

New 1,1'-Ring-substituted Vanadocene Dichlorides. Crystal Structures of $[V(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ and $[V(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$

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Abstract. The 1,1'-ring-substituted vanadocene dichlorides $[V(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]$ (R = CMe₃, SiMe₃, SiEt₃) have been prepared from VCl₄ and the appropriate lithiated cyclopentadiene, C₅H₄RLi, in 1:2 ratios. All complexes were characterized by elemental microanalysis and IR spectroscopy. The crystal structures of $[V(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ **3** and the parent compound $[V(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ **1** have been determined by X-ray diffraction and are in accordance with expectations. Compound **1**

crystallizes with two crystallographically independent molecules in its monoclinic unit cell. These two molecules are quite similar in their essential structural features. Compound **3** crystallizes in the triclinic space group P $\bar{1}$. The trimethylsilylcyclopentadienyl rings are bound in a staggered relative orientation.

Keywords: Vanadium; Vanadocene dichloride; Ring-substituted vanadocenes; Crystal structure

Neue 1,1'-ringsubstituierte Vanadocendichloride. Kristallstrukturen von $[V(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ und $[V(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$

Inhaltsübersicht. Die 1,1'-ringsubstituierten Vanadocendihalo-
genide $[V(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]$ (R = CMe₃, SiMe₃, SiEt₃) wurden
aus VCl₄ und dem geeigneten lithiierten Cyclopentadien,
C₅H₄RLi, im Molverhältnis 1:2 dargestellt. Alle Komplexe
wurden elementaranalytisch und IR spektroskopisch charak-
terisiert. Die Kristallstrukturen von $[V(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ **3**
und der Stammverbindung $[V(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ **1** wurden durch
Röntgenstrukturanalysen bestimmt und entsprechen den Er-

wartungen. Verbindung **1** kristallisiert mit zwei kristallogra-
phisch unabhängigen Molekülen in ihrer monoklinen Eleme-
ntarzelle. Diese zwei Moleküle sind ganz ähnlich in ihren
wesentlichen strukturellen Merkmalen. Verbindung **3**
kristallisiert in der triklinen Raumgruppe P $\bar{1}$. Die Trimethyl-
silylcyclopentadienylringe sind in einer gestaffelten relativen
Orientierung am Metall gebunden.

1 Introduction

The chemistry of vanadocene dichloride complexes has attracted interest for several reasons, notably on account of the high antitumor activity of the parent compound $[V(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ **1** [1, 2] and the nature of bonding and electronic structure in these *d*¹ molecules [3–5]. In contrast to a large number of ring-substituted titanocene dichloride derivatives which have been prepared and structurally studied [3, 6–11], little work has been reported on vanadium(IV) analogues [3, 12–15]. Such ring-substituted complexes are of interest because of the significant changes in reactivity, stability, catalytic and antitumor activity and other properties brought about by the substituents [16–19].

Here we describe the synthesis and characterization of some new stable complexes of the type $[V(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]$ (R = CMe₃ **2**, SiMe₃ **3**, SiEt₃ **4**) and the crystal structures of **3** and the parent compound $[V(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ **1**. The results compared to those of closely related molecules, help to identify overall structural trends in such complexes.

2 Experimental

Owing to the air sensitivity of the cyclopentadienide salts and vanadium(IV) chloride all preparations and other operations were carried out under a dry and oxygen-free argon atmosphere, using standard Schlenk techniques. Solvents were thoroughly dried and degassed before use. VCl₄ (Aldrich) and n-BuLi

(Merck) were obtained commercially and used as received. The substituted cyclopentadienes $C_5H_5(t-Bu)$ [20], $C_5H_5SiMe_3$ and $C_5H_5SiEt_3$ were prepared according to published procedures [21, 22]. Elemental C, H analyses were performed with a Perkin-Elmer 240C microanalyzer. IR spectra in the region $4000-600\text{ cm}^{-1}$ were obtained as KBr discs on a Perkin-Elmer 16PC FT-IR spectrophotometer. Magnetic susceptibilities were measured at room temperature by the Faraday method with a Cahn-Ventron RM-2 balance standardized with $Hg[Co(SCN)_4]$. All molar susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants (χ_M)_{corr}. Effective magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.83[(\chi_M)_{\text{corr}}T]^{1/2}$.

2.1 Preparation of the Complexes (1)–(4) (General Procedure):

To a solution of 48 mmol C_5H_5R ($R = H, t-Bu, SiMe_3$ or $SiEt_3$) in 15 mL petroleum ether, 30 mL (1.6 M, 48 mmol) of *n*-BuLi were added at room temperature, resulting in an immediate precipitation of a white solid. This was dissolved in ca. 25 mL THF and the solution was added dropwise to a suspension of 24 mmol VCl_4 in 15 mL petroleum ether at 0°C . The resulting green-brown suspension was stirred at 0°C

for 1 h and then heated at reflux for 2 h. Filtration of the reaction mixture, evaporation of the filtrate to ca. 5 mL and cooling to -25°C afforded the desired products $[V(\eta^5-C_5H_4R)_2Cl_2]$. **1**: 16% yield; light green crystals, m. p. 205°C (decomposition). $\mu_{\text{eff}}^{298} = 1.71\text{ BM}$. **2**: 10% yield; moss green microcrystals, m. p. 260°C (decomposition). $\mu_{\text{eff}}^{298} = 1.62\text{ BM}$. **3**: 14% yield; fibrous, light green crystals, m. p. 180°C (decomposition). $\mu_{\text{eff}}^{298} = 1.72\text{ BM}$. **4**: 19% yield; moss green microcrystals, m. p. 213°C (decomposition). $\mu_{\text{eff}}^{298} = 1.68\text{ BM}$.

2.2 Crystallographic Section

Slow vapour-diffusion-controlled recrystallization from CH_2Cl_2 /petroleum ether at room temperature gave green prismatic crystals of $[V(\eta^5-C_5H_5)_2Cl_2]$ **1** and $[V(\eta^5-C_5H_4SiMe_3)_2Cl_2]$ **3**. A crystal of **1** [$0.08 \times 0.14 \times 0.30\text{ mm}$] and of **3** [$0.34 \times 0.15 \times 0.05\text{ mm}$] was mounted in air. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11 < 2\theta < 24$ and they appear in Table 1, along with other crystal, data collection and refinement data. Three standard reflections monitored every 97 reflections showed less than 3%

Table 1 Summary of crystal, intensity collection and refinement data

Formula	$C_{10}H_{10}Cl_2V$	$C_{16}H_{26}Cl_2Si_2V$
fw	252.02	396.39
a (Å)	12.271(5)	6.769(1)
b (Å)	13.061(6)	12.907(2)
c (Å)	13.411(6)	12.712(3)
α , deg		67.227(7)
β , deg	109.255(12)	104.789(7)
γ , deg		97.599(6)
V, Å ³	2029(2)	989.4(3)
Z	8	2
Dcalc/Dmeasd (Mg m ⁻³)	1.650/1.62	1.331/1.31
Space group	P2 ₁ /a	P1
Temp, K	298	298
Radiation, λ	MoK α 0.7107	MoK α 0.7107
Abs coeff(μ), mm ⁻¹	1.450	0.885
Max. Abs. correction mode	1.19	1.36
Scan mode/speed (deg/min)	θ -2 θ /2.5	θ -2 θ /1.0
Scan range (deg)	2.5 + $\alpha_1\alpha_2$ separation	2.5 + $\alpha_1\alpha_2$ separation
θ range (deg)	1.61 to 25.00	1.71 to 22.50
Reflections collected	3743	2857
Independent reflections	3584 [R(int) = 0.0178]	2589 [R(int) = 0.0258]
Range of h, k, l	-14 → 13, -15 → 0, 0 → 15	-7 → 0, -13 → 13, -13 → 13
F(000)	1016	414
$[\Delta/\sigma]_{\text{max}}$	0.118	0.012
W ^{a)}	a = 0.0795 b = 6.0705	a = 0.0721 b = 1.4166
$[\Delta\rho]_{\text{max}}/[\Delta\rho]_{\text{min}}$ (e/Å ³)	0.598 and -0.533	0.550 and -0.781
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	3578/0/219	2581/0/262
Goodness-on-fit on F ²	1.041	1.122
R indices [2840 (2176) refs]	R1 = 0.0593, wR2 = 0.1551	R1 = 0.0503, wR2 = 0.1281
I > 2 σ (I) ^{b)}		
R indices (all data)	R1 = 0.0765, wR2 = 0.1802	R1 = 0.0612, wR2 = 0.1421

^{a)} $W = 1/[\sigma^2(F_o^2) + (a^*P)^2 + b^*P]$ and $P = (\text{Max}(F_o^2, 0) + 2^*F_c^2)/3$

^{b)} R1 based on F's, wR2 based on F²

variation and no decay. Lorentz, polarization and Ψ -scan absorption correction were applied using Crystal Logic software.

The structures were solved by direct methods using SHELXS-86 [23] and refined by full-matrix least-squares techniques with SHELXL-93 [24]. In complex **1** the asymmetric unit contains two independent molecules. The two cyclopentadi-

Table 2 Positional and equivalent thermal parameters ($\times 10^4$) of the non-H atoms. E. s. d.'s in parentheses. $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$

Atom	x	y	z	U_{eq}
[V(η^5-C₅H₅)₂Cl₂]				
V(1)	2177(1)	7097(1)	9668(1)	39(1)
Cl(1)	3714(1)	5954(1)	9657(1)	54(1)
Cl(2)	877(1)	5688(1)	8947(1)	59(1)
C(1)	2036(14)	7411(7)	7947(8)	46(3)
C(2)	2987(9)	7981(10)	8594(10)	55(3)
C(3)	2545(11)	8711(7)	9148(7)	47(3)
C(4)	1298(10)	8572(8)	8820(8)	46(3)
C(5)	1002(10)	7767(10)	8051(10)	55(3)
C(6)	1636(13)	7998(10)	10918(8)	42(3)
C(7)	2868(13)	8070(10)	11204(9)	51(3)
C(8)	3276(12)	7042(15)	11446(10)	57(4)
C(9)	2332(19)	6389(11)	11266(11)	61(4)
C(10)	1279(12)	6970(16)	10940(11)	61(4)
V(2)	2434(1)	-78(1)	4747(1)	39(1)
Cl(3)	3782(1)	1209(1)	4601(1)	55(1)
Cl(4)	995(1)	1254(1)	4339(2)	68(1)
C(11)	3814(8)	-164(10)	6405(7)	51(3)
C(12)	3339(12)	-1161(9)	6145(7)	54(3)
C(13)	2132(12)	-1107(9)	6048(7)	53(3)
C(14)	1890(9)	-97(11)	6235(8)	53(3)
C(15)	2890(13)	499(7)	6440(7)	50(3)
C(16)	1957(13)	-1666(8)	3988(8)	42(3)
C(17)	1109(13)	-993(16)	3439(15)	69(4)
C(18)	1637(16)	-283(9)	2929(9)	49(3)
C(19)	2792(15)	-478(11)	3161(11)	53(4)
C(20)	3046(12)	-1349(13)	3854(11)	56(4)
[V(η^5-C₅H₄SiMe₃)₂Cl₂]				
V	1558(1)	2508(1)	2695(1)	30(1)
Cl(1)	-1342(2)	3230(1)	1091(1)	47(1)
Cl(2)	-926(2)	1820(1)	3902(1)	45(1)
Si(1)	2954(2)	2830(1)	5650(1)	45(1)
Si(2)	1899(2)	2205(1)	-123(1)	42(1)
C(1)	1519(8)	4110(4)	3065(4)	43(3)
C(2)	2249(9)	4441(4)	2042(5)	50(3)
C(3)	4097(9)	3922(4)	2337(5)	49(3)
C(4)	4520(7)	3273(4)	3557(4)	41(2)
C(5)	2930(7)	3380(4)	4039(4)	36(2)
C(6)	753(8)	958(4)	2180(4)	40(3)
C(7)	1737(8)	556(4)	3378(4)	45(3)
C(8)	3728(8)	1015(4)	3478(4)	44(3)
C(9)	4003(7)	1666(4)	2333(4)	39(3)
C(10)	2148(7)	1643(4)	1511(4)	37(3)
C(11)	3588(13)	1319(6)	6338(6)	68(6)
C(12)	506(11)	3111(7)	5895(6)	83(5)
C(13)	5033(12)	3642(6)	6315(6)	68(5)
C(14)	2816(10)	3698(5)	-672(5)	59(4)
C(15)	3647(12)	1338(6)	-343(6)	76(6)
C(16)	-796(10)	1985(7)	-882(6)	81(4)

enyl rings of each molecule were found disordered and they were refined isotropically in two different positions. Only vanadium and chlorine atoms were refined anisotropically. Hydrogen atoms were not included in the refinement.

In complex **3** all hydrogen atoms (except those of C12, C14, C15 and C16 which were introduced at calculated positions as riding on bonded atoms) were located by difference maps and their positions were refined isotropically. All non-hydrogen atoms were refined anisotropically.

The positional parameters and the equivalent isotropic temperature factors for the non-hydrogen atoms are collected in Table 2. Hydrogen atomic coordinates and a list of structure

Table 3 Selected bond distances and angles for [V(η^5 -C₅H₅)₂Cl₂] **1** and [V(η^5 -C₅H₄SiMe₃)₂Cl₂] **3**

	1		3
	Molecule A	Molecule B	
A. Bond distances (Å)			
<i>Coordination about the vanadium atom</i>			
V—Cl(1)	2.409(2)	2.410(2)	2.419(2)
—Cl(2)	2.418(2)	2.409(2)	2.415(2)
—Cp(1)	1.97(1)	1.97(1)	1.986(1)
—Cp(2)	1.97(1)	1.98(1)	1.954(2)
<i>Cyclopentadienyl group</i>			
C(1)—C(2)	1.41(2)	1.42(1)	1.399(8)
C(2)—C(3)	1.42(2)	1.44(1)	1.394(8)
C(3)—C(4)	1.46(1)	1.39(1)	1.421(8)
C(4)—C(5)	1.43(2)	1.40(2)	1.412(7)
C(5)—C(1)	1.40(2)	1.44(1)	1.437(7)
<i>Trimethylsilyl group</i>			
Si—C(5)			1.887(5)
—C(11)			1.861(7)
—C(12)			1.867(6)
—C(13)			1.865(7)
B. Bond angles (°)			
<i>Coordination about the vanadium atom</i>			
Cl(1)—V—Cl(2)	86.6(1)	87.1(1)	85.39(5)
Cl(2)—V—Cp(1)	106.8(3)	107.3(3)	107.85(6)
Cp(1)—V—Cp(2)	131.2(5)	132.1(5)	134.32(8)
Cp(2)—V—Cl(1)	107.4(4)	106.3(3)	107.00(5)
Cl(1)—V—Cp(1)	107.4(4)	107.4(4)	106.69(5)
Cl(2)—V—Cp(2)	108.4(4)	107.2(3)	104.75(6)
<i>Cyclopentadienyl group</i>			
C(5)—C(1)—C(2)	110.7(9)	107.2(8)	110.1(5)
C(1)—C(2)—C(3)	107.1(9)	107.6(8)	107.5(5)
C(2)—C(3)—C(4)	107.5(8)	107.6(8)	108.1(5)
C(3)—C(4)—C(5)	107.5(8)	109.7(9)	109.4(4)
C(4)—C(5)—C(1)	107.1(8)	107.8(8)	104.8(4)
<i>Trimethylsilyl group</i>			
C(5)—Si(1)—C(11)			110.2(3)
C(5)—Si(1)—C(12)			111.0(3)
C(5)—Si(1)—C(13)			106.5(3)
C(11)—Si(1)—C(12)			113.3(4)
C(11)—Si(1)—C(13)			108.3(4)
C(11)—Si(1)—C(13)			107.3(4)

Cp refers to the centroids of the cyclopentadienyl rings

factors can be obtained from the authors. A selection of bond distances and bond angles is given in Table 3.

3 Results and Discussion

Complexes **1–4** were obtained as green crystalline, air-stable solids in 10–20% yield by reaction of VCl_4 with the appropriate lithiated cyclopentadiene, $\text{C}_5\text{H}_4\text{RLi}$, in 1:2 molar ratios in THF. They are soluble in all usual organic solvents. In water they form green unstable solutions. They are all paramagnetic with one unpaired electron. The IR spectra show the characteristic absorptions of η^5 -bonded cyclopentadienyl rings [3, 25] and trialkyl groups [26].

3.1 Crystal Structures of $[\text{V}(\eta^5\text{-C}_5\text{H}_3)_2\text{Cl}_2]$ **1** and $[\text{V}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ **3**

The unit cell of **1** contains two crystallographically independent but essentially identical molecules (A and B, Table 3). Their molecular structure is depicted in Fig. 1 together with the atomic numbering scheme. If the ring centroids are considered as coordination sites, the coordination geometry around the vanadium centre is a distorted tetrahedron, the other two coordination sites being occupied by the chlorine atoms. This stereochemistry is generally adopted by all monomeric metallocene complexes of the type $[\text{M}(\eta^5\text{-C}_5\text{H}_3)_2\text{X}_2]$ [27].

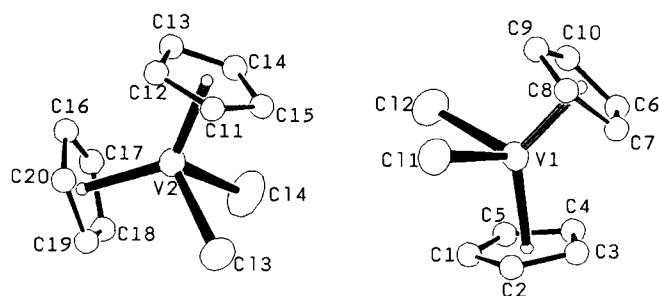


Fig. 1 ORTEP diagram showing the two independent molecules of **1** with the atomic labeling scheme

The metal-to-ring normal distances, which are less affected by thermal motion or disorder than the carbon-metal distances, are a little shorter than those found in $[\text{V}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Cl}_2]$ [3]. The Cl—V—Cl angle falls in the range 85–88° which corresponds to that expected for d^1 metallocene dichlorides [27]. Also the V—Cl bond lengths and Cp—V—Cp bond angle are normal and comparable with other published data (Table 4).

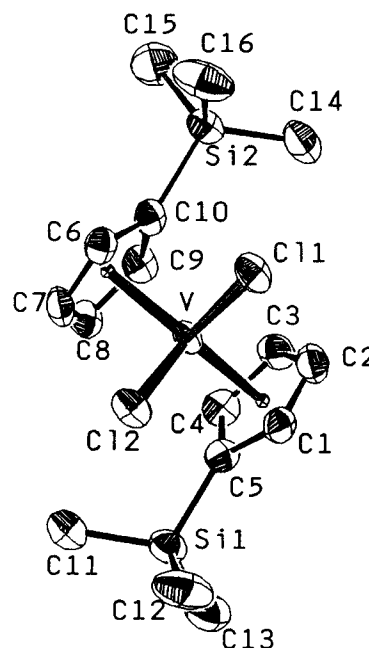


Fig. 2 ORTEP diagram of **3** with the atomic labeling scheme

The molecular structure of **3** is illustrated in Fig. 2. The compound is isostructural with $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ [31] and the stereochemistry about the metal centre is best described as distorted tetrahedral. The cyclopentadienyl rings have the staggered conformation with the SiMe_3 groups positioned at opposite sides of the molecule, directed away from each other. This structure, adopted only by molecules with bulky Cp-ring substi-

Table 4 Comparison of structural parameters (averaged values) for some $[\text{M}(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]$ compounds (R = H, Me, or SiMe_3)

Compound	M—Cp	M—Cl	Cp—M—Cp	Cl—M—Cl	Reference
$[\text{V}(\eta^5\text{-C}_5\text{H}_3)_2\text{Cl}_2]$	1.97	2.412	131.6	86.8	this work
$[\text{V}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$	1.991	2.398	133.4	87.1	[3]
$[\text{V}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$	1.970	2.417	134.3	85.4	this work
$[\text{Ti}(\eta^5\text{-C}_5\text{H}_3)_2\text{Cl}_2]$	2.058	2.364	131.0	94.5	[28]
$[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$	2.067	2.361	130.2	93.2	[3]
$[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$	2.062	2.365	131.0	91.6	[9]
$[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$	2.090	2.467	130.2	85.6	[27]
$[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$	2.078	2.462	131.7	84.8	[31]
$[\text{Zr}(\eta^5\text{-C}_5\text{H}_3)_2\text{Cl}_2]$	2.20	2.441	126.6	97.1	[27]
$[\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$	2.21	2.490	129.1	94.0	[30]

tments, contrasts with those of the methyl-substituted complexes $[M(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Cl}_2]$ ($M = \text{Ti, V}$) [3] in which the methyl substituents are located on the same side of the molecule above and below the MCl_2 group. This is attributable to the larger steric requirements of the SiMe_3 substituents. The Si atom shows almost tetrahedral coordination. The Si—C distances and angles about the silicium centre are normal.

If the structure of **3** is compared with those of its analogues $[M(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ (Table 4), the similar trends, observed previously in the unsubstituted $[M(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ complexes and concerning mainly the MCl_2 system, can be noted [27]. These trends are a consequence of the presence of the unpaired electron in d^1 complexes, which resides in a non-bonding but sterically significant orbital of approximate d_{z^2} character [3]. It is worth observing that the introduction of the SiMe_3 group into the cyclopentadienyl ring does not cause essential modifications in the bonding to the metal, as already reported for the titanium analogue [9].

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