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Methylcyclopentadienyl-vanadium(III) complexes

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Abstract

[(MeCp)VCl$_2$(PEt$_3$)$_2$] (1) and [(MeCp)$_2$VCl] (4) (MeCp = η^5-C$_5$H$_4$CH$_3$) have been obtained from the reaction between VCl$_3$ and NaMeCp in THF in the presence (1) and absence (4), respectively, of PEt$_3$. The reaction of VCl$_3$ and NaMeCp in the presence of CNt-Bu yielded (impure) [(MeCp)VCl$_2$(CNt-Bu)$_2$] (3) and, as a by-product, [(MeCp)$_2$V(CNt-Bu)$_2$][VCl$_4$(THF)$_2$] (2). The crystal and molecular structures of 1, 2 and 4 have been determined. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Increasing interest in the potential of cyclopentadienyl-vanadium chlorides as polymerisation catalysts [1], cancerostatic [2a] and bactericidal agents [2b], and active precursor compounds in a broad range of chemical reactions [3] has prompted us to re-evaluate and complement preparative and structural aspects of the chemistry of this group of compounds. There are essentially two routes that lead to V^{III} complexes of the types [CpVCl$_2$] and [Cp$_2$VCl], viz. (i) salt metathesis between VCl$_3$ (or THF-stabilised VCl$_3$) and Cp, where M = Tl [4,5] or Na [6,7], and (ii) reaction between [VCl$_3$(THF)$_3$] and NaCp or MgCp$_2$ in the presence of phosphines [8,9]. In the latter case, [CpVCl$_2$(PR$_3$)$_2$] is obtained (Cp = C$_5$H$_5^-$ and RC$_5$H$_4^-$; R = Me, Et), a reaction which we have employed to synthesise and structurally characterise the methylcyclopentadienyl (MeCp) complex [MeCpVCl$_2$(PEt$_3$)$_2$] (1). [CpVCl$_2$] by itself, i.e. without supporting ligands, does not seem to exist. Also, efforts to generate compounds with Cp-related six-electron donor ligands such as tris(pyrazolyl)borate

(HBpz) or amine-amidinate (amd) yielded ligand supported [(HBpz)VCl$_2$L] [10] and [(amd)VCl$_2$L] [11], e.g. L = THF. In the case of pentamethyl cyclopentadienide (Cp*), the trimer [Cp*VCl$_2$]$_3$ with bridging chloro ligands has been characterised [12,13]. Efforts to extend reaction (ii) to the generation of complexes stabilised by isocyanides have now lead to the isolation of [(MeCp)$_2$V(CNt-Bu)$_2$][VCl$_4$(THF)$_2$] (2).

While the reaction between VCl$_3$ and TlCp directly affords [Cp$_2$VCl] [4], VCl$_3$ and NaCp have been reported to yield either vanadocene (which can be converted to [Cp$_2$VCl] and [Cp$_2$VCl$_2$] by treatment with PCl$_3$) [7], or [Cp$_2$VCl$_2$] and an unnoticed reduction product [6], possibly vanadocene. We have now found that, in the case of MeCp, the disproportionation is accompanied by a non-redox side reaction, in which [(MeCp)$_2$VCl] (4) is formed.

2. Results and discussion

Complexes 1–4 were prepared according to Eqs. (1)–(3).
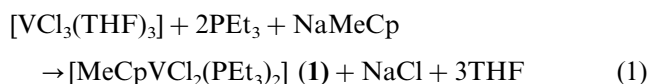
$$[VCl_3(THF)_3] + 2PEt_3 + NaMeCp$$
$$\rightarrow [MeCpVCl_2(PEt_3)_2] \text{ (1)} + NaCl + 3THF \qquad (1)$$
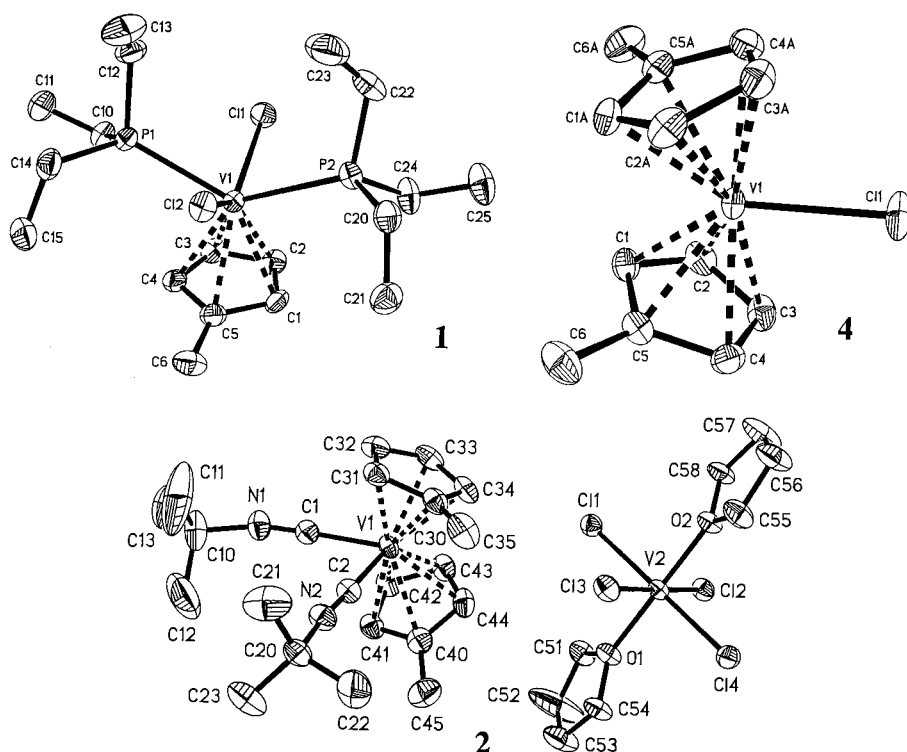
Fig. 1. ORTEP drawings (50% probability level) of **1**, **2** and **4**. H atoms were omitted for clarity.

$$[VCl_3(THF)_3] + 2CNt\text{-}Bu + NaMeCp$$

$$\rightarrow [MeCpVCl_2(CNt\text{-}Bu)_2]\ (\textbf{3}) + NaCl$$

$$+ 3THF\ (+ [(MeCp)_2V(CNt\text{-}Bu)_2][VCl_4(THF)_2]\ (\textbf{2}))$$

$$(2)$$

$$VCl_3 + 2NaMeCp$$

$$\rightarrow \{[(MeCp)_2VCl_2] + [(MeCp)_2V] + [(MeCp)_2VCl]\}(\textbf{4})$$

$$+ 2NaCl \tag{3}$$
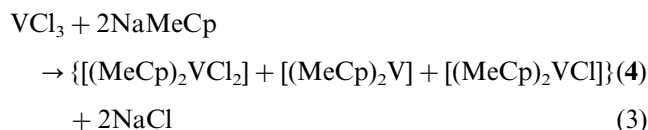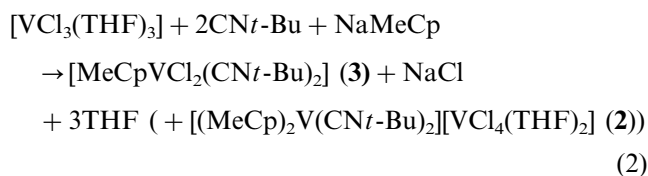
Reactions (1) and (2) proceed via $[VCl_3(PEt_3)_2]$ and $[VCl_3(CNt\text{-}Bu)_3]$ intermediates generated in situ when phosphine or isocyanide are added to a THF solution of VCl_3. The green $[VCl_3(CNt\text{-}Bu)_3]$ [$v_{CN} = 2208$ and $2168\ cm^{-1}$] has been described previously [14]. The main product obtained from reaction (2) is compound **3**, an isocyanide analogue of **1**. **3** could not be isolated free of sticking NaCl; its identity has been verified by, inter alia, IR [$v_{CN} = 2208$ and $2168\ cm^{-1}$, equal intensities] spectroscopy. The ^{1}H-NMR NMR spectrum shows two relatively broad signals at 3.98 and 2.94 ppm, which we attribute to contact-shifted methyl groups of the methyl-Cp and t-BuNC ligands. Orange crystals of **2** [$v_{CN} = 2125$ and $2155\ cm^{-1}$] have been obtained simultaneously as a by-product. **2** is analogous to the complexes $[Cp_2V(CNc\mathrm{Hex})_2]X$ (X = Cl, I, BPh$_4$) [15], none of which, however, has been structurally characterised to date. The $[(MeCp)_2V(CNt\text{-}Bu)_2]^+$ cation of **2**

is also reminiscent of the well known $[Cp_2V(CO)_2]^+$, which may be generated from $[Cp_2VCl]$ and CO [16].

If the reaction between VCl_3 and $NaCp'$ (Cp' = $RC_5H_4^-$) is conducted at a molar ratio $VCl_3:NaCp = 1:3$, $[Cp_2'V]$ is obtained [7]. In the case of a molar ratio $VCl_3:NaCp = 1:2$ and unsubstituted cyclopentadienide, the formation of $[Cp_2VCl_2]$ has been reported [6]. This reactions requires the simultaneous formation of a reduction product, a plausible candidate being $[Cp_2V]$. If this latter reaction is carried out with monomethyl-cyclopentadienide (Eq. (3)), the formation of $[(MeCp)_2VCl_2]$ and $[(MeCp)_2V]$, plus a third component, **4**, arising from a simple salt metathesis, is observed. Extremely air- and moisture-sensitive **4** makes up approximately one forth of the overall conversion of VCl_3 and has been separated in the form of blue crystals from a solution of the product mixture in THF/Et$_2$O.

The molecular structures of **1**, **2** and **4** are displayed in Fig. 1, with selected bonding parameters displayed in Table 1. Data for the structure determination and refinement are collated in Table 2.

In **2**, the pseudo-tetrahedral cation $[(MeCp)_2V(CNt\text{-}Bu)_2]^+$ is linked to the anion *trans*-$[VCl_4(THF)_2]^-$ (with the vanadium centre in an almost ideal octahedral array) by Coulomb forces and weak C···H–C hydrogen bonds involving the hydrogens on the Cp carbons C33, C34 and C35, the methyl carbon C35, and the t-Bu carbons C11, C12 and C22. The closest contact between anion and cation, C11···H33, amounts to 2.67 Å. The overall configuration in the cation is very much the

Table 1
Selected bond lengths (Å) and angles (°)

[MeCpVCl$_2$(PEt$_3$)] (1)		[(MeCp)$_2$VCl] (4)		[(MeCp)$_2$V(CNt-Bu)$_2$][VCl$_4$(THF)$_2$] (2)	
Bond lengths					
2.280(2)	V–C1	2.333(3)		V1–Cp$_c$(3)	1.928
2.290(2)	V–C2	2.292(3)		V1–Cp$_c$(4)	1.937
2.294(2)	V–C3	2.299(4)		V1–C1	1.995(5)
2.299(2)	V–C4	2.330(3)		V1–C2	2.004(5)
2.304(2)	V–C5	2.391(3)		C1–N1	1.163(6)
1.993	V–Cp$_c$[a]	1.950		C2–N2	1.164(6)
1.504(3)	C5–C6	1.504(5)		C30–C35	1.503(7)
2.411(1)	V–Cl1	2.400(1)		C40–C45	1.498(8)
	V–Cl2	2.408(1)		V2–Cl av.	2.375
	V–P1	2.566(1)		V2–O1	2.403(3)
	V–P2	2.573(1)		V2–O2	2.038(3)
Bond angles					
				Cp$_c$(3)–V–Cp$_c$(4)	137.19
	Cp$_c$–V–Cp$_c$	140.60		C1–V1–C2	82.6(2)
113.85/116.62	Cp$_c$–V–Cl	109.70		C1/2–V1–Cp$_c$ av.	105.9
113.13/113.42	Cp$_c$–V–P			V1–C1–N1	177.1(4)
129.52(4)	Cl1–V–Cl2			V1–C2–N2	178.0(4)
133.34(4)	P1–V–P2			V1–N1–C10	151.4(5)
79.74(3)	P–V–Cl1			C2–N2–C20	171.1(5)
80.47(3)	P–V–Cl2			Cl1–V2–Cl2	90.18(8)
79.11(4)	P2–V–Cl1			O1–V2–Cl1	179.31(12)
81.82(4)	P2–V–Cl2			O1–V2–Cl av. 89.8	89.8

[a] Cp$_c$ is the centroid of the cyclopentadienide.

same as in [Cp$_2$V(CO)$_2$][BPh$_4$] ([16]b), stressing the similarity between the carbonyl and isoncyanide ligands. While one of the isocyanides is somewhat bent [C1–N1–C10 = 151.4(5)°], the other one is approximately linear, as in other isocyanide-vanadium complexes such as [VX$_2$(CNR)$_4$] (X = Br, I; R = t-Bu, cHex) [17] and [VCl$_3$(CNt-Bu)$_3$] [14]. The C–N bond lengths in **2** are longer by ca. 0.03 Å than in [VX$_2$(CNR)$_4$] and [VCl$_3$(CNtBu)$_3$].

As in [(MeCp)$_2$VCl$_2$] [18], the MeCp ligands in the cation of **2** are oriented in such a way as to provide the approximate *syn* conformation with respect to the methyl groups [the torsion angle between the normals C30–C35 and C40–C45 (C30 and C40 are Cp carbons, C35 and C45 methyl carbons) in **2** amounts to 16.5°]. This is not so in **4**, where the methyl groups are positioned *anti* to each other (C_2 point symmetry). Other bonding parameters in **4** and [(MeCp)-VCl$_2$(PEt$_3$)$_2$] (**1**), such as the V–Cl bond lengths, the distance of vanadium to the centroid of the cyclopentadienide (Cp$_c$), the angles Cp$_c$–V–Cp$_c$, Cp$_c$–V–Cl and Cl–V–Cl, all compare to those of other Cp-chlorovanadium complexes, e.g. [Cp$_2$VCl] [5], [(RCp)$_2$-VCl$_2$] (R = Me [18], i-Pr, t-Bu [7]), [CpVCl$_2$(PMe$_3$)$_2$] [8] and [CpVCl(PEt$_3$)$_2$]$_2$ [19]. The V–P bond lengths in **1** [2.566(1) and 2.573(1) Å] exceed those in

[CpVCl$_2$(PMe$_3$)$_2$] [2.507(1) and 2.510(1) Å] and [CpVCl(PEt$_3$)$_2$]$_2$ [2.510(4) and 2.509(4) Å].

3. Experimental

All operations were carried out under inert gas, using the common Schlenk technique, and in absolute solvents. Starting materials (VCl$_3$, methylcyclopentadiene, t-butylisocyanide) were purchased from commercial sources. [VCl$_3$(THF)$_3$] was isolated by refluxing a slurry of VCl$_3$ in THF until dissolution (ca. 24 h) and cooling back the solution to room temperature. Addition of pentane increases the yield.

IR spectra were obtained as KBr pellets on a Perkin–Elmer 1720 FT spectrometer, the ^{1}H-NMR spectrum of **3** on a Varian Gemini 200 spectrometer with the usual setting parameters.

The X-ray structure determinations were carried out in the $\theta/2\theta$ scan mode on a Hilger and Watts (**1** and **4**) and CAD4 diffractometer (**2**), using monochromatic Mo–K$_\alpha$ ($\lambda = 71073$ Å) and Cu–K$_\alpha$ ($\lambda = 1.54178$ Å) radiation, respectively. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed into fixed positions and refined isotropically in the last cycles. Disorder problems had not to be considered.

Table 2
Crystal data and structure refinement

	1	**2**	**4**
Emperical formula	$C_{18}H_{37}Cl_2P_2V$	$C_{30}H_{48}Cl_4N_2O_2V_2$	$C_{12}H_{14}ClV$
Formula weight (g mol^{-1})	437.26	712.38	244.62
Temperature (K)	153	173	153
Wavelength (Å)	0.71073	1.54178	0.71073
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group	*Pbca*	*P$\bar{1}$*	*Pbcn*
a (Å)	13.497(3)	9.096(6)	10.525(2)
b (Å)	18.282(4)	13.290(9)	7.628(2)
c (Å)	18.672(4)	15.683(9)	13.745(3)
α (°)		110.49(5)	
β (°)		104.43(5)	
γ (°)		91.80(6)	
V (Å^3)	4607(2)	1705(2)	1103.5(4)
Z	8	2	4
$D_{calc.}$ (g cm^{-3})	1.261	1.388	1.472
Absorption coefficient (mm^{-1})	0.80	7.699	1.10
$F(000)$	1856	744	504
Crystal size (mm)	$0.3 \times 0.3 \times 0.2$	$0.2 \times 0.2 \times 0.1$	$0.3 \times 0.3 \times 0.15$
Theta range for data collection (°)	2.48–30.10	3.13–76.37	2.96–30.09
Index ranges	$0 < h < 16, 0 < k < 25,$ $0 < l < 26$	$0 < h < 11, -16 < k < 16,$ $-19 < l < 19$	$-4 < h < 14, -2 < k < 10,$ $-19 < l < 8$
Reflections collected	6758	7697	2919
Independent reflections	6437	7153	1624
R_{int}	0.0746	0.0544	0.0405
Parameters	215	369	67
Final R indices [$I > 2\sigma(I_0)$]	$R_1 = 0.0691,$ $wR_2 = 0.1998$	$R_1 = 0.0619, wR_2 = 0.1538$	$R_1 = 0.0495, wR_2 = 0.1304$
R indices (all data)	$R_1 = 0.0890,$ $wR_2 = 0.2207$	$R_1 = 0.0933, wR_2 = 0.1829$	$R_1 = 0.0592, wR_2 = 0.1387$
Largest difference peak and hole (e Å^{-3})	0.837 and -0.866	0.846 and -0.920	0.914 and -0.898

Absorption corrections (DIFABS) have been carried out for **4**. The program packages SHELXTL-Plus and SHELXL-97 were used throughout.

3.1. Dichloro-(η^5-methylcyclopenta-dienyl)-bis(triethylphosphine)vanadium(III), [(η^5-C$_5$H$_4$CH$_3$)VCl$_2${P(C$_2$H$_5$)$_3$}$_2$] (1)

The following modified synthesis is based on that reported by Nieman et al. [8]: 747 mg (2 mmol) of [VCl$_3$(THF)$_3$], dissolved in 50 ml of THF, was treated with 544 µl (4 mmol) of PEt$_3$. The initially rose solution immediately turned blue–black ([VCl$_3$(PEt$_3$)$_2$]). After cooling down to $-78°$C, a solution of 204 mg (2 mmol) of NaMeCp in 5 ml of THF was added. The solution was warmed to room temperature (r.t.) within 14 h, evaporated to dryness in vacuo, and the residue was redissolved in 20 ml of pentane of 0°C. After 10 min of stirring, the NaCl was filtered off and the filtrate allowed to stand at $-20°$C. Dark blue **1** crystallised within several hours. A selected crystal from this batch was used for structural analysis. The yield was 625 mg (1.54 mmol; 77%). Anal. Calc.: (C$_{18}$H$_{37}$Cl$_2$P$_2$V, $M =$

406.3 g mol^{-1}) C, 49.44; H, 8.53. Found C, 49.34; H, 8.27%.

3.2. Bis(η^5-methylcyclopentadienyl)-bis(t-butyliso-cyanide)vanadium(III) tetrachloro-bis(tetrahydro-furane)vanadate(III), [(η^5-C$_5$H$_4$CH$_3$)$_2$V-(CNtC$_4$H$_9$)$_2$]-[VCl$_4$(C$_4$H$_8$O)$_2$] (2), and dichloro-(η^5-methylcyclo-pentadienyl)-bis(t-butylisocyanide) vanadium(III), [(η^5-C$_5$H$_4$CH$_3$)VCl$_2$(CNtC$_4$H$_9$)$_2$] (3)

A 350 mg (0.93 mmol) sample of [VCl$_3$(THF)$_3$] was dissolved in 30 ml of THF, cooled to $-60°$C, and treated with 211 µl (1.87 mmol) of t-BuNC. The solution turned brown and finally green due to the formation of [VCl$_3$(CNt-Bu)$_3$] [IR (THF): $\nu_{CN} = 2197$s and 2157s; uncoordinated ligand: 2134 cm^{-1}]. To this solution was added 95 mg (0.93 mmol) of NaMeCp, resulting in a colour change to purple–brown. After filtration, 3 ml of pentane was added to the filtrate. After 48 h standing at $-20°$C, brown–red powdery **3** admixed with NaCl, and a few orange–red crystals of **2**, suitable for the X-ray structure determination, were isolated. Elemental analysis of **3** (C$_{16}$H$_{25}$Cl$_2$V, $M =$

367.2 g mol^{-1}) + NaCl revealed the correct C:H:N:V ratio and typically about one and a half equivalents of NaCl. Efforts to extract **3** from the mixture, or to separate the two components by gel chromatography failed. The identity of **3** was further established by mass spectrometry ($M^+ = 367$), IR [$\nu_{CN} = 2208s$ and 2168s cm^{-1} in KBr] and ^{1}H-NMR NMR spectroscopies. Since the samples isolated from THF proved insoluble in common solvents, the reaction was repeated in toluene to yield soluble **3**/NaCl, the ^{1}H-NMR of which in CDCl$_3$ showed two broad, contact-shifted resonances at $+3.98$ and $+2.94$ ppm, attributable to the methyl groups.

3.3. Chloro-bis(methylcyclopentadienyl)vanadium(III), [(η^5-$C_5H_4CH_3$)$_2$VCl] (4)

A 301 mg (2 mmol) sample of VCl$_3$ was suspended in 40 ml of THF and cooled to -30°C. Within 10 min, 408 mg (4 mmol) of NaMeCp was added in three portions. The blue solution was warmed to r.t. within 1 h, refluxed for 1 h and filtered through a filter plate (3 cm diameter) layered with 1 cm of diatomaceous earth. A light-purple coloured, sticky powder separated. The ink-blue filtrate was treated with 7 ml of diethyl ether and stored at -20°C. Blue crystals of **4**, suitable for the X-ray structure analysis, were collected after 24 h. Yield 120 mg (0.28 mmol, 25%). Anal. Calc.: (C$_{12}$H$_{14}$ClV, $M = 244.6$ g mol^{-1}) C, 58.91; H, 5.77. Found C, 58.72; H, 5.90%.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 103139, 103137, and 103139 for **1**, **2** and **4**, respectively.

Acknowledgements

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