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Bis(arene)vanadium(0) complexes as a source of vanadium(II) derivatives by both disproportionation of the $[V(\eta^6\text{-arene})_2]^+$ cations and oxidation of $[V(\eta^6\text{-arene})_2]$ *

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Abstract

The $[V(\eta^6\text{-arene})_2]^+$ cation (arene = benzene, toluene or mesitylene) is disproportionate to $[V(\eta^6\text{-arene})_2]$ and V^{II} compounds in ether solvents such as THF or 1,2-dimethoxyethane (DME). The extent of disproportionation depends on the nature of both the counteranion and the arene ligand. Addition of the filtered crude reaction mixtures, presumably containing the $[V(\eta^6\text{-arene})_2][Al_2X_7]$ derivatives, to THF gave $[V_2(\mu\text{-}X)_3(THF)_6[AlX_4]$ (arene = benzene or toluene; X = Cl or Br). For X = Cl and arene = toluene, addition to a THF solution of LiI yielded $[V_2(\mu\text{-}Cl)_3(THF)_6]I$. The atom connectivity was established for $[V_2(\mu\text{-}Cl)_3(THF)_6][AlCl_4]$, while $[V_2(\mu\text{-}Cl)_3(THF)_6]I$ was fully characterized by X-ray diffraction methods. Crystal data: $[V_2(\mu\text{-}Cl)_3(THF)_6]I$: monoclinic, space group $C2/c$ (no. 15), a 25.199(8), b 13.865(6), c 9.879(4) Å, β 103.98(2)°, V 3349.3 Å^3, $Z = 4$, D_c 1.523 g cm^{-3}, μ 17.256 cm^{-1}, $F(000) = 1560$. The vanadium(II) derivative $VI_2(THF)_{0.7}$ was obtained, together with $[V(\eta^6\text{-mesitylene})_2]$ in the reaction of $[V(\eta^6\text{-mesitylene})_2][AlI_4]$ with THF. By reaction of $[V(\eta^6\text{-mesitylene})_2]$ with CPh_3X (X = Br or I) in 1,2-dimethoxyethane (DME), the dihalides of vanadium(II), $[VX_2(DME)_2]$ have been isolated in good yields. The crystal and molecular structure of the monomeric *cis*-$[VI_2(DME)_2]$ of pseudo-octahedral geometry has been studied by X-ray diffraction methods. Crystal data: $[VI_2(DME)_2]$: monoclinic, space group $P2_1/n$ (non-standard No. 14), a 7.819(4), b 13.150(4), c 15.535(5) Å, β 90.23(3)°, V 1597.3(1) Å^3, $Z = 4$, D_c 2.017 g cm^{-3}, μ 44.231 cm^{-1}, $F(000) = 916$.

1. Introduction

The first report concerning a bis-(η^6-arene)vanadium derivative describes [1] the synthesis of $[V(\eta^6\text{-}C_6H_6)_2]$ by reaction of VCl_4 with $Al/AlCl_3$ in benzene followed by the treatment of the reaction mixture with an alkaline aqueous solution of $Na_2S_2O_4$. Some years later, $[V(\eta^6\text{-mesitylene})_2]I$ was isolated [2] from the system $VCl_3/Al/AlCl_3/1,3,5\text{-}Me_3C_6H_3$ (mesitylene) in the absence of water or any other proton-active species and it was shown that the behaviour of the $[V(\eta^6\text{-mesitylene})_2]^+$ cations in aqueous solution is best represented by disproportionation reactions such as those in eqns. (1) and (2):

$$2[V(\eta^6\text{-arene})_2]^+ \longrightarrow [V(\eta^6\text{-arene})_2] + V^{2+} + 2\ \text{arene} \quad (1)$$

$$[V(\eta^6\text{-arene})_2]^+ + V^{2+} \longrightarrow [V(\eta^6\text{-arene})_2] + V^{3+} \quad (2)$$

A situation similar to that reported in eqn. 2 was found [3] to operate in the $[V(dipy)_3]^+$ system, see eqn. (3) (dipy = 2,2′-bipyridine):

$$2[V(dipy)_3]^+ \longrightarrow [V(dipy)_3] + [V(dipy)_3]^{2+} \quad (3)$$

More recently, Teuben and coworkers verified that

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* Dedicated to Professor Gian Paolo Chiusoli, a pioneer in the field of metal-assisted organic reactions, on the occasion of his 70th birthday.

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$[V(\eta^6\text{-mesitylene})_2]I$ undergoes disproportionation according to eqn. (4) in the presence of Lewis bases such as THF, $P(OMe)_3$, acetonitrile, and pyridine at room temperature. No attempt was made to isolate the higher-oxidation-state vanadium species [4].

$$n[V(\eta^6\text{-mesitylene})_2]I \xrightarrow{L} (n-1)[V(\eta^6\text{-mesitylene})_2] + [VI_nL_{6-n}] + 2\ \text{mesitylene} \quad (4)$$

$(L = \text{THF}, P(OMe)_3, \text{acetonitrile, or pyridine};$
$n = 2 \text{ or } 3)$

In connection with our studies [5] concerning the synthesis and the reactivity of arene derivatives of early transition elements, we decided to investigate the disproportionation reaction of $[V(\eta^6\text{-arene})_2]^+$ cations in more detail.

In this paper we report that $[V_2(\mu\text{-X})_3(THF)_6]^+$ cations and $[V(\eta^6\text{-arene})_2]$ are the products from the treatment of $[V(\eta^6\text{-arene})_2]^+$ (arene = benzene or toluene) with THF at room temperature. Moreover, it has been found that the tendency of the $[V(\eta^6\text{-arene})_2]^+$ cations to disproportionate depends on the nature of both the arene ligand and the anion. The X-ray crystal structure of $[V_2(\mu\text{-Cl})_3(THF)_6]I$ is reported. Moreover, $[V(\eta^6\text{-mesitylene})_2]$ was found to undergo oxidation by triphenyl methyl bromide or iodide in DME to yield $[VX_2(DME)_2]$ (X = Br or I) and the X-ray crystal structure of *cis*-$[VI_2(DME)_2]$ is reported.

2. Experimental details

Unless otherwise stated, all the operations were carried out under an atmosphere of argon. Solvents were dried by conventional methods.

The commercial products VCl_3 (Fluka), aluminium powder (C. Erba) and triphenylmethyl bromide (Aldrich) were used without further purification. $AlCl_3$ (C. Erba) and $AlBr_3$ (Fluka) were sublimed prior to use. Vanadium tribromide, VBr_3 [6], triphenyl methyl iodide, CPh_3I [7], $[V(\eta^6\text{-mesitylene})_2]$ [5c] and the tetrahaloaluminates $[V(\eta^6\text{-mesitylene})_2][AlX_4]$ (X = Cl, Br, or I) [5c] were prepared according to the literature.

IR spectra were measured with Perkin–Elmer 283 or FT/1725X instruments in Nujol and/or polychlorotrifluoroethylene mulls prepared under rigorous exclusion of moisture and air.

2.1. Synthesis of $[V_2(\mu\text{-X})_3(THF)_6][AlX_4]$ (X = Cl or Br)

Only the reaction with arene = toluene is described in detail, the procedure with arene = benzene being substantially the same.

2.1.1. X = Cl

A mixture of VCl_3 (5.87 g, 37.3 mmol), Al (1.50 g, 55.6 mmol) and $AlCl_3$ (5.98 g, 44.9 mmol) in toluene (50 ml) was heated at the reflux temperature for 15 h. After this period, the reaction mixture consisted of two liquid layers; the lower one, which was dark brown, still contained the excess of aluminium. After filtration, the lower layer was slowly added (2 h) at room temperature to THF (50 ml). The brown precipitate which initially formed gradually dissolved to give a dark brown solution. After 15 h stirring at room temperature, the solution was cooled to *ca.* −30°C overnight. The large emerald-green crystals were filtered off, washed with cold THF (3 × 5 ml) and briefly dried *in vacuo* affording 5.36 g (71%) of $[V_2(\mu\text{-Cl})_3(THF)_6][AlCl_4]$. Anal. Found: Al, 3.0; Cl, 30.2; V, 13.2; $C_{24}H_{48}AlCl_7O_6V_2$ calc.: Al, 3.3; Cl, 30.6; V, 12.6%. IR spectrum (Nujol mull): $\tilde{\nu}$(C–O) (*asym*, THF) 1029, $\tilde{\nu}$(C–O) (*sym*, THF) 877, ν(Al–Cl) 493 cm^{-1}. The deep brown solution was dried *in vacuo* at room temperature, affording a dark tar which was extracted with boiling heptane (100 ml). After filtration, the volume of the resulting solution was reduced to *ca.* 30 ml. On cooling at *ca.* −78°C, dark brown crystals of $[V(\eta^6\text{-toluene})_2]$ (vanadium analysis) (3.51 g, 80% yield) were collected by filtration.

In the case of arene = benzene, $[V(\eta^6\text{-benzene})_2]$ and $[V_2(\mu\text{-Cl})_3(THF)_6][AlCl_4]$ were obtained in 60 and 75% yields, respectively.

2.1.2. X = Br

By using a similar procedure as reported in 2.1.1, green crystals of $[V_2(\mu\text{-Br})_3(THF)_6][AlBr_4] \cdot 2.5THF$ and $V(\eta^6\text{-toluene})_2$ were obtained in 76 and 51% yields, respectively, from the reaction of VBr_3 (3.29 g, 11.3 mmol) with Al (0.60 g, 22.2 mmol) and $AlBr_3$ (6.03 g, 22.6 mmol) in toluene (50 ml) at room temperature for 24 h followed by filtration of the excess aluminium and by treatment with THF at room temperature. Anal. Found: Al, 2.2; Br, 42.9; V, 7.2; $C_{34}H_{68}AlBr_7O_{8.5}V_2$ calc.: Al, 2.1; Br, 43.0; V, 7.8%. IR spectrum (Nujol mull): $\tilde{\nu}$(C–O) (*asym*, lattice THF) 1070, $\tilde{\nu}$(C–O) (*asym*, bonded THF) 1024, $\tilde{\nu}$(C–O) (*sym*, lattice THF) 921, $\tilde{\nu}$(C–O) (*sym*, bonded THF) 867, $\tilde{\nu}$(Al–Br) 400 cm^{-1}.

2.2. Synthesis of $[V_2(\mu\text{-Cl})_3(THF)_6]I$

A mixture of VCl_3 (7.51 g, 47.7 mmol), Al (1.80 g, 66.7 mmol) and $AlCl_3$ (7.70 g, 57.7 mmol) in toluene (50 ml) was refluxed for 15 h. The biphasic system was filtered and the lower layer was slowly added (2 h) to a solution of LiI (7.63 g, 57.0 mmol) in THF (100 ml) maintained at *ca.* 0°C. The brown precipitate which formed at the beginning of the addition gradually dissolved to give a dark brown solution. After 15 h stirring at room temperature, the solution was cooled to *ca.* −30°C overnight. The large emerald-green crystals were filtered off, washed with cold THF (3 × 5 ml) and briefly dried *in vacuo* affording 5.07 g (55%) of $[V_2(\mu\text{-}Cl)_3(THF)_6]I$. Anal. Found: C, 36.9; H, 6.15; total halogen 30.8; V, 12.8; $C_{24}H_{48}Cl_3IO_6V_2$ calc.: C, 37.5; H, 6.3; total halogen, 30.4; V, 13.3%. IR spectrum (Nujol mull): $\tilde{\nu}$(C–O) (*asym*, THF) 1030, $\tilde{\nu}$(C–O) (*sym*, THF) 877 cm^{-1}. The deep brown solution was evaporated *in vacuo* at room temperature affording a dark tar which was extracted with boiling heptane (100 ml). The suspension was filtered and the volume of the filtrate was reduced to *ca.* 30 ml. By cooling to *ca.* −78°C, black crystals of $V(\eta^6\text{-toluene})_2$ (2.25 g, 40% yield) were collected by filtration (spectroscopic and analytical identification).

2.3. *Crystal data and structure refinement of $[V_2(\mu\text{-}Cl)_3(THF)_6]I$*

A green needle of approximate dimensions 0.15 × 0.20 × 0.50 mm, obtained from THF at low temperature, was sealed under argon in a glass capillary. The lattice parameters (Table 1) were refined on a Enraf-Nonius CAD4 diffractometer with graphite monochromator using 25 reflections in the range $9.9° \leq \Theta \leq 14.3°$ and Mo Kα radiation (λ 0.71069 Å). The data collection was at room temperature. During the data collection three intensity reflections were monitored every 3 h showing no intensity decay. After merging, 2493 unique data with $I > 3\sigma(I)$ remained and were used for the subsequent calculations. The position of the V and I atoms were obtained from a Patterson synthesis [8]. Subsequent difference Fourier syntheses showed the chlorine as well as the oxygen and carbon atoms of the THF ligands. Refinement with isotropic temperature parameters converged to $R = 0.175$. An empirical absorption correction with the program DIFABS [9] improved the R value to 0.143. Anisotropic thermal parameters were then assigned to all the atoms resulting in $R = 0.061$. By taking into account the hydrogen atoms in the calculated positions during the structure factor calculations, and after refinement of the extinction coefficient [10] a final R value of 0.061 was obtained. A list of positional parameters is reported in Table 2.

TABLE 1. Lattice constants and parameters of the structure determination of $[V_2(\mu\text{-}Cl)_3(THF)_6]I$ and *cis*-$VI_2(DME)_2$

		$[V_2(\mu\text{-}Cl)_3(THF)_6]I$	*cis*-$VI_2(DME)_2$
Formula		$C_{24}H_{48}Cl_3IO_6V_2$	$C_8H_{20}I_2O_4V$
Molecular weight		767.8	485.0
Size of the crystal (mm)		0.15 × 0.2 × 0.5	0.15 × 0.15 × 0.25
Crystal system		monoclinic	monoclinic
Space group		$C2/c$ (No. 15)	$P2_1/n$ (non-standard No. 14)
Lattice constants (Å or degrees)	a	25.199(8)	7.819(4)
	b	13.865(6)	13.150(4)
	c	9.879(4)	15.535(5)
	β	103.98(2)	90.23(3)
Cell volume (Å^3)	V	3349.3(10)	1597.3(10)
Temperature of data collection (°C)		18	20
Formula units	Z	4	4
$F(000)$		1560	916
Density (g cm^{-3})	D_c	1.523	2.017
Radiation (λ, Å)		Mo Kα (0.71069)	Mo Kα (0.71069)
Absorption coefficient (cm^{-1})	μ	17.256	44.231
Scan type		$\omega/2\theta$	ω
Range of data collection (degrees)	θ	3–31	5–26
Range of data collection (h, k, l)		0,36; 0,16; −14,14	0,9; 0,16; −19,19
No. of reflection measured		5398	3495
No. of independent reflection with $I > 3\sigma(I)$		2493	1528
No. of parameters		238	136
Absorption correction		DIFABS [9]	DIFABS [9]
Minimum, maximum correction		0.4619; 1.2408	0.6200; 1.1897
Extinction coefficient		2.26725×10^{-7}	–
$R = \Sigma \vert \Delta F \vert / \Sigma \vert F_o \vert$		0.061	0.046
$R_w = [\Sigma w(\Delta F)^2 / \Sigma w F_o^2]^{1/2}$		0.059	0.047

TABLE 2. Fractional atomic coordinates for $[V_2(\mu\text{-Cl})_3(THF)_6]I$ (estimated standard deviations in parentheses refer to the least significant digit)

Atom	x	y	z	B (Å^2)
I1	0.750	0.250	0.000	12.30(4)
V1	0.55632(4)	0.25949(6)	0.22459(9)	2.73(2)
Cl1	0.52773(6)	0.3307(1)	0.4257(1)	3.51(3)
Cl2	0.500	0.1166(1)	0.250	3.85(4)
O1	0.5784(2)	0.2054(3)	0.0439(4)	3.89(9)
O2	0.6284(2)	0.1912(3)	0.3503(4)	3.74(9)
O3	0.6054(2)	0.3843(3)	0.2134(4)	3.63(9)
C11	0.5884(3)	0.2719(6)	−0.0614(7)	5.3(2)
C12	0.5890(4)	0.2119(7)	−0.1887(8)	7.8(2)
C13	0.5848(5)	0.1109(7)	−0.1448(8)	8.0(3)
C14	0.5598(4)	0.1156(5)	−0.0253(8)	5.8(2)
C21	0.6648(3)	0.1275(5)	0.3030(7)	5.0(2)
C22	0.7103(3)	0.1079(8)	0.430(1)	7.9(2)
C23	0.6838(4)	0.1149(7)	0.5494(9)	7.4(2)
C24	0.6349(3)	0.1757(6)	0.4973(7)	6.2(2)
C31	0.5842(3)	0.4801(5)	0.183(1)	6.8(2)
C32	0.6318(4)	0.5446(6)	0.197(1)	8.8(3)
C33	0.6795(4)	0.4873(6)	0.231(1)	10.0(3)
C34	0.6632(3)	0.3908(5)	0.275(1)	6.2(2)

2.4. Reaction of $[V(\eta^6\text{-mesitylene})_2][AlX_4]$ with THF

2.4.1. $X = Cl$

No reaction was observed when $[V(\eta^6\text{-mesitylene})_2][AlCl_4]$ (1.74 g, 3.78 mmol) was dissolved in THF (30 ml) and stirred for 15 h at room temperature and for 8 h at the boiling point of the mixture.

2.4.2. $X = Br$

A suspension of $[V(\eta^6\text{-mesitylene})_2][AlBr_4]$ (8.61 g, 13.5 mmol) in THF (50 ml) was stirred for 15 h at room temperature. No apparent change of the reaction mixture was observed. When the mixture was heated at the boiling point, the brown solid disappeared and a pale brown solid formed which was filtered and dried *in vacuo* (8.6 g). This solid had a vanadium content of 1.1%. The deep brown solution was dried *in vacuo* at room temperature affording a dark tar which was extracted with boiling heptane (100 ml). The red-brown mixture was filtered and the volume of the filtrate was reduced to *ca.* 10 ml. On cooling at *ca.* −78°C, dark brown crystals of $V(\eta^6\text{-mesitylene})_2$ (0.46 g, 23% yield) were collected.

2.4.3. $X = I$

A suspension of $[V(\eta^6\text{-mesitylene})_2][AlI_4]$ (1.35 g, 1.63 mmol) in THF (30 ml) was stirred for 15 h at room temperature. The brown orange solid initially present disappeared and a red-brown solution was present. The solution was evaporated to dryness *in vacuo* at room temperature affording a dark tar which was extracted with boiling heptane (30 ml). The red-brown mixture was filtered and the volume of the filtrate was reduced to *ca.* 10 ml. On cooling to *ca.* −78°C, dark brown crystals of $[V(\eta^6\text{-mesitylene})_2]$ (0.18 g, 76% yield) were collected. The residue from the extraction with heptane was treated with THF (10 ml) obtaining a light yellow-green solid which was filtered, washed with THF (2 ml) and dried *in vacuo* affording 0.176 g (61% yield) of $VI_2(THF)_{0.7}$ in the form of a greenish solid very sensitive to oxygen and moisture. Anal. Found: I, 71.3; V, 14.1; $C_{2.8}H_{5.6}I_2O_{0.7}V$ calc.: I, 71.4; V, 14.3%. IR spectrum (Nujol mull): $\tilde{\nu}$(C–O) (*asym*, THF) 1018, $\tilde{\nu}$(C–O) (*sym*, THF) 862 cm^{-1}. $\chi_M^{corr} = 5897 \times 10^{-6}$ cgsu; diam. corr. $= -141 \times 10^{-6}$ cgsu; μ_{eff} (293 K) $=$ 3.72 BM.

2.5. Reaction of $[V(\eta^6\text{-mesitylene})_2]$ with CPh_3X in DME

2.5.1. $X = Br$

A solution of CPh_3Br (3.028 g, 9.37 mmol) in DME (75 ml) was introduced into a dropping funnel and slowly added to a solution of $[V(\eta^6\text{-mesitylene})_2]$ (0.91 g, 3.12 mmol) in the same solvent (50 ml). During the slow addition of the first equivalent of CPh_3Br, a brown solid and a yellow solution were obtained, the former then changing to a green solid, while the solution turned red. After the addition of the second equivalent of CPh_3Br the green solid in a light yellow solution was filtered off, washed with DME (2 × 5 ml) and dried *in vacuo*, affording 0.88 g (72%) of $[VBr_2(DME)_2]$. Anal. Found: Br, 40.5; V, 12.9; $C_8H_{20}Br_2O_4V$ calc.: Br, 40.9; V, 13.0%. IR spectrum (Nujol mull): $\tilde{\nu}$(C–O) (DME) 1050 cm^{-1}. $\chi_M^{corr} = 6532 \times 10^{-6}$ cgsu; diam. corr. $= -201 \times 10^{-6}$ cgsu; μ_{eff} (293 K) $=$ 3.92 BM. The solution was evaporated to dryness affording 1.04 g of $C_{38}H_{30}$ (the triphenylmethyl dimer) identified from its IR spectrum in Nujol, in comparison with the literature data [11].

2.5.2. $X = I$

A suspension of CPh_3I (1.95 g, 5.27 mmol) in DME (25 ml) was treated with $[V(\eta^6\text{-mesitylene})_2]$ (0.77 g, 2.64 mmol). An immediate reaction was observed on mixing the reagents: the resulting brown solid was converted to a green precipitate, which was filtered off, washed with DME (2 × 5 ml) and dried *in vacuo* affording 0.804 g (63% yield) of $[VI_2(DME)_2]$. Anal. Found: I, 52.3; V, 10.6; $C_8H_{20}I_2O_4V$ calc.: I, 52.3; V, 10.5%. IR spectrum (Nujol mull): $\tilde{\nu}$(C–O) (DME): 1048 cm^{-1}. $\chi_M^{corr} = 7112 \times 10^{-6}$ cgsu; diam. corr. $=$ -229×10^{-6} cgsu; μ_{eff} (293 K) $=$ 4.08 BM.

TABLE 3. Fractional atomic coordinates for *cis*-$[VI_2(DME)_2]$ (estimated standard deviations in parentheses refer to the least significant digit) [a]

Atom	x	y	z	B ($Å^2$)
I1	0.0423(1)	0.60171(8)	0.78538(6)	5.91(2)
I2	0.1544(1)	0.76603(9)	1.01120(7)	7.06(3)
V	−0.1188(2)	0.7412(2)	0.8956(1)	3.94(4)
O1	−0.337(1)	0.7444(7)	0.8107(6)	6.0(2)
O2	−0.064(1)	0.8684(7)	0.8152(6)	6.6(2)
O3	−0.245(1)	0.6323(8)	0.9755(6)	7.5(3)
O4	−0.269(1)	0.839(1)	0.9756(6)	8.4(3)
C1	−0.482(2)	0.683(2)	0.809(2)	10.9(6)
C2	0.111(2)	0.899(1)	0.792(1)	8.2(4)
C3	−0.224(2)	0.528(2)	0.987(1)	11.9(6)
C4	−0.246(3)	0.942(2)	0.985(2)	14.8(7)
C12	−0.355(2)	0.838(1)	0.761(1)	10.1(5)
C21	−0.172(2)	0.867(2)	0.735(1)	10.7(6)
C34	−0.360(3)	0.674(2)	1.034(1)	13.9(8)
C43	−0.334(3)	0.785(2)	1.049(1)	14.7(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)(a^2\beta_{1,1} + b^2\beta_{2,2} + c^2\beta_{3,3} + ab(\cos\gamma)\beta_{1,2} + ac(\cos\beta)\beta_{1,3} + bc(\cos\alpha)\beta_{2,3})$.

2.6. *Crystal data and structure refinement of cis-$[VI_2(DME)_2]$*

A green crystal obtained from DME by slow cooling to *ca.* −30°C was sealed under argon in a glass capillary and mounted on an Enraf-Nonius CAD 4 diffractometer equipped with graphite monochromator and Mo Kα radiation (λ 0.71069 Å) (see Table 1). The data collection was at room temperature. During the data collection, three reflections have been monitored every 3 h showing no intensity decay. The vanadium and the iodine atoms were located by direct methods [12], the oxygen and the carbon atoms by difference Fourier syntheses. An empirical absorption correction with the program DIFABS [9] was applied to the unmerged data set. All non-hydrogen atoms were refined anisotropically to R 0.046 and R_w 0.047. A list of positional parameters is reported in Table 3.

3. Results and discussion

3.1. *Disproportionation of $[V(\eta^6\text{-arene})_2]^+$*

The treatment of VCl_3 with $Al/AlCl_3$ in refluxing benzene or toluene followed by filtration to eliminate the excess of aluminium gave the well-known biphasic liquid system [5c] which was added to THF at room temperature to afford an orange-red suspension changing to a red-brown solution with time. The solution, upon standing at about −30°C, separated green crystals which were identified as the dinuclear, chloride-bridging, vanadium(II) derivative $[V_2(\mu\text{-Cl})_3(THF)_6][AlCl_4]$ [13*]. The organometallic compounds of zerovalent vanadium, $[V(\eta^6\text{-benzene})_2]$ and $[V(\eta^6\text{-toluene})_2]$, respectively, were isolated in good yields from the mother liquor.

Earlier work [5c] had shown that addition, after filtration from the excess of aluminium, to THF of the primary reduction product [14*] resulting from the $VCl_3/Al/AlCl_3$/mesitylene system, affords the ionic $[V(\eta^6\text{-mesitylene})_2][AlCl_4]$; this differs from the corresponding benzene and toluene derivatives, which are sufficiently stable (*vide infra*) to be isolated under these conditions.

The benzene or toluene $[V(\eta^6\text{-arene})_2]^+$ cations in the presence of THF undergo disproportionation, which can best be represented by eqn. (5).

$$4[V(\eta^6\text{-arene})_2][Al_2Cl_7] + 20\ THF \longrightarrow 2[V(\eta^6\text{-arene})_2] + [V_2(\mu\text{-Cl})_3(THF)_6][AlCl_4] + 7[AlCl_3(THF)_2] + 4\ \text{arene} \quad (5)$$

The products of this reaction are three: the dinuclear ionic derivative of vanadium(II) is the least soluble in the reaction medium (consisting of THF and the parent hydrocarbon in the approximate ratio 1/1) and can be easily separated by crystallization at low temperature. A large contribution to the driving force of reaction (5) presumably originates from the formation of the THF adducts of both vanadium(II) and $AlCl_3$ [15].

The bromide $[V_2(\mu\text{-Br})_3(THF)_6][AlBr_4]$ was obtained in a similar way from the $VBr_3/Al/AlBr_3$/toluene system, followed by filtration and reaction of the resulting biphasic mixture with THF at room temperature.

In an attempt to isolate the iodide $[V(\eta^6\text{-toluene})_2]I$ by a procedure similar to that reported [2] for $[V(\eta^6\text{-mesitylene})_2]I$, (*i.e.* addition of the biphasic system deriving from the $VCl_3/Al/AlCl_3$/toluene reaction mixture after elimination of the excess of aluminium to a solution of LiI in THF), formation of an orange solid was observed which promptly dissolved affording a deep brown-red solution. Working up of this reaction mixture afforded $[V_2(\mu\text{-Cl})_3(THF)_6]I$ and $[V(\eta^6\text{-toluene})_2]$ in good yields suggesting the disproportionation of eqn. (6).

$$4[V(\eta^6\text{-toluene})_2][Al_2Cl_7] + LiI + 16\ THF \xrightarrow{THF} 2[V(\eta^6\text{-toluene})_2] + [V_2(\mu\text{-Cl})_3(THF)_6]I + 8[AlCl_3(THF)_2] + LiCl + 4\ \text{toluene} \quad (6)$$

To the best of our knowledge, $[V_2(\mu\text{-Cl})_3(THF)_6]I$ represents the first "mixed" halo complex of vanadium(II) to be reported. Also, it is the first example of a

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* Reference number with asterisk indicates a note in the list of references.

TABLE 4. Selected bond distances (Å) and angles (°) in $[V_2(\mu\text{-}Cl)_3(THF)_6]I$. (estimated standard deviations in parentheses refer to the least significant digit)

V1'-Cl1	2.485(2)	O2-C21	1.433(9)
V1-Cl1	2.476(2)	O2-C24	1.440(8)
V1'-Cl2	2.486(2)	O3-C31	1.437(8)
V1-Cl2	2.486(2)	O3-C34	1.438(9)
V1-O1	2.136(4)		
V1-O2	2.153(4)		
V1-O3	2.145(4)		
O1-C11	1.460(9)		
O1-C14	1.444(8)		
Cl1-V1-Cl1'	87.14(6)	O1-V1-O2	88.5(2)
Cl1-V1-Cl2	87.21(5)	O1-V1-O3	88.3(2)
Cl1-V1-O1	176.5(1)	O2-V1-O3	88.3(2)
Cl1-V1-O2	94.6(1)	V1-O1-C11	120.2(4)
Cl1-V1-O3	90.2(1)	V1-O1-C14	125.5(5)
Cl1'-V1-Cl2	87.37(5)	V1-O2-C21	126.8(3)
Cl1'-V1-O1	89.8(1)	V1-O2-C24	121.5(4)
Cl1'-V1-O2	177.3(1)	V1-O3-C31	124.7(4)
Cl1'-V1-O3	93.7(2)	V1-O3-C34	124.4(4)
Cl2-V1-O1	94.5(1)		
Cl2-V1-O2	90.7(1)		
Cl2-V1-O3	177.2(1)		
V1-Cl1-V1'	74.46(5)		
V1-Cl2-V1'	74.26(6)		

derivative of the $[V_2(\mu\text{-}Cl)_3(THF)_6]^+$ cation not containing a complex anion.

The vanadium(II) cations, $[V_2(\mu\text{-}X)_3(L)_6]^+$ ($X = Cl$ or Br; L = THF or 3-MeTHF) are known, obtained by reduction of $[VCl_3(L)_3]$ (L = THF or 3-MeTHF) with Zn powder [16a–d] or by reaction of $[VX_3(L)_3]$ with $AlR_2(OR)$ (X = Cl, L = THF, R = Me or Et) [16d,f]; X = Br, L = THF, 3-MeTHF, R = Et [16e]). Moreover, the structures of compounds with $[Zn_2Cl_6]^{2-}$ [16a–c], $[BPh_4]^-$ [16c–e] and $[AlEt_2Cl_2]^-$ [16f] as counteranion have been reported.

In view of the ready availability of the $[V(\eta^6\text{-arene})_2]^+$ cations, the disproportionation in THF is proposed as an alternative synthesis of the vanadium(II) halide-bridged dimeric compounds.

It is possible, in principle, to envisage a contribution to the disproportionation of the $[V(\eta^6\text{-arene})_2]^+$ cation from a reaction such as 2, which was found [2] to operate in aqueous solution, with formation of vanadium(0) and vanadium(III). However, we never observed any product of vanadium in an oxidation state higher than II.

The new derivative $[V_2(\mu\text{-}Cl)_3(THF)_6]I$ has been characterized by single-crystal X-ray analysis. A list of bond distances and angles are reported in Table 4. Figure 1 shows a SCHAKAL plot of the molecular structure of the cationic part of $[V_2(\mu\text{-}Cl)_3(THF)_6]I$.

The bond distances and angles reported in the literature [16a–e] for the cation are the same as in our complex within experimental error. The cationic complex in $[V_2(\mu\text{-}Cl)_3(THF)_6]I$ exhibits the crystallographic point symmetry C_2 with the two-fold axis of the space group $C2/c$ passing through the atom Cl(2), thus indicating that the two vanadium centres are equivalent. The V–Cl distances within the chloride bridges are in the range 2.476(2) and 2.486(2) Å. The chloride bridges are symmetrical with V–Cl distances longer than the sum of the covalent radii of V and Cl {2.21 Å [17]}, as expected for bridging chlorides.

The bond angles V–Cl–V {74.36(5)° (mean value)} are slightly larger than the ideal values of 70.53° for face-sharing octahedra, indicating a repulsion between the metal centres of d^3 electronic configuration. As a consequence, the bond angles Cl–V–Cl (87.2°) are smaller than the expected values for octahedral coordination. In agreement with these observations, the $V \cdots V$ distance is 2.999(1) Å, suggesting that vanadium–vanadium interactions, if present, are weak. This distance is substantially identical to the $V \cdots V$ distance of 2.993(1) Å reported earlier [16] for the same dinuclear cation in the hexachlorodizincate derivative [16c].

The average V–O distance of 2.145(4) Å is similar to the mean V–O bond distances observed in other complexes of vanadium(II) containing oxygen-bonded ligands. Some examples are: $[V_2(\mu\text{-}X)_3(THF)_6]$ BPh_4 (2.147(7) Å, X = Cl [16d]; 2.142(8) Å, X = Br [16e]), $[V(CH_3OH)_6]Cl_2$ (2.132(4) Å) [16f], $[V(H_2O)_6][CF_3SO_3]_2$ (2.120 Å) [18], $(NH_4)_2[V(H_2O)_6](SO_4)_2$ (2.15(2) Å) [19] and $[V(THF)_4][V(CO)_6]_2$ (2.170 Å) [20].

We studied the stability of the recently isolated [5c] tetrahaloaluminate derivatives $[V(\eta^6\text{-mesitylene})_2][AlX_4]$ in THF. It has been found that the stability of these compounds is strongly influenced by the nature of the anion. $[V(\eta^6\text{-mesitylene})_2][AlCl_4]$ is not affected by THF even after prolonged heating at the boiling point; $[V(\eta^6\text{-mesitylene})_2][AlBr_4]$ is stable at room temperature for some hours but readily reacts at temperatures above the ambient; $[V(\eta^6\text{-mesitylene})_2][AlI_4]$ is stable in THF only for short periods even at room temperature.

In the reaction of $[V(\eta^6\text{-mesitylene})_2][AlI_4]$ with THF it has been possible to isolate both the organometallic and the inorganic compounds, namely $[V(\eta^6\text{-mesitylene})_2]$ and "VI_2". This suggests that also in the case of the tetrahaloaluminato- derivatives of $[V(\eta^6\text{-mesitylene})_2]^+$, the reaction with THF proceeds according to the proposal by Teuben *et al.* [4], *i.e.*, disproportionation of V^I to V^0 and V^{II} (see eqn. (4)).

The inorganic product from the disproportionation of $[V(\eta^6\text{-mesitylene})_2][AlI_4]$ has the composition $VI_2 \cdot 0.7$ THF. This is presumably a polynuclear product containing coordinated THF, as suggested by the IR data (see Experimental details). Vanadium(II) iodide has been reported to be obtained by reaction of vanadium metal with diiodine at *ca.* 160–170°C for some days [21a] or by decomposition of $\mathrm{VI_3}$ at about 400°C [21b] and has been shown [21a] to have a polynuclear iodide-bridged structure of the $\mathrm{CdI_2}$-type.

Compounds of formula $\mathrm{VX_2L_2}$ (X = Cl, Br or I; L = THF, $\mathrm{CH_3OH}$, pyridine, acetonitrile or dioxane) have been prepared by electrochemical reduction of $\mathrm{VCl_3}$ or $\mathrm{VBr_3}$ in methanol/HX systems followed by ligand exchange [21c,d] or by electrochemical oxidation of vanadium metal in acetonitrile [21e]. It is noteworthy that the compound $\mathrm{VCl_2(THF)_2}$ was claimed [22] to be obtained by zinc reduction of $\mathrm{VCl_3}$ in THF. This formulation was later questioned [16a,b].

3.2. Oxidation of $[\mathrm{V}(\eta^6\text{-mesitylene})_2]$

The reaction of $[\mathrm{V}(\eta^6\text{-mesitylene})_2]$ with $\mathrm{CPh_3X}$ has been used in attempts to isolate ionic $[\mathrm{V}(\eta^6\text{-mesitylene})_2]\mathrm{X}$ derivatives similar to $[\mathrm{V}(\eta^6\text{-mesitylene})_2]\mathrm{I}$ [2] to be used in comparative tests of stability towards disproportionation, as already done with the $\mathrm{AlX_4^-}$ derivatives. The reaction of $[\mathrm{V}(\eta^6\text{-mesitylene})_2]$ with $\mathrm{CPh_3Br}$ has been studied in some detail. By operating in aliphatic hydrocarbon solution, we have not been able to isolate $[\mathrm{V}(\eta^6\text{-mesitylene})_2]\mathrm{Br}$ due to further oxidation by the organic bromide even with a $[\mathrm{V}(\eta^6\text{-mesitylene})_2]/\mathrm{CPh_3Br}$ molar ratio of 1. Nevertheless, in DME as medium, we have observed that the addition of a pale yellow solution of $\mathrm{CPh_3Br}$ to a dark-red solution of $[\mathrm{V}(\eta^6\text{-mesitylene})_2]$ produces a pale brown solid. Without further addition of $\mathrm{CPh_3Br}$, after some minutes the solid turns bright green and the solution acquires the typical colour of $[\mathrm{V}(\eta^6\text{-mesitylene})_2]$. Two equivalents of the organic bromide are required to consume the vanadium(0) complex initially present with formation of $[\mathrm{VBr_2(DME)_2}]$ and the $\mathrm{C_{38}H_{30}}$ *i.e.*, the rearranged dimeric form of the triphenylmethyl radical [11] (eqn. (7)):

$$\mathrm{V}(\eta^6\text{-mesitylene})_2 + 2\,\mathrm{CPh_3Br} + 2\,\mathrm{DME} \longrightarrow [\mathrm{VBr_2(DME)_2}] + \mathrm{C_{38}H_{30}} + 2\ \text{mesitylene} \qquad (7)$$

These results suggest that reaction (7) proceeds via a one-electron oxidation of $\mathrm{V^0}$ to $\mathrm{V^I}$ by the organic bromide, followed by fast disproportionation of the intermediate vanadium(I) bis-arene cation to $\mathrm{V^0}$ and $\mathrm{V^{II}}$ as in reaction sequence (8):

$$[\mathrm{V}(\eta^6\text{-mesitylene})_2] \xrightarrow{\mathrm{CPh_3Br}} [\mathrm{V}(\eta^6\text{-mesitylene})_2]\mathrm{Br} \xrightarrow{\mathrm{DME}} [\mathrm{VBr_2(DME)_2}] + [\mathrm{V}(\eta^6\text{-mesitylene})_2] \qquad (8)$$

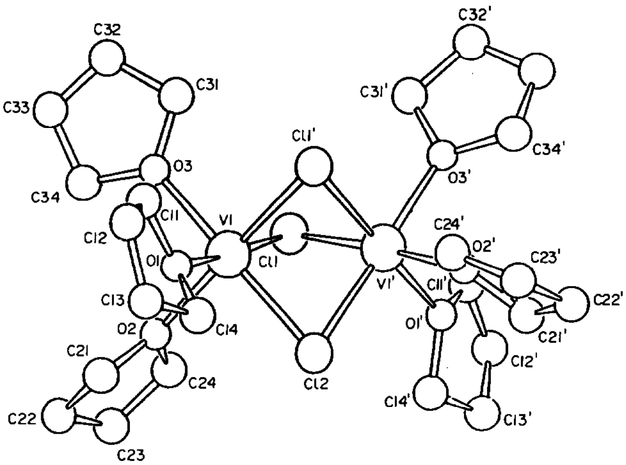

Fig. 1. SCHAKAL plot of the molecular structure of $[\mathrm{V_2}(\mu\text{-Cl})_3(\mathrm{THF})_6]\mathrm{I}$.

The reaction of $[\mathrm{V}(\eta^6\text{-mesitylene})_2]$ with $\mathrm{CPh_3I}$ in DME does not offer any possibility to observe the intermediate vanadium(I) species due to the further oxidation to vanadium(II): addition of a solution of $\mathrm{CPh_3I}$ to a solution of $[\mathrm{V}(\eta^6\text{-mesitylene})_2]$ immediately gives a green solid which has been identified as $[\mathrm{VI_2(DME)_2}]$, (eqn. (9)):

$$[\mathrm{V}(\eta^6\text{-mesitylene})_2] + 2\,\mathrm{CPh_3I} + 2\,\mathrm{DME} \longrightarrow [\mathrm{VI_2(dme)_2}] + \mathrm{C_{38}H_{30}} + 2\ \text{mesitylene} \qquad (9)$$

The iodide *cis*-$[\mathrm{VI_2(DME)_2}]$ is the first monomeric iodide of vanadium(II) to be reported. Other halo-complexes of vanadium(II) of formula $[\mathrm{VCl_2L_4}]$ or $[\mathrm{VCl_2(LL)_2}]$ have been reported. Some examples are: $[\mathrm{VCl_2(pyridine)_4}]$ [23a], $[\mathrm{VCl_2(dmpe)_2}]$ (dmpe = 1,2 bis-dimethylphosphino-ethane) [23b], $[\mathrm{VCl_2(CH_3COOH)_4}]$ [23c] and $[\mathrm{VCl_2(TMEDA)_2}]$ (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediammine) [23d]. Due to the paucity of data on simple vanadium(II) halides, it was decided to investigate the well-crystallized iodide by X-ray diffraction methods.

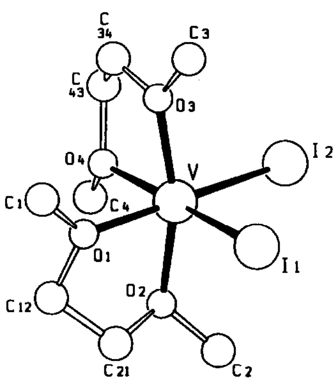

Fig. 2. SCHAKAL plot of the molecular structure of *cis*-$[\mathrm{VI_2(DME)_2}]$.

TABLE 5. Selected bond distances (Å) and angles (degrees) in *cis*-$[VI_2(DME)_2]$ (estimated standard deviations in parentheses refer to the least significant digit)

V–I1	2.811(2)	O2–C2	1.48(2)
V–I2	2.805(2)	O2–C21	1.50(3)
V–O1	2.156(9)	O3–C3	1.40(2)
V–O2	2.13(1)	O3–C34	1.39(2)
V–O3	2.14(2)	O4–C4	1.37(2)
V–O4	2.14(1)	O4–C43	1.43(2)
O1–C1	1.40(2)	C12–C21	1.53(3)
O1–C12	1.46(2)	C34–C43	1.49(4)
I1–V–I2	97.13(7)	O1–V–O4	84.7(4)
I1–V–O1	89.8(3)	O2–V–O3	163.6(4)
I1–V–O2	93.7(3)	O2–V–O4	88.9(5)
I1–V–O3	97.2(3)	O3–V–O4	79.1(4)
I1–V–O4	173.3(3)	V–O1–C1	131(2)
I2–V–O1	171.9(3)	V–O1–C12	114.6(9)
I2–V–O2	97.5(3)	V–O2–C2	123.2(9)
I2–V–O3	93.3(3)	V–O2–C21	111(1)
I2–V–O4	88.7(3)	V–O3–C3	133(2)
O1–V–O2	77.7(4)	V–O3–C34	114(1)
O1–V–O3	90.1(4)	V–O4–C4	126(1)
		V–O4–C43	111(1)

A SCHAKAL plot of the molecular structure of *cis*-$[VI_2(DME)_2]$ is reported in Fig. 2; selected bond distances and angles are listed in Table 5. The coordination around the vanadium atom is that of a distorted octahedron with angles at vanadium [I1–V–O4 173.3(3)°; I2–V–O1 171.9(3)°; O2–V–O3 163.6(4)°] which significantly deviate from 180°. The compound has a *cis* arrangement of ligands with a I1–V–I2 angle of 97.13(7)°. The increase of this angle with respect to the theoretical value expected for an octahedral geometry is probably due to the steric hindrance of the iodide ligands.

Once the difference of the ionic radii of choride {1.81 Å [17]} and iodide {2.16 Å [17]} are taken into consideration, the vanadium–iodide distance (2.808(2) Å, mean value) compares well with that reported for $[VCl_2(pyridine)_4]$ (2.462 Å, mean value) [23a], $[VCl_2(dmpe)_2]$ (2.440 Å, mean value) [23b], $[VCl_2(CH_3COOH)_4]$ (2.496(1) Å, mean value) [23c] and $[VCl_2(TMEDA)_2]$ (2.487(1) Å, mean value) [23d].

The V–O distances (2.13(1)–2.156(9) Å) are in the range of values observed in other vanadium(II) derivatives containing oxygen-bonded ligands (*vide supra*) [16d–f,18–20].

4. Conclusions

The stability of $[V(\eta^6\text{-arene})_2]^+$ cations in the presence of THF towards disproportionation depends on both the arene and the anion. The stability follows the trend:

mesitylene > toluene ≈ benzene

$AlCl_4 > AlBr_4 > AlI_4$

The effect of the aromatic hydrocarbon must be related to the general higher stability of π-arene complexes of transition elements [24] by increasing methyl substitution on the ring, arene substitution by the solvent and/or by the solvated X^- being presumably an important step in the disproportionation. The effect of the halide in the $[AlX_4]^-$ counteranion has probably to do with the fission of $[AlX_4]^-$ by THF to give solvated X^-. In view of the decreasing tendency to solvation in the sequence $Cl^- > Br^- > I^-$, the heavier halide is better available for attack at the vanadium centre.

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13 Enraf-Nonius CAD4 single crystal diffractometer, graphite monochromator, Mo Kα radiation, T 291 K, Crystal data: $[V_2(\mu\text{-Cl})_3(THF)_6][AlCl_4]$: orthorhombic, space group $Pna2_1$ (No. 33) a 23.921(7), b 12.207(2), c 13.394(2) Å, V 3911.1 Å^3, $Z = 4$, D_c 1.375 g cm^{-3}, μ 9.984 cm^{-1}, $F(000) = 1672$. The lattice parameters were refined using 25 carefully measured reflections between $8.5° \le \Theta \le 14.9°$. The data collection at room temperature with the $\omega/2\theta$ scan technique between $\Theta = 3$ and $\Theta = 27°$ resulted in 8254 reflections. Because of the poor quality of the diffraction

data and the extensive decomposition of the crystal during the data collection (total loss of intensity of 27.3%), 760 unique intensity values with $I > 2\sigma(I)$ remained after merging and could be used for the refinement. Direct methods [12] revealed the structural model including the vanadium, chlorine and oxygen atoms of the cation. A difference Fourier synthesis revealed the atoms of the $[AlCl_4]^-$ anion and the carbon atoms of the THF ligands, the latter showing severe disorder. Refinement with isotropic thermal parameters converged at $R = 0.117$. An empirical absorption correction [9] and further refinement improved the R value to 0.109. With anisotropic thermal parameters for the vanadium, aluminium, and chlorine atoms of the cation an R value of 0.108 was obtained. A refinement with anisotropic thermal parameters for the chlorine atoms of the anion did not result in satisfactory values. Nevertheless, it can be stated that the atom connectivity is the same as that of the iodide derivative $[V_2(\mu\text{-}Cl)_3(THF)_6]I$, *vide infra*. Some selected distances are: $V \cdots V$: 3.01(1) Å; V–Cl: 2.38(2)–2.54(2) Å; V–O (mean value): 2.19(4) Å; V–Cl–V (mean value): 74.9°; Cl–V–Cl (mean value): 86.8°.

14 The primary reduction product of VCl_3 is believed to be $[V(\eta^6\text{-mesitylene})_2][Al_2Cl_7]$ as suggested by the observation [5c] that the sparingly (in mesitylene) soluble $[V(\eta^6\text{-mesitylene})_2][AlCl_4]$ becomes more soluble by addition of one equivalent of $AlCl_3$.

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