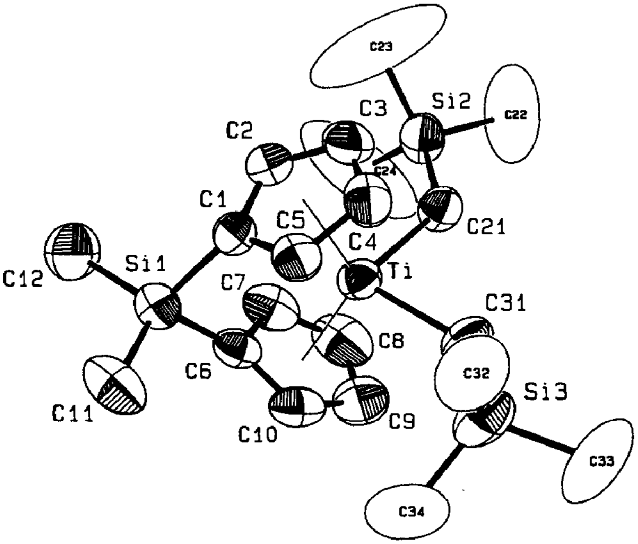


Fig. 1. Perspective ORTEP drawing of **4**. Thermal ellipsoids scaled at 50% level. Selected bond lengths (pm) and angles (°) are given in Table 2.

to the parent C_5H_5 complex, this effect being attributed to a net electron withdrawal by the $Si(CH_3)_3$ group. Thus the shift to higher fields for the C(1) signal in our complexes **4** and **5** implies that there is a bonding contribution by the electron withdrawing Si 3*d* orbitals in the silylene bridged ring which modifies the π-electron distribution in the ring, resulting in shielding of the C(1) atom but deshielding of the remaining ring carbon atoms. In order to obtain additional information, we recorded the UV-VIS spectra of **1** and **2**. It has recently been reported that for a series of different ring-substituted titanocene dichlorides the symmetry-forbidden $A_1 \rightarrow A_2$ transition between λ 500 and 560 nm moves to lower energy as more electron-donating substituents are introduced into the rings (523 nm for $(\eta^5\text{-}C_5H_5)_2TiCl_2$ [4]; 334 for $(\eta^5\text{-}C_5H_5)_2ZrCl_2$). We found absorption bands with maxima at 542 nm (for **1**) and 356 nm (for **2**); the value observed for the novel titanocene dichloride is comparable to that for $[\eta^5\text{-}1,2,4\text{-}C_5H_2(CH_3)_3]_2TiCl_2$ (536 nm).

This behaviour provides further experimental evidence for the net effect due to the electron distribution in the ring produced by the silylene group, without modification of the electronic situation at the metal center. The change in electron distribution in the ring for compound **1** has been confirmed by the distortions observed in the crystal structure [2a]. This confers interesting structural and electronic properties on compounds of this type, and their behaviour in reduction and C–H bond activation processes is being studied.

The structure of compound **4** was determined by X-ray diffraction. A perspective view and important parameters of the molecular structure is presented in Fig. 1, along with the appropiate atom-labeling scheme. The molecular parameters about the central atom are comparable to those reported for several group 4 metallocenophane dichlorides [2a]. Two C_5H_4 ring centroids and two $CH_2Si(CH_3)_3$ groups in **4** define a tetrehadron like that in $[(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2]TiCl_2$. In contrast to reports on **4** [2a] no significant π-bonding contribution from a η^3-allyl,η^2-olefin resonance structure could be detected in the X-Ray structure. It is true that the distances Ti–C3 (244.5(2) pm), Ti–C4 (244.3(2) pm), Ti–C8 (246.0(3) pm) and Ti–C9 (246.1(2) pm) are significantly longer than the other six Ti–C bonds, which range from 238.4(1) to 241.7(2) pm, but there is no shortening for C3–C4 (140.7(2) pm) and C8–C9 (139.5(3) pm). This effect reflects the difference in the titanium carbon ring bonding interactions arising from the electron ring distribution induced by the silicon atom and controlled by the steric hindrance imposed by the other two substituents bonded to the metal [5].

Experimental

Preparation of $[(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2]Ti[CH_2Si(CH_3)_3]_2$ *(4)*

A suspension of $[(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2]TiCl_2$ (**1**) (600 mg, 1.97 mmol) in 40 ml of diethyl ether was treated with $Li[CH_2Si(CH_3)_3]$ (370 mg, 3.94 mmol) at −30 °C. The mixture was allowed to warm slowly to room temperature and then stirred for 2–3 h. The yellow suspension formed was filtered and filtrate was evaporated under vacuum to about half of its volume, then kept at −18 °C to give orange crystals of **4**. Yield: 563 mg (70%).

Table 1

Positional parameters and their estimated standard deviations

(Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq} = (4/3)\cdot[a^2\cdot B_{1,1} + \ldots + ab(\cos\gamma) * B_{1,2} + \ldots]$ (Å^2). Cp denotes the centroid of the cyclopentadienyl ligand.)

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Ti	0.25079(5)	0.30132(5)	0.26364(4)	4.11(1)
Si1	0.23970(9)	0.15898(9)	0.51389(7)	5.02(2)
Si2	0.08760(9)	0.19936(9)	0.06022(8)	5.56(2)
Si3	0.42510(11)	0.56073(11)	0.25182(8)	6.82(2)
C1	0.1126(3)	0.3066(3)	0.4415(2)	4.3(1)
C2	0.0230(3)	0.3012(3)	0.3658(3)	4.9(1)
C3	−0.0122(3)	0.4198(4)	0.2976(3)	5.5(1)
C4	0.0577(3)	0.5004(3)	0.3271(3)	5.3(1)
C5	0.1357(3)	0.4298(3)	0.4142(2)	4.6(1)
C6	0.3683(3)	0.1155(3)	0.3893(3)	4.6(1)
C7	0.3407(3)	0.0643(3)	0.2995(3)	5.7(1)
C8	0.4280(4)	0.0888(4)	0.2064(3)	7.4(1)
C9	0.5094(3)	0.1604(4)	0.2322(3)	7.3(1)
C10	0.4724(3)	0.1779(3)	0.3430(3)	5.8(1)
C11	0.3203(4)	0.2093(4)	0.6174(3)	7.4(1)
C12	0.1553(4)	0.0292(4)	0.5711(4)	8.7(1)
C21	0.1813(3)	0.2988(3)	0.1085(3)	4.9(1)
C22	0.0812(6)	0.2375(5)	−0.0844(4)	17.1(2)
C23	−0.1006(5)	0.2354(6)	0.1236(5)	24.7(2)
C24	0.1690(6)	0.0216(5)	0.0843(5)	25.2(2)
C31	0.3464(3)	0.4549(3)	0.1951(3)	5.4(1)
C32	0.2874(4)	0.6937(4)	0.3291(4)	8.9(1)
C33	0.5177(5)	0.6448(4)	0.1361(4)	12.6(1)
C34	0.5674(4)	0.4619(4)	0.3444(4)	9.9(1)
Cp1	0.0633	0.3915	0.3692	
Cp2	0.4237	0.1213	0.2940	

^{1}H NMR (270 MHz, C_6D_6, 28 °C): $\delta[(CH_3)_2Si]$ 0.07 (s, 6H); $\delta[(CH_3)_3Si]$ 0.12 (s, 18H); $\delta(TiCH_2Si)$1.00 (s, 4H); $\delta(C_5H_4)$5.51 (t, J 2.3 Hz, 4H$^\alpha$); 7.19 (t, J 2.2 Hz, 4H$^\beta$).

^{13}C NMR (67.8 MHz, C_6D_6, 28 °C): $\delta[(CH_3)_2Si]$ −5.71; $\delta[(CH_3)_3Si]$ 3.35; $\delta(TiCH_2Si)$ 65.2; $\delta[(C_5H_4)(C_1)]$ 102.4; $\delta[(C_5H_4)(C_3)]$ 114.1; $\delta[(C_5H_4)(C_2)]$ 124.5.

EI-MS (70 eV): $m/z = 321$ ($[M - CH_2Si(CH_3)_3]^+$, 40%); 234 ($[M - 2CH_2Si(CH_3)_3]^+$, 100%). The C, H analysis was as expected.

Crystal data: "STRUX-II, Programmsystem zur Verarbeitung von Roentgendaten, Universität Marburg (1980) und TU München (1985, 1987), BRD. Orange crystals from diethyl ether (−78 °C; irregular shape); triclinic space group $P\bar{1}$ (Int. Tab. No. 2); cell dimensions from a least squares fit of 25 reflections in the range $35.8° < 2\theta < 41.8°$: a 985.7(1), b 1077.7(1), c 1252.6(1) pm, α 81.08(1), β 80.01(1)°, γ 69.28(1)°; V 1219×10^6 pm^3; empirical formula: $C_{20}H_{36}Si_3Ti$, fw 408.7; $Z = 2$; $F(000) = 440$; ρ(cal.) 1.113 g cm^{-3}; Enraf–Nonius CAD-4, Mo-K_α-radiation (λ 71.073 pm), graphite monochromator; T 23 ± 1 °C; ω-scans in the range $2.0° \leq \theta \leq 30.0°$; scan width $(1.20 + 0.30\ \mathrm{tg}\theta)° \pm 25\%$ before and after each reflection for background determination; t_{max} 45 s; 5773 measured reflections ($-h, \pm k, \pm l$), 381 reflections with negative intensity rejected. 4001 independent reflections of which

Table 2

Selected bond lengths (pm) and bond angles (°)

Ti–C1	239.9(1)	Si1–C1	186.0(2)
Ti–C2	238.4(1)	Si1–C6	183.9(2)
Ti–C3	244.5(2)	Si1–C11	186.8(3)
Ti–C4	244.3(2)	Si1–C12	186.2(2)
Ti–C5	239.2(2)	Si2–C21	186.1(2)
Ti–C6	241.7(2)	Si2–C22	180.1(3)
Ti–C7	238.6(2)	Si2–C23	181.5(3)
Ti–C8	246.0(3)	Si2–C24	179.5(4)
Ti–C9	246.1(2)	Si3–C31	186.4(2)
Ti–C10	241.2(2)	Si3–C32	185.2(2)
Ti–C21	217.7(2)	Si3–C33	186.4(2)
Ti–C31	217.9(2)	Si3–C34	189.0(3)
Ti–Cp1 [a]	209.5		
Ti–Cp2	211.4		
C1–C2	142.4(3)	C6–C7	143.2(2)
C2–C3	139.0(2)	C7–C8	137.4(3)
C3–C4	140.7(2)	C8–C9	139.5(3)
C4–C5	140.6(2)	C9–C10	139.7(3)
C5–C1	140.6(2)	C10–C6	141.5(2)
C21–Ti–C31	91.7(1)	C1–Si1–C6	93.0(1)
C21–Ti–Cp1	107.7	C1–Si1–C11	111.3(1)
C21–Ti–Cp2	108.2	C1–Si1–C12	112.6(1)
C31–Ti–Cp1	106.9	C6–Si1–C11	112.5(1)
C31–Ti–Cp2	107.9	C6–Si1–C12	113.0(2)
Cp1–Ti–Cp2	128.4	C11–Si1–C12	112.9(2)
Ti–C21–Si2	134.1(1)		
Ti–C31–Si3	135.1(1)		

[a] Cp denotes the centroid of the cyclopentadienyl ligand.

719 reflections with $I < 3.0\sigma(I)$ are supressed; 230 parameters full matrix least squares refined; $R = \Sigma(\| F_o | - | F_c |)/\Sigma | F_o | = 0.049$, $R_w = [\Sigma w(| F_o | - | F_c |)^2/\Sigma | F_o |^2]^{1/2} = 0.049$ and $\mathrm{GOF} = [\Sigma W(| F_o | - | F_c |)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2} = 4.668$ with $w = 1/\sigma^2(F_o)$. The structure solution was by Patterson's method and difference Fourier techniques. No absorbtion correction (μ 4.9 cm^{-1}) was applied. Correction was made for decomposition (85.5 h; −32.8%). The hydrogen atoms were placed in calculated positions (C–H 95 pm) and included in the structure factor calculations (with common isotropic temperature factors for the H atoms of each C atom) but not refined. Anomalous dispersion was taken into account. Shift error < 0.001 in the last refinement cycle; residual electron density: $+0.53$ e/A^3 and -0.43 e/$\mathrm{Å}^3$ respectively. Positional parameters are listed in Table 1 and selected bond lengths and bond angles in Table 2. Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (West-Germany), by quoting the depository number CSD 53449, the names of the authors, and the journal reference.

Preparation of $[(C_5H_4)_2Si(CH_3)_2]Zr[CH_2Si(CH_3)_3]$ *(5)*

The procedure described for **4** gave **5** in 65% yield.

^{1}H NMR (80 MHz, C_6D_6, 28 °C): $\delta[(CH_3)_2Si]$ 0.11 (s, 6H); $\delta[(CH_3)_3Si]$ 0.17 (s, 18H); $\delta(ZrCH_2Si)$ 0.19 (s, 4H); $\delta(C_5H_4)$ 5.71 (t, J 2.3 Hz, 4H$^\alpha$); 6.71 (t, J 2.3 Hz, 4H$^\beta$).

^{13}C NMR (17.8 MHz, C_6D_6, 28 °C): $\delta[(CH_3)_2Si] - 4.91$ (q, J 113.23 Hz); $\delta[(CH_3)_3Si]$ 3.70 (q, J 116.61 Hz); $\delta(ZrCH_2Si)$ 46.88 (t, J 106.94 Hz); $\delta[(C_5H_4)(C_1)]$ 99.70 (m); $2\delta[(C_5H_4)(C_3)]$ 111.63 (dm, J 150.19 Hz.); $\delta[(C_5H_4)(C_2)]$ 120.34 (dm, J 150.19 Hz.). The C, H analysis was as expected.

Acknowledgement

We greatly appreciate financial support from CICYT (PB86-0093), Acción Integrada (MEC-DAAD No. 1/51 B), and also thank the Deutsche Akademische Austauschdienst (Acciones Integradas Hispano-Alemanas) for generous support of this work.

References

1 J.A. Smith and H.H. Brintzinger, J. Organomet. Chem., 218 (1981) 159.
2 (a) C.S. Bajgur, W.R. Tikkanen and J.L. Petersen, Inorg. Chem., 24 (1985) 2539; and ref. cited therein; (b) H. Yasuda, K. Nagasuna, M. Akita, K. Lee and A. Nakamura, Organometallics, 3 (1984) 1470.
3 M.F. Lappert, C.J. Pickett, P.I. Riley and P.I. Yarrow, J. Chem. Soc. Dalton Tans., (1981) 805.
4 W.C. Finch, E.V. Anslyn and R.H. Grubbs, J. Am. Chem. Soc., 110 (1988) 2406.
5 R. Gómez, T. Cuenca, P. Royo, unpublished results.