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Binuclear vanadium complexes containing sulfur and selenium ligands: the reactions of the half-sandwich compounds $CpV(CO)_4$ and $Cp^{\star}V(CO)_4$ with dichalcogenides E_2R_2 (E = S, Se; R = Me, Ph). The X-ray crystallographic structures of $Cp^{\star}{}_2V_2(CO)_4(\mu\text{-}SR)_2$ (R = Me, Ph; $Cp^{\star} = C_5Me_5$)

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Abstract

Both the photo-induced reaction of $CpV(CO)_4$ (**1**) and $Cp^{\star}V(CO)_4$ (**1***) ($Cp = C_5H_5$, $Cp^{\star} = C_5Me_5$) with diorganochalcogenides, E_2R_2 (E = S, Se; R = Me, Ph) at room temperature in THF solution and the thermal reaction of the kinetically labile derivatives $CpV(CO)_3(SMe_2)$ (**7**) and $Cp^{\star}V(CO)_3(SMe_2)$ (**7***) with E_2R_2 in solution lead to binuclear, diamagnetic complexes Cp_2– and $Cp_2^{\star}$–$V_2(CO)_4(\mu\text{-}ER)_2$ (**8**, R = Me and **9**, R = Ph). In the presence of excess E_2R_2, further decarbonylation takes place to give paramagnetic Cp_2– and $Cp_2^{\star}$–$V_2(\mu\text{-}ER)_4$ (**10**, R = Me and **11**, R = Ph). With H_2S, both **1*** and **7*** can be converted into a labile intermediate $Cp^{\star}{}_2V_2(CO)_4(\mu\text{-}S)_2$ (**12***) which tends to lose the CO ligands. No carbonyl-containing intermediates were observed in the reactions of **1*** and **7*** with excess sulfur or selenium to give $Cp^{\star}{}_2V_2E_5$ (E = S (**2a***) and Se (**2b***)) and $Cp^{\star}{}_2V_2E_4$ (E = S, **3a*** and Se, **3b***), respectively. The carbonylvanadium complexes were characterized by their ^{1}H, ^{13}C and ^{51}V NMR spectra. X-Ray crystallographic structure analyses carried out for $Cp^{\star}{}_2V_2(CO)_4(\mu\text{-}SMe)_2$ (**8a***) and $Cp^{\star}{}_2V_2(CO)_4(\mu\text{-}SPh)_2$ (**9a***) revealed a bent $V_2(\mu\text{-}SR)_2$ core. The $Cp^{\star}$ ligands are arranged *cis* to each other, and the organo substituents occupy the *exo/exo* positions. The vanadium–vanadium distance is 3.083(1) Å in **8a*** and 3.070(1) Å in **9a***.

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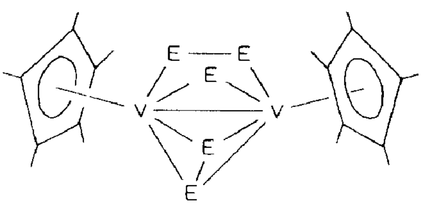
Introduction

The oxidative decarbonylation of carbonylmetal and cyclopentadienylcarbonylmetal complexes by chalcogens (E = S, Se) and dichalcogenides E_2R_2 (E = S, Se; R = alkyl, aryl) often leads to carbonyl-containing intermediates in the first step. These primary products may allow conclusions to be drawn about the route by which the stepwise loss of CO ligands takes place. The following account describes our attempts to obtain carbonylvanadium complexes containing bridging sulfur and selenium ligands.

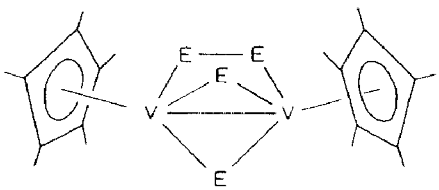
Carbonylvanadium complexes containing unsubstituted chalcogen ligands are rare: Only a few binuclear compounds $[V(CO)_3(dppe)]_2(\mu\text{-}E)$ (dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$) with an almost linear V=E=V multiple-bond system (E = S, Se, Te) have been described [1].

The thermal reactions of the half-sandwich complexes * $CpV(CO)_4$ (**1**) [2] and $Cp^{\star}V(CO)_4$ (**1***) [3,4] with excess sulfur in boiling toluene lead to complete displacement of all CO ligands. The binuclear main products, of the known compositions $Cp_2V_2S_5$ [2,5] and $Cp^{\star}_2V_2S_5$ [6], are also accessible by thermolysis in solution of the mononuclear bis(cyclopentadienyl)vanadium complexes $Cp_2V(S_5)$ [5] and $Cp^{\star}_2V(S_2)$ [6], respectively. The binuclear structure is supported by X-ray crystallographic structure determinations carried out for the methylcyclopentadienyl complexes $Cp'_2V_2S_5$ [7] and $Cp'_2V_2Se_5$ [8]. As demonstrated by Rauchfuss and coworkers [9–11], chalcogen abstraction from the pentachalcogenides $Cp_2V_2E_5$ by tri(^{n}butyl)phosphane is a good route to the tetrachalcogenides $Cp_2V_2E_4$ (E = S, Se); an X-ray crystallographic structure analysis of $(\eta^5\text{-}C_5H_4{}^iPr)_2V_2S_4$ [10] is available. In all binuclear complexes, the chalcogens always occupy bridging positions between the two vanadium atoms for which a bonding interaction can be formulated on the basis of the vanadium-vanadium distances in the range of 2.6 Å (E = S) and 2.8 Å (E = Se). Terminal chalcogenido ligands are absent.

In our studies [3,4] of the reactions between $Cp^{\star}V(CO)_4$ (**1***) and both sulfur and selenium, we always isolated carbonyl-free products such as $Cp^{\star}_2V_2E_5$ (E = S (**2a***), Se (**2b***)), $Cp^{\star}_2V_2E_4$ (E = S (**3a***), Se (**3b***)) and $Cp^{\star}_2V_2E_3O$ (E = S (**4a***), Se (**4b***)). The binuclear structures of the pentamethylcyclopentadienylvanadium complexes are assumed to be analogous to those of the less-highly ring-substituted compounds prepared by Rauchfuss and coworkers [7,8,10].



$Cp^{\star}_2V_2E_5$ (E = S (**2a***)
E = Se (**2b***))



$Cp^{\star}_2V_2E_4$ (E = S (**3a***)
E = Se (**3b***))

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* Abbreviations: Cp = cyclopentadienyl, $\eta^5\text{-}C_5H_5$; Cp′ = methylcyclopentadienyl, $\eta^5\text{-}C_5H_4Me$; $Cp^{\star}$ = pentamethylcyclopentadienyl, $\eta^5\text{-}C_5Me_5$. The notation $Cp^{(\star)}$ indicates that both the unsubstituted (Cp) and the permethylated ($Cp^{\star}$) cyclopentadienyl complexes were used.

The pentachalcogenides (**2a***,**2b***) are the predominant products if excess chalcogen E is available. The tetrachalcogenides (**3a***,**3b***) were isolated from photo-induced reactions of **1*** in the presence of a limited amount of chalcogen (V/E 1/3). Complexes containing an oxo bridge such as $Cp^{\star}{}_2V_2E_3O$ (**4a***,**4b***) were generally observed as side-products [3], the molecular structure of $Cp^{\star}{}_2V_2Se_3O$ (**4b***) has been determined [12]. Finally, chalcogen abstraction from the pentachalcogenides $Cp^{\star}{}_2V_2E_4$ (**3a***,**3b***) using excess tri(n-butyl)phosphane led to the trichalcogenides. $Cp^{\star}{}_2V_2E_3$ (E = S (**5a***), Se (**5b***)) [3].

Up to the present time, no carbonyl-containing intermediates of the reactions between $Cp^{\star}V(CO)_4$ (**1***) and chalcogens (E = S, Se) to give the binuclear products **2a***,**2b***–**5a***,**5b*** have been identified. This is surprising in view of the fact that both mononuclear and binuclear half-sandwich carbonylmetal complexes of the first-row transition metals chromium, manganese, iron and cobalt are known to form derivatives containing both carbonyl groups and unsubstituted chalcogens as ligands [cf. 13]. Thus, the reactions of elemental sulfur with $Cp_2Cr_2(CO)_6$ [14–17], $CpMn(CO)_3$ [13] and $Cp_2Fe_2(CO)_4$ or $Cp'_2Fe_2(CO)_4$ [2,18–21] have been studied in detail, and sulfur complexes containing pentamethylcyclopentadienylcarbonylmetal fragments are also well-known, e.g. with chromium [22,23], molybdenum and tungsten [24,25], manganese and rhenium [13], ruthenium [26,27] and rhodium [28,29], as are related selenium and tellurium complexes [cf. 30]. It is widely assumed that the transformation of half-sandwich carbonylmetal compounds into chalcogen-rich binuclear complexes proceeds under stepwise loss of carbonyl ligands [15,17,20,25,29].

With the aim to obtain carbonyl-containing precursors of the binuclear vanadium-chalcogen complexes **2a***,**2b***, **3a***,**3b*** and **5a***,**5b***, we have used reactive derivatives of the half-sandwich complex $Cp^{\star}V(CO)_4$ (**1***) of the type $Cp^{\star}V(CO)_3L$ (L = acetonitrile (**6***) or dimethylsulfide (**7***)) for the reactions with elemental sulfur and selenium. We have also studied the reactions of **1***, **6*** and **7*** with diorganodichalcogenides E_2R_2 (E = S, Se; R = Me, Ph) and with hydrogen sulfide, H_2S. Similar reactions between $CpNb(CO)_3L$ (L = tetrahydrofuran) and both MeSH and H_2S had been reported by Herrmann, Ziegler and coworkers [31] to give binuclear complexes of the type $Cp_2Nb_2(CO)_4(\mu\text{-SMe})_2$ and $Cp_2Nb_2(CO)_4(\mu\text{-S})_n$ (n = 2, 3) which were structurally characterized (cf. [49*,50]).

Results and discussion

Synthetic studies

Photolytic displacement of a CO ligand from either $CpV(CO)_4$ (**1**) [32–33,46] or $Cp^{\star}V(CO)_4$ (**1***) in the presence of a two-electron ligand L in solution leads to the formation of monosubstituted derivatives, $CpV(CO)_3L$ and $Cp^{\star}V(CO)_3L$. Although numerous cyclopentadienyl compounds of the type $CpV(CO)_3L$ are known [46*], apparently no pentamethylcyclopentadienyl complexes $Cp^{\star}V(CO)_3L$ have been described so far. The acetonitrile compound **6*** tends to decompose if the THF/CH_3CN mixture used as a solvent is removed, however, the dimethyl sulfide

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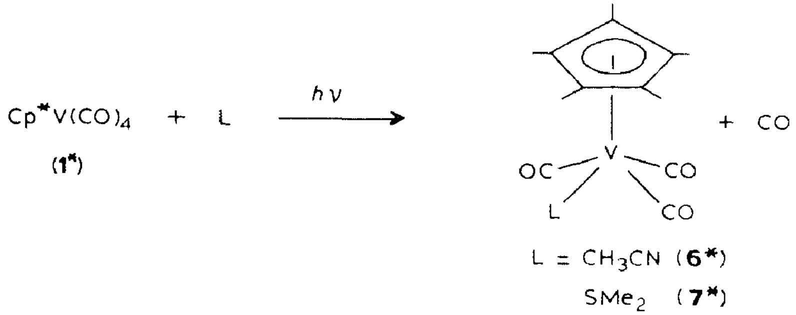
* Reference number with asterisk indicates a note in the list of references.

complex **7*** can be easily isolated in the crystalline state.



The corresponding cyclopentadienyl complexes CpV(CO)$_3$L (L = CH$_3$CN (**6**) [34] and SMe$_2$ (**7**) [33]) had been obtained earlier. The four-leg pianostool structure of CpV(CO)$_3$(SMe$_2$) (**6**) was supported by an X-ray structure analysis [33].

The reactions of **6*** (in acetonitrile solution) and **7*** (in toluene) with either sulfur or selenium at room temperature lead to the same carbonyl-free binuclear products **2a***–**4a*** and **2b***–**4b*** which are also formed in the thermal and photochemical reactions of Cp*V(CO)$_4$ (**1***) with sulfur and selenium, respectively. Attempts to detect carbonyl-containing intermediates in the ν(CO) region of the infrared spectra were unsuccessful, only the decrease of the starting material **1*** (ν (CO) 2011 and 1906 cm^{-1}, in toluene) could be monitored. The ^{51}V NMR spectra gave no indication of intermediates either. It is obvious that CO-containing precursors of the binuclear sulfur- or selenium-bridged complexes **2a***,**2b***–**4a***,**4b*** are not present in appreciable amounts in the reaction mixtures, although the thermal decarbonylation of 1 mmol **1*** in boiling toluene in the presence of chalcogen requires about 16 h in the case of selenium and about 28 h in the case of sulfur. Preliminary attempts to carbonylate Cp$^{\star}_2$V$_2$S$_3$ (**5a***) under CO pressure (60 bar) were also unsuccessful. (The spontaneous and induced carbonylation of (C$_5$Me$_4$Et)$_2$Ru$_2$S$_4$ has been described recently [27].)

In contrast to the oxidative decarbonylation of CpV(CO)$_4$ (**1**) [2] and Cp*V(CO)$_4$ (**1***) [3] by sulfur and selenium which leads directly to carbonyl-free products, the corresponding reaction of **1** and **1*** with diorganodichalcogenides, E$_2$R$_2$, can be conducted as a two-step process. For example, the photo-induced reaction of **1** with MeSSMe in THF solution results in the formation of a bis(methylthiolato)-bridged, diamagnetic complex Cp$_2$V$_2$(CO)$_4$(μ-SMe)$_2$ (**8a**) [35], which, upon prolonged irradiation or thermolysis, is completely decarbonylated to give the tetrakis(methylthiolato)-bridged, paramagnetic Cp$_2$V$_2$(μ-SMe)$_4$ (**10a**):

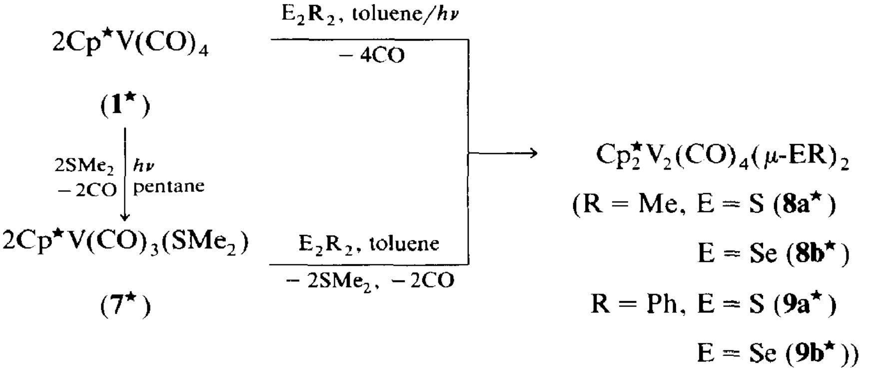
$$\underset{(\mathbf{1})}{2\mathrm{CpV(CO)_4}} \xrightarrow[\substack{(\mathrm{THF},\ h\nu) \\ -4\mathrm{CO}}]{+\mathrm{MeSSMe}} \underset{(\mathbf{8a})}{\mathrm{Cp(CO)_2V(\mu\text{-}SMe)_2V(CO)_2Cp}}$$

$$\Big\downarrow \begin{array}{l} +\mathrm{MeSSMe} \\ -4\mathrm{CO} \end{array}$$

$$\underset{(\mathbf{10a})}{\mathrm{CpV(\mu\text{-}SMe)_4VCp}}$$

The stepwise oxidative substitution of CO ligands by 2 equivalents of dimethyldisulfide corresponds to an increase of the formal oxidation state of vanadium from +1 (in **1**) through +2 (in **8a**) to +3 (in **10a**). The paramagnetic final product **10a** had been directly obtained before from the reaction of **1** with either MeSSMe or MeSH [36]. The analogous phenyl complexes $Cp_2V_2(\mu\text{-}EPh)_4$ (E = S (**11a**), Se (**11b**)) were similarly prepared using E_2Ph_2 [37,38].

In the context of our ^{51}V NMR studies [3], we have synthesized a series of 8 bis(μ-chalcogenido)vanadium complexes $Cp_2^{(\star)}V_2(CO)_4(\mu\text{-}ER)_2$ in order to estimate the influence of the ring ligand (Cp or Cp*), the chalcogen (E = S or Se) and the organyl substituent (R = Me or Ph). Both the direct photolysis of **1** or **1*** in the presence of E_2R_2 (in THF or toluene solution) and the reaction of the substituted intermediate $Cp^{(\star)}V(CO)_3(SMe_2)$ (**7**, **7***) with E_2R_2 give acceptable yields of the binuclear carbonyl-containing products around 40–50% (when R = Me) and 20–40% (when R = Ph), e.g.



The binuclear, carbonyl-containing complexes **8a**,**8b**, **8a***,**8b***, **9a**,**9b** and **9a***,**9b*** were purified by column chromatography over silica and characterized by their IR as well as their ^1H, ^{13}C and ^{51}V NMR spectra (Table 1). X-Ray crystallographic structure analyses for **8a*** and **9a*** have confirmed the binuclear structure with two RE bridges.

In addition to the carbonyl-containing diamagnetic complexes of the type $Cp_2^{(\star)}V_2(CO)_4(\mu\text{-}ER)_2$ (**8** and **9**), some carbonyl-free, paramagnetic material is generally obtained. The amount of the paramagnetic side-product increases if E_2R_2 is used in excess and the solutions are refluxed or irradiated for extended periods. According to the electron-impact mass spectra, the paramagnetic complexes correspond to the composition $Cp_2^{(\star)}V_2(ER)_4$ and are therefore considered to be the tetra-bridged products $Cp_2V_2(\mu\text{-}ER)_4$ (R = Me, E = S (**10a**), Se (**10b**), R = Ph, E = S (**11a**), Se (**11b**)) and $Cp^\star{}_2V_2(\mu\text{-}ER)_4$ (R = Me, E = S (**10a***), Se (**10b***), R = Ph (E = S (**11a***), Se (**11b***) some of which (e.g. **10a** [35,36], **11a**,**11b** [37,38]) had been described earlier. The assumed structure has been confirmed for $Cp_2V_2(\mu\text{-}SeMe)_4$ (**10b**) [51].

If, instead of dichalcogenides E_2R_2, hydrogen sulfide, H_2S, is allowed to interact with the pentamethylcyclopentadienylcarbonylvanadium compounds **1*** and **7***, a labile binuclear complex **12*** can be isolated to which the formula $Cp^\star{}_2V_2(CO)_4(\mu\text{-}S)_2$ is tentatively assigned. The orange-brown material **12*** is formed both by irradiation of $Cp^\star V(CO)_4$ (**1***) in THF solution in the presence of H_2S and by stirring solutions of $Cp^\star V(CO)_3(SMe_2)$ (**7***) in contact with H_2S. It is difficult to exclude

Table 1. Spectroscopic data

Complex	IR spectra ^{a} ν(CO) (cm^{-1})			NMR spectra ^{b}						
				$\delta(^{51}V)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	$\delta(^{13}C)$ (ppm)			$\delta(^1H)$ (ppm)	
						C_5Me_5	(Cp*)	ER	Cp*	ER
CpV(CO)$_4$	2030s,	1935vs,	1902w	−1512	37		90.4(m)		5.07	
(1)										
Cp*V(CO)$_4$	2015s,	1915vs,	1885w	−1466	95	10.8	103.8		1.90	
(1*)										
CpV(CO)$_3$(CH$_3$CN) (cf. [34])	1968,	1866,	1843sh ^{c}	−715 ^{c}	–					
(6)										
Cp*V(CO)$_3$(CH$_3$CN)	1953m	1853vs,	1825sh ^{c}	−759 ^{c}	–					
(6*)										
CpV(CO)$_3$(SMe$_2$) (cf. [33])	1965s,	1880s,	1862vs	−859	100		92	25.5	4.56	1.36
(7)										
Cp*V(CO)$_3$(SMe$_2$)	1949s,	1861s,	1951vs	−886	140	10.5	103.59	25.5 ^{d}	1.80	2.09
(7*)										
Cp$_2$V$_2$(CO)$_4$(μ-SMe)$_2$	1997m,	1990vs,	1933s	−788	635		94.03	23.48	5.03	2.15
(8a)							93.65	23.71	5.06	2.12
Cp*$_2$V$_2$(CO)$_4$(μ-SMe)$_2$	1971vs,	1910s,		−777	1235	11.2	103.70	22.5	1.75	1.99
(8a*)										
Cp$_2$V$_2$(CO)$_4$(μ-SeMe)$_2$	1992,	1988s,	1935s	−815	740		92.38	6.78	5.05	2.06
(8b)							92.47		5.02	1.98
Cp*$_2$V$_2$(CO)$_4$(μ-SeMe)$_2$	1969vs,	1912s		−772	1220	11.9	103.08	4.66	1.81	1.93
(8b*)										
Cp$_2$V$_2$(CO)$_4$(μ-SPh)$_2$	1995vs,	1955s,	1916m,b ^{e}	−686	835		95.33	143.12(a), 131.51(b) ^{f}	5.28	7.28 (m)
(9a)								128.25(c) 126.24(d)	5.21	7.20 (m)
Cp*$_2$V$_2$(CO)$_4$(μ-SPh)$_2$	1971vs	1933m,	1886w	−712	1020	10.94	102.75	141.66(a), 133.44(b) ^{f}	1.58	7.45 (m)
(9a*)								127.46(c), 126.16(d)		7.14 (m)
Cp$_2$V$_2$(CO)$_4$(μ-SePh)$_2$	1993vs,	1948s,	1917sh ^{e}	−727	1030		93.31	133.43(b) ^{f}	5.23	7.32 (m)
(9b)							93.60	128.29(c), 126.71(d)	5.20	7.20 (m)
Cp*$_2$V$_2$(CO)$_4$(μ-SePh)$_2$	1972vs,	1933s,	1887m	−723	1030	11.67	103.94	130.90(a), 134.48(b) ^{f}	1.68	7.49 (m)
(9b*)								127.72(c), 126.69(d)		7.16(m)
Cp*$_2$V$_2$(CO)$_4$(μ-S)$_2$	1983vs,	1920s,b		−721	1200	11.82	103.65 ^{g}		1.60 ^{g}	
(12*)										

[a] In hexane solution. [b] In chloroform-*d* solution. [c] In acetonitrile solution. [d] At −20 °C. [e] In toluene solution. [f] *J*-modulated spectrum, the small characters indicate the carbon atoms in the phenyl substituent ((a), Cl; (b), C2/6; (c), C3/5; (d) C4. [g] In benzene-d_6 solution.

the possibility that **12*** is the thiolato-bridged complex $Cp^\star_2V_2(CO)_4(\mu\text{-}SH)_2$. The field desorption mass spectra (*m/e* 550) are in agreement with this composition. However, no ν(S–H) absorptions could be identified in the IR spectra. An orange-brown material which has exactly the same IR, ^1H and ^{51}V NMR spectra is obtained when D_2S (from B_2S_3/D_2O) was used instead of H_2S in the reaction with **7***; no ^2D NMR signals could be observed. Attempts to methylate **12*** using diazomethane led to immediate loss of the CO ligands, as did the treatment with n-butyllithium. The ν(CO) pattern in the IR spectra of **12*** is very similar to that of the bis(methylthiolato) complex **8a***. We assume that **12*** is analogous to the binuclear niobium complex for which the sulfur-bridged structure $Cp_2Nb_2(CO)_4(\mu\text{-}S)_2$ had been deduced [31] on the basis of an X-ray crystal structure analysis. (See, however, refs. 49* and 50.)

Attempts to purify **12*** by recrystallization, chromatography or sublimation resulted in loss of the CO ligands, the main decomposition product being $Cp^\star{}_2V_2S_4$ (**3a***). In the presence of excess elemental sulfur, **12*** reacts to give a mixture of the CO-free complexes **2a***, **3a*** and **5a***. With selenium, mixed-chalcogen complexes of the types $Cp^\star{}_2V_2E_3$ and $Cp^\star{}_2V_2E_4$ (containing both S and Se) were formed which can be characterized on the basis of their ^{51}V NMR spectra after extrapolation from the homoleptic chalcogen complexes **5a***,**5b*** and **3a***,**3b***. These results will be discussed in a forthcoming paper.

Spectroscopic characterization

The relevant IR and NMR data of the carbonyl-containing complexes are given in Table 1.

In the ν(CO) region of the IR spectra, only bands of terminal CO ligands can be observed. As expected, the pattern of the ν(CO) absorptions is found at somewhat lower frequencies in the pentamethylcyclopentadienyl compounds, indicating stronger $V \rightarrow CO$ back-bonding in the Cp* than in the Cp complexes. The ν(CO) frequencies of analogous complexes containing either sulfur or selenium are almost identical. The solutions of the cyclopentadienyl complexes $Cp_2V_2(CO)_4(\mu\text{-}EMe)_2$ (E = S (**8a**), Se (**8b**)) presumably contain isomers, as may be deduced from the observation of two high-frequency bands of differing intensity at ca 1990 cm^{-1} in hexane solution.

Additional information concerning the presence of isomers in solution can be deduced from the ^{13}C and ^1H NMR spectra of the cyclopentadienyl complexes **8a**,**8b** and **9a**,**9b**. In agreement with the results reported for **8a** [35], we find that the ^1H NMR spectra of these compounds consistently contain two singlets of differing intensity for the Cp ring protons. Furthermore, the ^1H NMR spectra of the methyl complexes **8a**,**8b** also show two slightly separated singlets for the methyl substituents. These results taken together indicate that at least two isomers are present in solution. Both *cis-trans* isomerism of the two Cp ring ligands with respect to the V–V axis and/or *endo-exo* isomerism of the organyl substituents at the two chalcogenido bridges are possible. Signals ascribed to isomeric species are also observed in the ^{13}C NMR spectra of **8a**,**8b** and **9b**. No indications for the presence of isomers can be detected in the ^1H and ^{13}C NMR spectra of the pentamethylcyclopentadienyl complexes **8a***,**8b*** and **9a***,**9b***. It is interesting to note that the complexes containing permethylated ring ligands (Cp*) have a much higher tendency to crystallize than the corresponding Cp compounds.

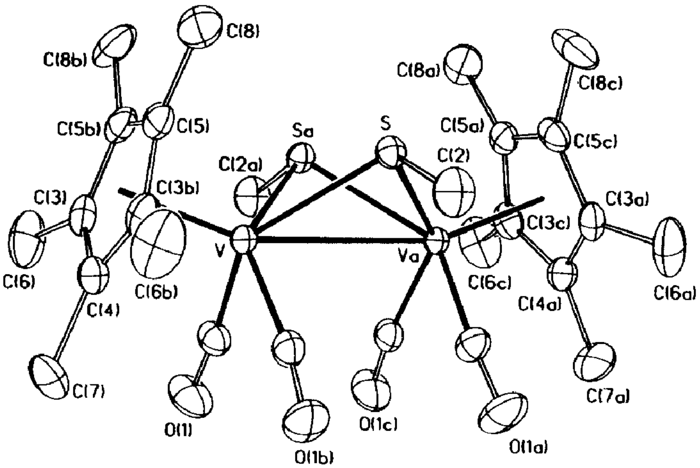


Fig. 1. Molecular structure of $Cp^{\star}_2V_2(CO)_4(\mu\text{-}SMe)_2$ (**8a***).

Although the ^{51}V NMR spectra are appropriate for the rapid identification of these binuclear vanadium compounds [cf. 3], it is not possible to identify slightly differing vanadium centers owing to the large line-widths (600–1250 Hz).

X-Ray structures of $Cp^{\star}{}_2V_2(CO)_4(\mu\text{-}SR)_2$ *(R = Me (8a*), Ph (9a*))*

The solid-state structures of two typical pentamethylcyclopentadienylvanadium complexes, **8a*** and **9a***, were determined in order to characterize the central (pseudo-tetrahedral) core V_2E_2 and the positions of the bridge substituents R. The molecular structures of the two binuclear compounds are presented in Fig. 1 and 2, selected interatomic distances and angles are compared in Table 2.

The methyl complex **8a*** possesses high crystallographic symmetry. The molecule contains two symmetry planes, one containing the metal atoms and the centers of the five-membered ring ligands, the other one being determined by the sulfur and

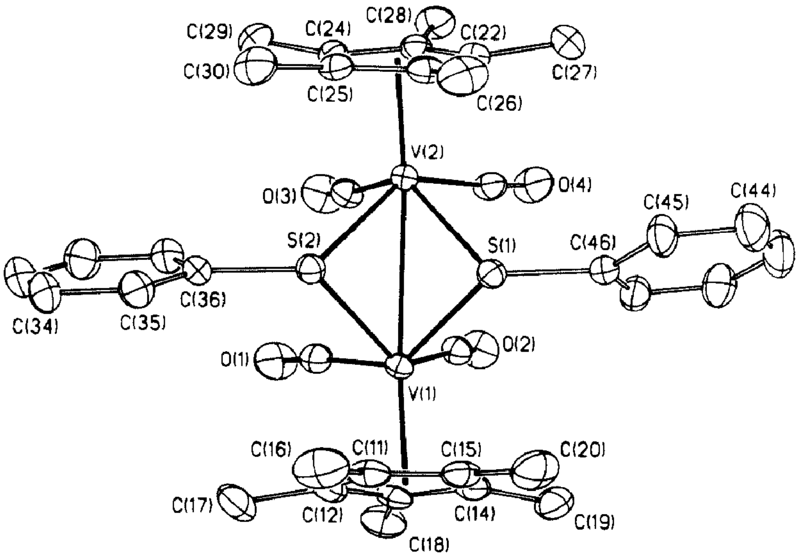


Fig. 2. Molecular structure of $Cp^{\star}_2V_2(CO)_4(\mu\text{-}SPh)_2$ (**9a***).

Table 2

Selected bond distances and angles

$\mathrm{Cp}^{\star}{}_2\mathrm{V}_2(\mathrm{CO})_4(\mu\text{-SMe})_2$ (**8a***)		$\mathrm{Cp}^{\star}{}_2\mathrm{V}_2(\mathrm{CO})_4(\mu\text{-SPh})_2$ (**9a***)	
Bond distances (Å)			
V–V(a)	3.083(1)	V(1)–V(2)	3.070(1)
V–S	2.425(1)	V(1)–S(1)	2.443(1)
		V(1)–S(2)	2.450(1)
		V(2)–S(1)	2.450(1)
		V(2)–S(2)	2.442(1)
V–CNT [a]	1.964(3)	V(1)–CNT(1)	1.967(2)
		V(2)–CNT(2)	1.965(2)
V–C(1)	1.939(3)	V(1)–C(1)	1.948(4)
		V(1)–C(2)	1.943(4)
		V(2)–C(3)	1.938(4)
		V(2)–C(4)	1.952(4)
Bond angles (deg)			
V–S–V(a)	78.9(1)	V(1)–S(1)–V(2)	77.7(1)
		V(1)–S(2)–V(2)	77.7(1)
S–V–S(a)	71.2(1)	S(1)–V(1)–S(2)	69.1(1)
		S(1)–V(2)–S(2)	69.1(1)
C(1)–V–C(1b)	80.3(2)	C(1)–V(1)–C(2)	75.6(2)
		C(3)–V(2)–C(4)	77.6(2)
V–S–C(2)	113.2(1)	V(1)–S(1)–C(46)	120.1(1)
		V(1)–S(2)–C(36)	116.6(1)
		V(2)–S(1)–C(46)	115.4(1)
		V(2)–S(2)–C(36)	119.6(1)
Dihedral angles (deg)			
[V,V(a),S]–[V,V(a),S(a)]	97.8	[V(1),S(1),V(2)]–[V(1),S(2),V(2)]	93.6
Torsion angles (deg)			
CNT–V–V(a)–CNT(a)	0.0	CNT(1)–V(1)–V(2)–CNT(2)	−28.2

[a] CNT = Center of the Cp* ring.

carbon atoms of the methylthiolato bridges (Fig. 1). The complex $\mathrm{Cp}^{\star}{}_2\mathrm{V}_2(\mathrm{CO})_4(\mu\text{-SMe})_2$ (**8a***) has the same geometry as $\mathrm{Cp}_2\mathrm{Nb}_2(\mathrm{CO})_4(\mu\text{-SMe})_2$ [31]. In both **8a*** and **9a***, the two Cp* ring ligands are arranged *cis* to each other, and both substituents R occupy *exo* positions, being directed towards the $\mathrm{V}_2(\mathrm{CO})_4$ part of the molecule. The planes of the phenyl rings in **9a*** comprise an angle of ca 36°. The angle which is enclosed by the two (nearly linear) carbonyl groups is 75.6(2)° and 77.6(2)° in the phenyl compound **9a***, 80.3(2)° in the methyl complex **8a*** and 84.3(19)°, in the methylniobium complex $\mathrm{Cp}_2\mathrm{Nb}_2(\mathrm{CO})_4(\mu\text{-SMe})_2$ [31].

The diamagnetism established by the NMR studies of solutions containing $\mathrm{Cp}_2^{(\star)}\mathrm{V}_2(\mathrm{CO})_4(\mu\text{-ER})_2$ (**8**, **9**) suggests that the binuclear complexes contain a formal vanadium–vanadium single bond and obey the 18-electron (EAN) rule. The acute angles at the sulfur atoms (V–S–V 78.9(1)° in **8a*** and 77.1(1)° in **9a***) can be taken as an indication for such a bonding metal–metal interaction. However, the vanadium–vanadium distance (3.083(1) Å in **8a***, 3.070(1) Å in **9a***) is unusually long if compared with vanadium–vanadium bond lengths observed in other binuclear cyclopentadienyl complexes for which a V–V bond has been established, e.g. $Cp_2V_2(CO)_5$ (2.462(2) Å) [39], $Cp_2V_2(CO)_4(PPh_3)$ (2.466(1) Å) [40], $(C_5H_4{}^iPr)_2V_2S_4$ (2.610(1) Å) [10], $Cp'_2V_2S_5$ (2.658(1) Å) [7] and $Cp'_2V_2Se_5$ (2.779(4) Å) [8]. A "normal" V–V single bond is expected to have a length of about 2.7 Å, but longer V ··· V distances have been observed, e.g. in $Cp^\star{}_2V_2Cl_2(\mu\text{-}S)_2$ (2.829(3) Å) [41] and $Cp_2V_2(PEt_3)_2(\mu\text{-}Cl)_2$ (3.245(3) Å) [42]. The nature of the interaction between the vanadium centers in these complexes (antiferromagnetic coupling?) is a matter of discussion [cf. 41]. A long metal–metal distance has also been found in the niobium complexes $Cp^\star{}_2Nb_2(CO)_4(\mu\text{-}SMe)_2$ (3.164(9) Å), $Cp^\star{}_2Nb_2(CO)_4(\mu\text{-}S)_2$ (3.143(1) Å) and $Cp^\star{}_2Nb_2(CO)_4(\mu\text{-}S)_3$ (3.555(1) Å) [31]. A binuclear vanadium complex without metal–metal bond is $Cp^\star{}_2V_2O_2Cl_2(\mu\text{-}O)$ (V ··· V 3.395(1) Å) [43].

The sulfur–sulfur separation in **8a**★ (2.81 Å) and **9a**★ (2.78 Å) is consistent with the presence of two almost independent three-electron RS bridges. The S–S bond distance in $Re_2(CO)_6[\mu\text{-}Br]_2[\mu\text{-}MeSSMe]$ which contains an intact dimethyldisulfide ligand is 2.111(13) Å [44]. The angles formed by the V_2S planes and the R–S vector are 120.6(2)° for **8a**★ and (av) 127.0(2)° for **9a**★.

Table 3

Crystallographic data for **8a**★ and **9a**★

	8a★	**9a**★
Formula	$C_{26}H_{36}O_4S_2V_2$	$C_{36}H_{40}O_4S_2V_2$
Crystal system	orthorhombic	monoclinic
Space group	*Ccmm* (non-std, No. 63)	$P2_1/n$ (No. 14)
a Å	8.396(2)	11.919(3)
b Å	21.952(4)	14.527(4)
c Å	15.135(4)	20.019(6)
β deg		97.03(2)
V Å^3	2790(1)	3440(1)
Z	4	4
D (calcd), g cm^{-3}	1.38	1.36
μ(Mo-K_α), cm^{-1}	8.8	7.3
T, K	296	296
Size mm	0.28×0.30×0.45	0.21×0.30×0.31
Color	red brown	deep red
Diffractometer	Nicolet R3m/μ	Nicolet R3m/μ
Radiation	Mo-K_α (λ 0.71073 Å)	Mo-K_α (λ 071073 Å)
Monochromator	graphite	graphite
Scan limits, deg	$4 \le 2\theta \le 52$	$4 \le 2\theta \le 48$
Scan method	Wyckoff	Wyckoff
Reflections collected	2930	5771
Independent reflections	1471	5364
Obsd. reflections ($n\sigma F_o$)	1129	3857
Std reflections	3 std/197 reflections	3 std/197 reflections
Decay, %	< 1%	< 1%
R(F), %	2.92	3.91
R(WF), %	3.25	4.30
GOF	0.924	1.130
Δ/σ	0.045	0.092
$\Delta(\rho)$, ΔÅ^{-3}	0.25	0.32
N_0/N_v	9.18	10.34

Experimental

All reactions and the purification procedures were carried out under an atmosphere of dry argon in dry, Ar-saturated solvents.

The half-sandwich complex $CpV(CO)_4$ (**1**) was obtained by normal-pressure carbonylation of VCp_2 in THF solution [47], $Cp^{\star}V(CO)_4$ (**1***) was prepared by the reaction of $V(CO)_6$ with $Cp^{\star}H$ in hexane solution [43,48].

The ligand SMe_2 (Merck) and the dichalcogenides S_2Me_2 (Fluka), Se_2Me_2 (Aldrich), S_2Ph_2 (Merck) and Se_2Ph_2 (Fluka) were commercial products and used without further purification. Grey selenium metal (Fluka) was used.

The photo-induced CO eliminations were performed using a high-pressure mercury lamp TQ 718 (700 W, Original Hanau).

$Cp^{\star}V(CO)_3(SMe_2)$ ($7^{\star}$)

A solution containing 0.32 g (1.07 mmol) $Cp^{\star}V(CO)_4$ (**1***) and 0.4 ml (5.45 mmol) dimethylsulfide, SMe_2, in 30 ml pentane was irradiated at 0 °C for 30 min. Carbon monoxide evolved and was removed periodically by intermittant application of the aspirator vacuum. The deep-red solution was concentrated to 20 ml and kept over dry-ice (−78 °C) over night. The deep-red crystals (dec. 70 °C) were washed twice with cold pentane. Yield 0.30 g (84%).

General procedure for the preparation of binuclear bis(μ-organylchalcogenido)-bis(pentamethylcyclopentadienyl)-tetracarbonyldivanadium, $Cp^{\star}_2V_2(CO)_4(\mu\text{-}ER)_2$

(a) A solution of 1 mmol (0.30 g) $Cp^{\star}V(CO)_4$ (**1***) and 0.3 ml (4.1 mmol) SMe_2 in 30 ml pentane is photolysed at 0 °C until the IR absorptions of **1*** have disappeared (30–40 min). Then 1 mmol dimethyl or diphenyl dichalcogenide, E_2R_2, is added and the dark-red solution of **7*** is stirred for 3 h. The reaction mixture is brought to dryness, the residue redissolved in a small amount of pentane/toluene and purified by column chromatography over silica. The binuclear complex $Cp^{\star}_2V_2(CO)_4(\mu\text{-}ER)_2$ (E = S, Se; R = Me, Ph) is eluted as an orange to red zone using pentane/toluene (2/1 for **8a***,**8b***; 1/2 for **9a***,**9b***).

Table 4

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for $Cp^{\star}_2V_2(CO)_4(\mu\text{-}SMe)_2$ (**8a***)

	x	*y*	*z*	*U* [a]
V	2960(1)	4298(1)	2500	23(1)
S	1494(1)	5000	3432(1)	28(1)
O(1)	5808(3)	4313(1)	1210(2)	65(1)
C(1)	4721(3)	4347(1)	1674(2)	39(1)
C(2)	2175(5)	5000	4576(2)	47(1)
C(3)	2590(3)	3409(1)	1737(2)	38(1)
C(4)	3559(4)	3294(2)	2500	39(1)
C(5)	1060(3)	3582(1)	2966(2)	38(1)
C(6)	3020(6)	3253(2)	796(2)	72(1)
C(7)	5205(6)	3017(2)	2500	70(2)
C(8)	−376(4)	3683(2)	3543(3)	67(1)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

(b) A tetrahydrofuran solution (15 ml) containing 0.50 mmol (0.15 g) Cp*V(CO)$_4$ (**1***) and 1 mmol E_2R_2 is photolysed at 0 °C for 20–30 min. The solvent is removed and the product purified by chromatography over silica.

Table 5

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for Cp*$_2$V$_2$(CO)$_4$(μ-SPh)$_2$ (**9a***)

	x	y	z	U [a]
V(1)	3178(1)	8345(1)	1148(1)	29(1)
V(2)	5085(1)	8257(1)	2325(1)	28(1)
S(1)	4696(1)	7214(1)	1363(1)	31(1)
S(2)	3169(1)	7638(1)	2258(1)	32(1)
O(1)	2299(3)	10165(2)	1687(2)	71(1)
O(2)	4481(3)	9980(2)	631(2)	59(1)
O(3)	4611(3)	10307(2)	2565(2)	65(1)
O(4)	6669(3)	9366(2)	1510(2)	65(1)
C(1)	2632(4)	9463(3)	1537(2)	44(1)
C(2)	4094(3)	9320(3)	830(2)	39(1)
C(3)	4675(3)	9526(3)	2467(2)	41(1)
C(4)	6054(3)	8928(3)	1775(2)	42(1)
C(11)	1709(4)	7344(3)	757(2)	43(2)
C(12)	1305(3)	8272(3)	759(2)	47(1)
C(13)	1873(3)	8780(3)	281(2)	41(1)
C(14)	2637(3)	8166(3)	10(2)	42(1)
C(15)	2516(3)	7283(3)	295(2)	44(1)
C(16)	1258(4)	6543(3)	1122(2)	69(2)
C(17)	332(4)	8597(4)	1107(3)	69(2)
C(18)	1616(4)	9743(3)	38(3)	64(2)
C(19)	3295(4)	8368(4)	−571(2)	64(2)
C(20)	3065(4)	6417(3)	86(2)	67(2)
C(21)	5968(3)	7036(3)	2929(2)	38(1)
C(22)	6791(3)	7677(3)	2757(2)	41(1)
C(23)	6599(3)	8525(3)	3095(2)	37(1)
C(24)	5661(3)	8391(3)	3468(2)	34(1)
C(25)	5290(3)	7469(3)	3371(2)	36(1)
C(26)	5900(4)	6027(3)	2745(2)	62(2)
C(27)	7777(4)	7455(4)	2383(2)	64(2)
C(28)	7356(3)	9356(3)	3149(2)	56(2)
C(29)	5235(4)	9049(3)	3962(2)	53(2)
C(30)	4428(4)	7000(3)	3747(2)	55(2)
C(31)	2180(2)	9023(2)	3007(1)	53(2)
C(32)	1376	9308	3414	77(2)
C(33)	585	8681	3602	87(3)
C(34)	598	7771	3383	81(2)
C(35)	1402	7486	2975	56(2)
C(36)	2193	8112	2787	41(1)
C(41)	6090(2)	7864(1)	406(1)	47(1)
C(42)	6974	7743	18	62(2)
C(43)	7555	6908	37	72(2)
C(44)	7252	6194	445	70(2)
C(45)	6368	6314	833	51(1)
C(46)	5787	7149	814	36(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

$Cp^\star{}_2V_2(CO)_4(\mu\text{-}SMe)_2$ (**8a★**): orange-brown crystals, m.p. 209 °C (dec). Yield 150 mg (51.8%) and 70 mg (48.4%) by methods (a) and (b), respectively. Anal. Found: C, 53.79; H, 6.37; O, 11.2; S, 11.0%. Molecular mass 578 (M^+) by EI MS. $C_{26}H_{36}O_4S_2V_2$ (578.59) calcd.: C, 53.97, H, 6.27; O, 11.06 and S, 11.08%.

$Cp^\star{}_2V_2(CO)_4(\mu\text{-}SePh)_2$ (**9b★**): red crystals, m.p. 192 °C (dec.). Yield 70 mg (17.6% and 80 mg (20.0%) by methods (a) and (b), respectively.

Photolysis of $Cp^\star V(CO)_4$ (1★) in the presence of H_2S

A slow stream of H_2S was blown through a solution of 0.14 g (0.47 mmol) $Cp^\star V(CO)_4$ in 20 ml THF for 1/2 min. The solution was irradiated at 0 °C for 10–15 min until the gas evolution ceased. The solvent was removed under high vacuum, and the orange-brown residue (**12★**) washed twice with cold pentane. Decomposition involving loss of CO takes place slowly both in solution and in the solid state at room temperature.

Crystal structure determinations

Crystallographic data for both structures are collected in Table 3. Crystals of **8a★** and **9a★** were fixed to glass fibers with epoxy cement. The space group for **8a★** was determined by systematic absences and diffraction symmetry, and distinguished from its acentric alternatives by the presence of perpendicular mirror planes in the unit cell. No corrections for absorption were judged necessary.

The structures of both compounds were solved by direct methods and completed by difference Fourier syntheses. The phenyl rings for **9a★** were constrained to rigid, planar hexagons (d(CC) 1.395 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized isotropic contributions.

All computations used SHELXTL (5.1) software (G. Sheldrick, Nicolet XRD, Madison WI (USA)). Atomic coordinates are given in Tables 4 and 5.

Complete tables of the crystallographic data (anisotropic thermal parameters, hydrogen-atom coordinates and structure factors) may be obtained from one of the authors (ALR).

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