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Cyclopentadienyl- and methylcyclopentadienyl-vanadium complexes containing chalcogen bridges: dechalcogenation to pseudocubane clusters

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Abstract

In extension of previous studies with pentamethylcyclopentadienyl (Cp*, η^5-C_5Me_5) vanadium complexes, decarbonylations in the presence of elemental chalcogens of the halfsandwich compounds Cp(')V(CO)$_4$ and Cp(')V(CO)$_3$L (L = SMe$_2$, MeCN) containing either the unsubstituted cyclopentadienyl (Cp, η^5-C_5H_5) or the monomethyl-substituted (Cp', η^5-C_5H_4Me) cyclopentadienyl ring ligand have been investigated. (The notation Cp(') indicates that both the unsubstituted (Cp) and the monomethyl-substituted (Cp') cyclopentadienyl complexes were used.) The main products obtained from Cp(')V(CO)$_3$L and an excess of chalcogen were binuclear pentachalcogenides Cp(')$_2$V$_2$E$_5$ (1) (E = S, Se) and oxo-tritellurides Cp(')$_2$V$_2$E$_3$O (4) (E = Te), respectively. Oxygen-containing side-products such as $Cp'_2V_2E_3O$ (E = S, Se), $Cp'_2V_2S_4O$ and Cp'VO(S$_5$) were isolated from the reactions starting from Cp'V(CO)$_4$. Chalcogen abstraction from **1** by use of one equivalent of tri(n-butyl)phosphane (P^{n}Bu$_3$) gave the tetrachalcogenides Cp(')$_2$V$_2$E$_4$ (**2**), while further addition of P^{n}Bu$_3$ gave pseudocubane clusters Cp(')$_4$V$_4$E$_4$ (**7**) (E = S, Se). Small amounts of trisulfides Cp(')$_2$V$_2$S$_3$ (**3**) were observed by ^{51}V NMR spectroscopy in solutions of **1** and **2** in the presence of P^{n}Bu$_3$. Binuclear tetracarbonyl-dichalcogenides Cp(')$_2$V$_2$(CO)$_4$E$_2$ (**6**) (E = S, Te) were made by treating solutions of Cp(')V(CO)$_3$(SMe$_2$) with H_2S and by photolysing Cp(')V(CO)$_4$ in the presence of either H_2S or TeP^{n}Bu$_3$. The reactions of $Cp'_2V_2(CO)_4S_2$ (**6a'**) with an excess of an oligochalcogenide Na$_2$E$_5$ (E = Se, Te) gave the mixed-chalcogenide complexes $Cp'_2V_2E_2S_2$ (E = Se (**2d'**) and Te (**2f'**)), which react with two equivalents of P^{n}Bu$_3$ or NiCp$_2$ to the pseudocubane cluster $Cp'_4V_4S_4$ (**7a'**). Thermal decarbonylation of the tetracarbonyl-dichalcogenides Cp(')$_2$V$_2$(CO)$_4$E$_2$ (**6**) in toluene solution gave the tetranuclear clusters Cp(')$_4$V$_4$E$_4$ (**7**) (E = S, Te) directly. The analogous pentamethylcyclopentadienyl compounds $Cp^*_4V_4E_4$ (**7***) (E = S, Te) were also prepared. The spectroscopic data for the new CpV and Cp'V complexes are compared with those of the corresponding Cp*V compounds.

Introduction

In previous communications [1–3] we have described binuclear pentamethylcyclopentadienyl vanadium complexes in which the bridging framework between the

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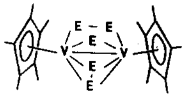
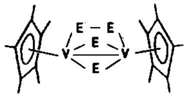
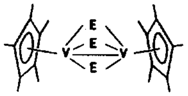
two vanadium centers contains three, four, or five chalcogen atoms. Thermal and photo-induced decarbonylation of the parent halfsandwich complex $Cp^{*}V(CO)_4$ by either sulfur or selenium leads to the homoleptic-bridged pentachalcogenides $Cp^{*}_{2}V_{2}E_{5}$ (**1**) and tetrachalcogenides $Cp^{*}_{2}V_{2}E_{4}$ (**2**) (E = S, Se) [1]. The corresponding trichalcogenides $Cp^{*}_{2}V_{2}E_{3}$ (**3**) are accessible by dechalcogenation of either **1** or **2** with tri(n-butyl)phosphane, $P^{n}Bu_3$ [2]. Side-products such as $Cp^{*}_{2}V_{2}E_{3}O$ (**4**) and $Cp^{*}_{2}V_{2}E_{4}O$ (**5**) contain an additional oxo bridge between the vanadium centers.



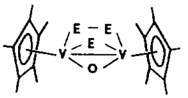
(1)
(E = S, Se)



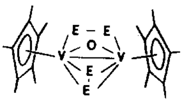
(2)
(E = S, Se)



(3)
(E = S, Se)



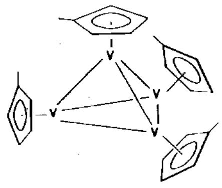
(4)
(E = S, Se, Te)



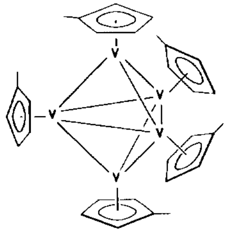
(5)
(E = S)

If the kinetically labile complexes $Cp^{*}V(CO)_3L$ (L = SMe_2, MeCN) are used as starting materials instead of the parent halfsandwich $Cp^{*}V(CO)_4$, the decarbonylation by chalcogens to give **1**, **2**, **4** and **5** can be conducted under milder conditions. It is then possible to prepare heteroleptic-bridged compounds containing a mixed S/Se framework [2] and even tellurium [3] between the vanadium atoms. All pentamethylcyclopentadienyl vanadium chalcogenide complexes (E = S, Se, Te) obtained so far are binuclear; the dechalcogenation of **1** and **2** using $P^{n}Bu_3$ leads to **3** almost quantitatively.

On the other hand, the methylcyclopentadienyl (Cp′) vanadium sulfide compounds $Cp'_{2}V_{2}S_{5}$ (**1a′**) [4] and $Cp'_{2}V_{2}S_{4}$ (**2a′**) [5] are known to give clusters such as $Cp'_{4}V_{4}S_{4}$ (**7a′**) and $Cp'_{5}V_{5}S_{6}$ upon desulfurization [6,7]. We therefore decided to study the influence of the ring ligands Cp and Cp′ on the existence and stability of binuclear vanadium chalcogenides (including the selenides and tellurides). In earlier studies the pentasulfide $Cp_{2}V_{2}S_{5}$ (**1a**) was assumed to be polymeric [8,9].



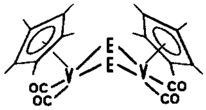
(7a′)
$Cp'_{4}V_{4}(\mu_{3}\text{-}S)_{4}$



$Cp'_{5}V_{5}(\mu_{3}\text{-}S)_{6}$

(The sulfido bridges are omitted for the sake of clarity)

The clusters $Cp'_{4}V_{4}S_{4}$ (**7a′**) and $Cp'_{5}V_{5}S_{6}$ were also previously obtained by treating vanadocenes $Cp'_{2}V$ with thiols [10–12]. An additional route was examined in the present study: it originated in our view that decarbonylation of the binuclear, chalcogen-bridged tetracarbonyl complexes $Cp_2^*V_2(CO)_4E_2$ (**6**) [3] would also lead to pseudocubane clusters.



$Cp_2^*V_2(CO)_4(\mu\text{-}E)_2$ (**6**)
($E = S, Se, Te$)

A similar decarbonylation of $Cp_2^*M_2(CO)_2(\mu\text{-}Se)_2$ ($M = Co, Rh$) has been used to generate tetramers $Cp_4^*M_4Se_4$ [13]. Pseudocubane clusters $Cp_4^*M_4E_4$ of first row transition metals M that contain only pentamethylcyclopentadienyl ring ligands are rare. Other examples are $Cp_4^*Co_4Te_4$ [14] and $Cp_4^*Cr_4E_4$ ($E = O$ [15], S [16,17]).

Results and discussion

Table 1 gives the numbering system for the vanadium chalcogenide compounds, in accordance with the notations used in the preceding papers [2,3]. The superscripts * and ′ indicate $\eta^5\text{-}C_5(CH_3)_5$ (Cp*) and $\eta^5\text{-}C_5H_4(CH_3)$ (Cp′) complexes, as distinct from compounds containing unsubstituted $\eta^5\text{-}C_5H_5$ (Cp) rings.

Binuclear pentachalcogenides and tetrachalcogenides

Reaction of Cp(′)V(CO)$_4$ and Cp(′)V(CO)$_3$L ($L = SMe_2$ or MeCN) with an excess of sulfur or selenium gives the pentachalcogenides Cp(′)$_2V_2E_5$ (**1**) ($E = S$, Se) in good yields, along with by-products. In contrast to the previously described procedure for the preparation of $Cp_2V_2S_5$ (**1a**) [8], mild reaction conditions could be used owing to the higher reactivity of the kinetically labile starting complexes, Cp(′)V(CO)$_3$L, although only moderate improvements of the yields were achieved by using Cp(′)V(CO)$_3$L in place of Cp(′)V(CO)$_4$. The formation of side-products was not mentioned in the literature. In the synthesis of **1a**, the side-product is $Cp_2V_2S_4$ (**2a**), which can be isolated almost without decomposition by rapid chromatography on a short silica column. In the synthesis of **1a**′, a variety of side-products were isolated (including **2a**′, **4a**′ and **5a**′), all corresponding to the by-products formed in the analogous preparation of **1a***.

In the reactions leading to the pentaselenides Cp(′)$_2V_2Se_5$ (**1b**, **1b**′), the tetraselenides Cp(′)$_2V_2Se_4$ (**2b**, **2b**′) could not be obtained from the product mixtures. The by-product in the synthesis of Cp(′)$_2V_2Se_5$ (**1b**′) was $Cp_2'V_2Se_3O$ (**4b**′), again consistent with the results in the synthesis of $Cp_2^*V_2Se_5$ (**1b***) [1]. Neither penta- nor tetratellurides were formed in the analogous reactions with tellurium, as expected from the observations on the Cp*V system [3].

The best method of preparing the homoleptic-bridged tetrachalcogenides Cp(′)$_2V_2E_4$ (**2**) ($E = S$, Se) involves stoichiometric dechalcogenation of the pentachalcogenides **1**:

$$\underset{(\mathbf{1})}{Cp(')_2V_2E_5} + P^nBu_3 \rightarrow \underset{(\mathbf{2})}{Cp(')_2V_2E_4} + EP^nBu_3$$
$$E = S, Se$$

The stability of the tetrachalcogenides **2** thus formed increases with the number of methyl groups attached to the cyclopentadienyl ring ligand. The sulfido complex

Table 1

Numbering scheme

Type of complex [a] (E = S, Se or Te)	$Cp_2V_2E_5$ (1)	$Cp_2V_2E_4$ (2)	$Cp_2V_2E_3$ (3)	$Cp_2V_2E_3O$ (4)
	1a, a′, a* $Cp_2V_2S_5$	2a, a′, a* $Cp_2V_2S_4$	3a, a′,a* $Cp_2V_2S_3$	4 a′, a* $Cp_2V_2S_3O$
	1b, b′, b* $Cp_2V_2Se_5$	2b, b′, b* $Cp_2V_2Se_4$	3 b* $Cp_2V_2S_3$	4 b′, b* $Cp_2V_2Se_3O$
	1 c′, c* $Cp_2V_2SeS_4$	2 c* $Cp_2V_2SeS_3$	3 c′,c* $Cp_2V_2SeS_2$	4 c* $Cp_2V_2SeS_2O$
	1 d′, d* $Cp_2V_2Se_2S_3$	2 d′, d* $Cp_2V_2Se_2S_2$		4 d* $Cp_2V_2Se_2SO$
	1 e′, e* $Cp_2V_2Se_3S_2$	2 e* $Cp_2V_2Se_3S$		4e, e′, e* $Cp_2V_2Te_3O$
	1 f′, f* $Cp_2V_2Se_4S$	2 f′, f* $Cp_2V_2Te_2S_2$		4 f* $Cp_2V_2TeS_2O$
		2 g* $Cp_2V_2Te_2Se_2$		4 g* $Cp_2V_2TeSeSO$
				4 h* $Cp_2V_2TeSe_2O$
				4 i* $Cp_2V_2Te_2SO$
				4 j* $Cp_2V_2Te_2SeO$
Type of complex [a] (E = S, Se or Te)	$Cp_2V_2E_4O$ (5)	$Cp_2V_2(CO)_4E_2$ (6)	$Cp_4V_4E_4$ (7)	
	5 a′, a* $Cp_2V_2S_4O$	6a, a′, a* $Cp_2V_2(CO)_4S_2$	7a, a′,a* $Cp_4V_4S_4$	
		6 b* $Cp_2V_2(CO)_4Se_2$	7b, b′ $Cp_4V_4Se_4$	
		6c, c′, c* $Cp_2V_2(CO)_4Te_2$	7 c′,c* $Cp_4V_4Te_4$	

[a] Cp denotes a cyclopentadienyl ring ligand such as η^5-C_5H_5 (Cp), η^5-$C_5H_4CH_3$ (Cp′) or η^5-$C_5(CH_3)_5$ (Cp*).

$Cp_2V_2S_4$ (**2a**) decomposed slowly on contact with silica; the selenido compound $Cp_2V_2Se_4$ (**2b**) could not be purified at all by column chromatography on silica.

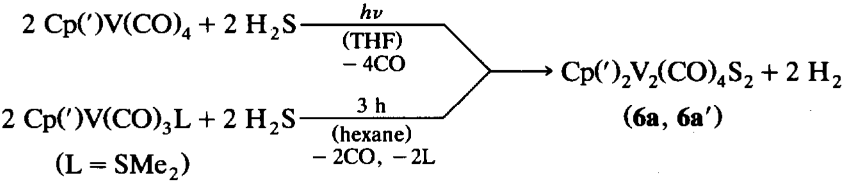
Heteroleptic-bridged tetrachalcogenides $Cp(')_2V_2Te_3O$ (**4e**, **4e**′) are formed in the reactions of $Cp(')V(CO)_3(SMe_2)$ with either tellurium or oligotelluride, Na_2Te_5. The identification of **4e** and **4e**′ was based on ^1H, ^{13}C, and ^{51}V NMR data as well as on IR spectroscopic comparison with the Cp^* analogue **4e***. The low stability of **4e** and **4e**′ made characterization by mass spectrometry difficult. For example, the field desorption mass spectrum of $Cp'_2V_2Te_3O$ (**4e**′) gave a parent peak corresponding to $Cp'_4V_4Te_4$ (**7c**′).

An elegant route to heteroleptic-bridged tetrachalcogenides such as $Cp'_2V_2Te_3O$ (**4e**′) and $Cp'_2V_2E_2S_2$ (E = Se (**2d**′), Te (**2f**′)) makes use of the binuclear tetracarbonyl-dichalcogenides $Cp'_2V_2(CO)_4E_2$ (E = S, Te) as intermediates (see below).

Binuclear tetracarbonyl-dichalcogenides

Previous studies [2,3] have shown that chalcogen-bridged pentamethylcyclopentadienyl complexes $Cp^*_2V_2(CO)_4E_2$ (E = S (**6a***) [18] and Te (**6c***) [3]) can be used as precursors for binuclear vanadium compounds with a mixed-chalcogen framework [2,3]. It was assumed, that the cyclopentadienyl and methylcyclopentadienyl complexes $Cp(')_2V_2(CO)_4E_2$ might be used in a similar way.

The sulfido-bridged derivatives **6a** and **6a**′ were prepared by two routes, one involving photolysis of $Cp(')V(CO)_4$ in the presence of H_2S in THF solution, as described for the Cp^* analogue **6a*** [18], and the other stirring of a solution of $Cp(')V(CO)_3(SMe_2)$ under an atmosphere of H_2S:



$$\left.\begin{array}{l} 2\,Cp(')V(CO)_4 + 2\,H_2S \xrightarrow[\text{(THF)}\ -4CO]{h\nu} \\ 2\,Cp(')V(CO)_3L + 2\,H_2S \xrightarrow[\text{(hexane)}\ -2CO,\ -2L]{3\ h} \\ (L = SMe_2) \end{array}\right\} \longrightarrow \begin{array}{c} Cp(')_2V_2(CO)_4S_2 + 2\,H_2 \\ (\mathbf{6a}, \mathbf{6a}') \end{array}$$

The tellurido-bridged tetracarbonyls **6c** and **6c**′ were obtained in nearly quantitative yields by irradiating $Cp(')V(CO)_4$ in the presence of TeP^nBu_3, a photolabile tellurium source, in highly dilute hexane solutions.

$$2\,Cp(')V(CO)_4 + 2\,TeP^nBu_3 \xrightarrow[\text{(hexane)}]{h\nu} \underset{(\mathbf{6c},\ \mathbf{6c}')}{Cp(')_2V_2(CO)_4Te_2} + 4\,CO + 2\,P^nBu_3$$

Similar attempts to prepare the selenium-bridged analogues (**6b**, **6b**′) by the above routes using either H_2Se or SeP^nBu_3 were unsuccessful, as with the Cp^* system (*cf.* [3]).

The stability of the sulfido-bridged tetracarbonyls **6a** and **6a**′ is comparable to that of **6a***, whereas the tellurido-bridged compounds **6c** and **6c**′ are less stable than **6c***. In solution **6c** rapidly decomposed. The reactions of **6a**′ were investigated in more detail. In the presence of chalcogen sources such as oligoselenide (Na_2Se_5) and oligotelluride (Na_2Te_5), respectively, heteroleptic-bridged tetrachalcogenides $Cp'_2V_2E_2S_2$ were found to be formed in good yields.

$$\begin{array}{lcll} Cp'_2V_2(CO)_4S_2 + 2\,E & \rightarrow & Cp'_2V_2E_2S_2 & + 4\,CO \\ (\mathbf{6a}') & & E = Se\ (\mathbf{2d}') & \\ & & \quad\ \ Te\ (\mathbf{2f}') & \end{array}$$

The oxidative decarbonylation of **6a**′ in the presence of chalcogen is faster than that of $Cp'V(CO)_3L$ (L = SMe_2, MeCN). The reaction of **6a**′ with oligoselenide also produced an inseparable mixture of pentachalcogenides $Cp'_2V_2Se_nS_{5-n}$ (**1b**′–**1f**′), which were identified by ^{51}V NMR spectroscopy (Table 2). However, no by-products were isolated in the reaction of **6a**′ with oligotelluride.

The decarbonylation of $Cp'_2V_2(CO)_4Te_2$ (**6c**′) in the presence of Na_2Te_5 led once more to the oxo-tritellurides $Cp'_2V_2Te_3O$ (**4e**′); homoleptic-bridged tetratellurides could not be isolated. Again, the oxidative decarbonylation of the binuclear precursor **6c**′ was faster than that of the mononuclear $Cp'V(CO)_3(SMe_2)$.

When solutions of the tetracarbonyl-dichalcogenides **6** in toluene are heated in the absence of additional chalcogen, decarbonylation takes place and the tetranuclear clusters **7** are formed:

$$\begin{array}{ccccc} Cp(')_2V_2(CO)_4E_2 & \xrightarrow[\text{(toluene)}]{\text{1–4 h}} & \text{“}[Cp(')_2V_2E_2]\text{”} & \longrightarrow & 1/2\,Cp(')_4V_4E_4 \\ (\mathbf{6}) & & \text{not isolated} & & (\mathbf{7}) \\ (E = S, Te) & & & & \end{array}$$

It is conceivable that the thermal decarbonylation of **6** proceeds through a coordinatively unsaturated intermediate “$[Cp(')_2V_2E_2]$”, which either adds chalcogens or dimerizes.

Tetranuclear clusters

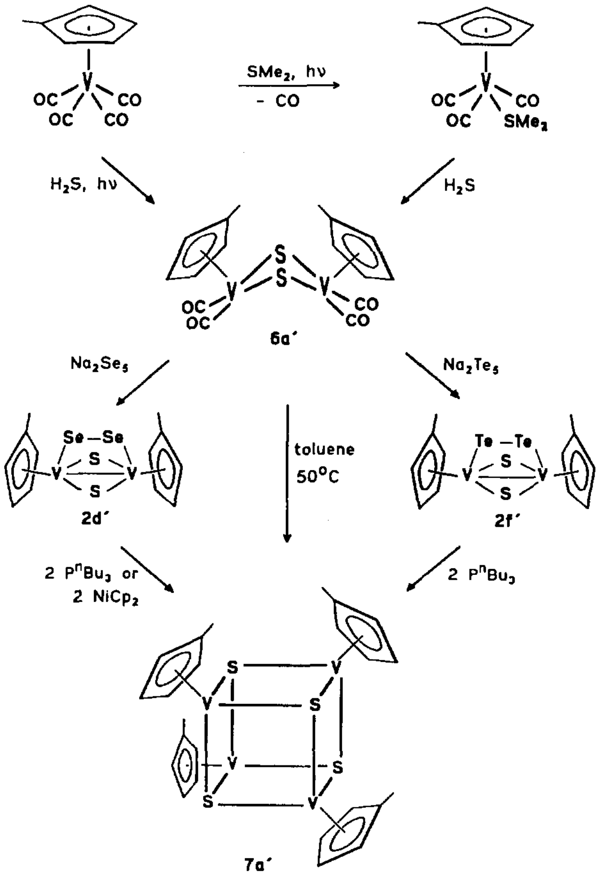
When an excess of P^nBu_3 was added to either $Cp(')_2V_2S_5$ (**1a**, **1a**′) or $Cp(')_2V_2S_4$ (**2a**, **2a**′), sulfur was removed from the complex, and the tetranuclear and pentanuclear clusters reported by Rauchfuss *et al.* [6,7] were formed. The methylcyclopentadienyl complex $Cp'_4V_4S_4$ (**7a**′) was isolated in even higher yields when $Cp'_2V_2E_2S_2$ (E = S (**2d**′) and Te (**2f**′)) was treated with either P^nBu_3 or nickelocene, $NiCp_2$, as a chalcogen abstraction reagent (Scheme 1).

However, no reaction was observed between $Cp^*_2V_2E_2S_2$ (**2d***, **2f***) and $NiCp_2$, not even in boiling toluene. Since $Cp^*_2V_2Se_2S_2$ (**2d***) reacts with P^nBu_3 to give $Cp^*_2V_2SeS_2$ (**3c***) [2], the lack of reactivity towards $NiCp_2$ might be ascribed to the presence of the bulky Cp* ligand, which apparently blocks the approach of $NiCp_2$ to the chalcogen framework.

Reactions in NMR tubes between $Cp_2V_2S_5$ (**1a**) and stoichiometric amounts (1 : 1) of P^nBu_3 showed the formation of a small amount of $Cp_2V_2S_3$ (**3a**) in addition to $Cp_2V_2S_4$ (**2a**) (Fig. 1). The analogous experiment with $Cp'_2V_2S_5$ (**1a**′) also gave a trace of **3a**′ along with $Cp'_2V_2S_4$ (**2a**′). The mixed-chalcogen complex $Cp'_2V_2Se_2S_2$ (**2d**′) was partially deselenized to give $Cp'_2V_2SeS_2$ (**3c**′), but in the reaction of $Cp_2V_2Se_5$ (**1b**) with P^nBu_3 (1 : 1) no trace of (the unknown) $Cp_2V_2Se_3$ (**3b**) could be detected (Fig. 1).

Addition of three equivalents of P^nBu_3 to $Cp(')_2V_2Se_5$ (**1b** and **1b**′) gave $Cp(')_4V_4Se_4$ (**7b** and **7b**′) exclusively. The clusters were characterized by mass spectrometry; no evidence for the presence of $Cp(')_5V_5Se_6$ was found. The paramagnetism of $Cp(')_4V_4Se_4$ (**7b** and **7b**′) suggests that two electrons occupy a t_2 set of orbitals [7], in agreement with the model for cubane clusters developed by Dahl *et al.* [19].

Attempts to obtain pseudocubanes containing different chalcogens by treating equimolar mixtures of $Cp'_2V_2S_4$ (**2a**′) and $Cp'_2V_2Se_4$ (**2b**′) with two equivalents of



Scheme 1. Formation of $Cp'_4V_4S_4$ (**7a'**) via $Cp'_2V_2(CO)_4S_2$ (**6a'**).

P^nBu_3 were unsuccessful. According to the EI mass spectra, the product mixture contained only the homoleptic-bridged tetramers $Cp'_4V_4S_4$ (**7a'**) and $Cp'_4V_4Se_4$ (**7b'**); apparently **2a'** is more reactive towards the phosphane than **2b'**. However, cubane clusters containing different ring ligands, e.g. $Cp'_2Cp_2V_4S_4$ (from $Cp'_2V_2S_4$ (**2a'**) and two equivalents of vanadocene [7]) are known.

Whereas the dechalcogenation of the pentamethylcyclopentadienyl complexes $Cp^*_2V_2E_5$ (**1***) and $Cp^*_2V_2E_4$ (**2***) ($E = S$, Se) by P^nBu_3 generally stops at the trichalcogenide stage, $Cp^*_2V_2E_3$ (**3***), and cannot be continued to tetranuclear clusters, the thermal decarbonylation of the tetracarbonyl-dichalcogenide compounds $Cp^*_2V_2(CO)_4E_2$ (**6***) can actually be used to synthesize pseudocubane clusters (**7***) containing a Cp* ring ligand on every metal. The new complexes $Cp^*_4V_4S_4$ (**7a***) and $Cp^*_4V_4Te_4$ (**7c***) belong to the small group of $Cp^*_4M_4E_4$ clusters [13–17] containing a first-row transition element.

Spectroscopic studies

The Cp and Cp' complexes were characterized by NMR, IR and mass spectroscopy (Table 2). The most important method for the identification of the new

Table 2

Spectroscopic data

Complex	Colour	Molecular ion[a] (m/e)	NMR spectra[b]							IR spectra
			$\delta(^{51}V)$ (ppm)	$\nu_{1/2}$ (Hz)	$\delta(^{1}H)$ (ppm) CH ring	CH_3	$\delta(^{13}C)$ (ppm) C_1	C–H	CH_3	ν(V–O–V) (cm^{-1})
1a $Cp_2V_2S_5$	Black	392	417	150	6.60			104.8		
1a′ $Cp'_2V_2S_5$	Black	420	449	130	6.60(1)	2.36(3)	119.5	107.5	16.5	
					6.57(1)			106.5		
					6.40(2)			104.3		
								103.9		
1b $Cp_2V_2Se_5$	Green	628	880	160	6.57			106.8		
1b′ $Cp'_2V_2Se_5$	Green	656	938	180	6.59(2)	2.34(3)	116.9	106.7	16.7	
					6.43(1)			105.5		
					6.38(1)			102.0		
1c′ $Cp'_2V_2SeS_4$			601	180	6.71	2.34				
					6.51					
1d′ $Cp'_2V_2Se_2S_3$			684	180	6.72	2.32	120.4	109.1		
					6.64		118.2	108.8	14.0	
							117.6	108.4		
							114.1	99.6		
								97.5		
1e′ $Cp'_2V_2Se_3S_2$			735	180	6.33	2.29				
					6.25					
1f′ $Cp'_2V_2Se_4S$			803	190	6.37	2.15				
					6.29					
2a $Cp_2V_2S_4$	Orange	360	1454	290	6.72			107.0		
2a′ $Cp'_2V_2S_4$	Orange-red	388	1461	330	6.65(2)	2.43(3)	122.2	108.5	16.0	
					6.54(2)			106.0		
2b $Cp_2V_2Se_4$	Green		2136	400	7.13			107.9		
2b′ $Cp'_2V_2Se_4$	Green	578	2154	560	6.26(2)	2.25(3)	119.6	102.9	16.4	
					6.12(2)			99.8		
2d′ $Cp'_2V_2Se_2S_2$	Red-brown	484	1627	400	6.72(2)	2.38(3)	121.5	108.4	16.3	
					6.47(2)			105.5		

2f' $Cp'_2V_2Te_2S_2$	Green	580	1810	450	6.93(2) 6.43(2)	2.26(3)	116.6	107.6 104.1	16.8	
3a $Cp_2V_2S_3$	Violet	328	1592	450	6.20			107.3		
3a' $Cp'_2V_2S_3$	Red		1605	540						
3c' $Cp'_2V_2SeS_2$	Turquoise		1725	570						
4a' $Cp'_2V_2S_3O$	Orange	372	1252	420	6.74(1) 6.70(1) 6.49(1) 6.42(1)	2.30(3)	121.2	109.4 108.3 107.4 104.4	15.0	746
4b' $Cp'_2V_2Se_3O$	Orange	516	1622	440	6.95(1) 6.90(1) 6.41(1) 6.28(1)	2.14(3)	120.3	113.8 108.8 107.4 106.1	17.2	728
4e $Cp_2V_2Te_3O$	Green		2285	940	5.08			108.2		770
4e' $Cp'_2V_2Te_3O$	Green		2382	890	4.98(1) 4.72(1) 4.38 4.34 (2)	2.38(3)	120.0	110.8 95.1 91.4 91.0	16.1	788
5a' $Cp'_2V_2S_4O$	Green	404	437	290	6.68(1) 6.64(2) 6.50(1)	2.27(3)	120.3	107.6 106.4 106.0	15.2	723
6a $Cp_2V_2(CO)_4S_2$	Orange		-747^{c}	470	4.57^{c}			94.3^{c}		$2003vs^{d}$ 1943s,br
6a' $Cp'_2V_2(CO)_4S_2$	Orange		-736^{c}	490	$4.52(2)^{c}$ 4.45(2)	$1.66(3)^{c}$	109.8^{c}	95.4^{c} 92.8	15.5^{c}	$1999vs^{d}$ 1937s,br
6c $Cp_2V_2(CO)_4Te_2$	Dark red		-1045^{c}	730						$1963s^{e}$ 1920s,br
6c' $Cp'_2V_2(CO)_4Te_2$	Dark red		-974^{c}	750	$4.43(2)^{c}$ 4.36(2)	$1.70(3)^{c}$	96.0^{c}	91.4^{c} 89.3	13.8^{c}	$1978vs^{d}$ 1929s,br

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[a] EI mass spectra (ref. to ^{51}V, ^{32}S, ^{80}Se and ^{128}Te). [b] In $CDCl_3$ solution (^{51}V NMR spectra were recorded at 15°C, ^{1}H and ^{13}C NMR spectra at 25°C). [c] In C_6D_6 solution. [d] $\nu(CO)$ in hexane solution. [e] $\nu(CO)$ in THF solution.

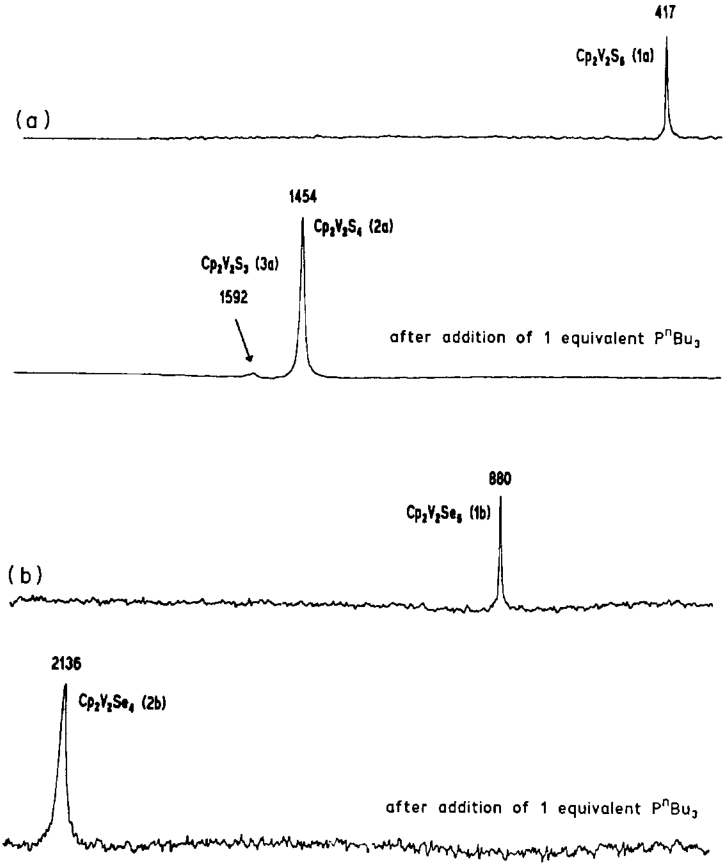


Fig. 1. Dechalcogenation of (a) $Cp_2V_2S_5$ (**1a**) and (b) $Cp_2V_2Se_5$ (**1b**) by tri(n-butyl)phosphane (P^nBu_3) in $CDCl_3$ solution, as monitored by ^{51}V NMR spectroscopy ($\delta(^{51}V)$ (ppm) ref. $VOCl_3$, 15°C).

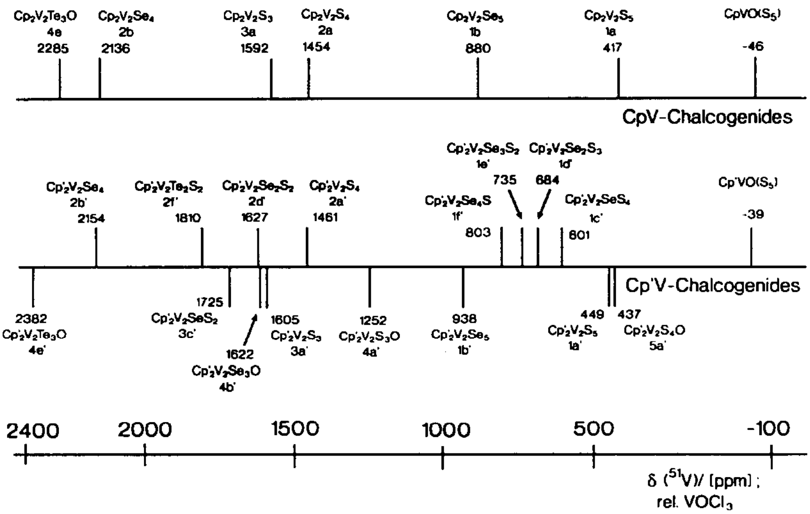
compounds is ^{51}V NMR spectroscopy. Because of the favorable NMR parameters of the ^{51}V nucleus ($I = 7/2$), such as high natural abundance (99.76%), low quadrupole moment ($Q = -0.052 \times 10^{-28}$ m^2) and high receptivity (0.381 ref. to ^1H) [20], rapid accumulation is possible, and even traces of diamagnetic vanadium complexes can be unequivocally identified (Scheme 2).

The following features can be discerned from the available ^{51}V NMR data (Table 2 and Scheme 2):

(a) if the number of chalcogen atoms in the bridge system is reduced (in the series of complex types **1**–**2**–**3**), the ^{51}V signal moves to lower field [1,2];

(b) if the number of heavier chalcogens increases in the bridge system of the vanadium(V) complexes **1**–**5**, the ^{51}V signal is shifted to lower field [3], *i.e.* $\delta(^{51}V)$ increases in the order O < S < Se < Te ("inverse chalcogen dependence" (ICD));

(c) the tetracarbonyl-dichalcogenides (**6**) have their ^{51}V signals at high field, like other carbonylvanadium complexes, and the signal moves upfield if the chalcogen is changed from sulfur to tellurium ("normal chalcogen dependence" (NCD)).



Scheme 2. Chemical shifts $\delta(^{51}V)$ of cyclopentadienyl- and methylcyclopentadienyl-vanadium chalcogenide complexes.

	$\delta(^{51}V)$		$\delta(^{51}V)$
$Cp_2V_2(CO)_4S_2$ (**6a**)	−747	$Cp_2V_2(CO)_4Te_2$ (**6c**)	−1045
$Cp'_2V_2(CO)_4S_2$ (**6a′**)	−736	$Cp'_2V_2(CO)_4Te_2$ (**6c′**)	−974
$Cp^{*}_2V_2(CO)_4S_2$ (**6a***)	−721	$Cp^{*}_2V_2(CO)_4Te_2$ (**6c***)	−853

It can be assumed that whether ICD or NCD is observed depends on the valence shell electron configuration of the observed nucleus, as discussed for normal and inverse halogen dependence [21,22]. Inverse halogen dependence has been related to the change in sign in spin-orbit coupling at the half-filled subshell [22].

Similar conclusions can be derived from the observed ^{51}V chemical shifts of the chalcogenide complexes **1–5** (d^0 configuration, ICD) and the tetracarbonyl-chalcogenides **6** (d^2 configuration, NCD). The binuclear vanadium-chalcogenide compounds **1–6** provide a good example that both ICD and NCD can be observed with the same central metal.

(d) if the cyclopentadienyl ring ligand varies in the series Cp–Cp′–Cp*, the signal is shifted downfield:

	$\delta(^{51}V)$		$\delta(^{51}V)$		$\delta(^{51}V)$
$CpV(CO)_4$	−1512	$Cp_2V_2S_5$ (**1a**)	417	$Cp_2V_2Se_5$ (**1b**)	880
$Cp'V(CO)_4$	−1504	$Cp'_2V_2S_5$ (**1a′**)	449	$Cp'_2V_2Se_5$ (**1b′**)	938
$Cp^{*}V(CO)_4$	−1477	$Cp^{*}_2V_2S_5$ (**1a***)	596	$Cp^{*}_2V_2Se_5$ (**1c***)	1119

(This rule is not valid, however, in the very low-field region, *e.g.* for $Cp^{*}_2V_2Se_4$ (**2b***) and $Cp^{*}_2V_2Te_3O$ (**4e***), *cf.* [3]).

The line-widths of the vanadium signals are significantly smaller for Cp and Cp′ complexes than for the corresponding Cp* compounds [1–3].

The ^1H and ^{13}C NMR spectra (Table 2) of the Cp′ complexes provide information about the symmetry of the central divanada-chalcogenide framework and thus indicate the possible chirality of the vanadium centers. A mirror plane including the two metal atoms is characteristic of the central framework in $Cp'_2V_2E_4$ (E = S (**2a′**), Se (**2b′**)), $Cp'_2V_2E_2S_2$ (E = Se (**2d′**), Te (**2f′**)) and $Cp'_2V_2(CO)_4E_2$ (E = S (**6a′**), Te(**6c′**)), as indicated by the observation of only two multiplets for the ring protons in the ^1H and only four signals (C^1, C^2/C^5, C^3/C^4 and CH_3) in the ^{13}C NMR spectra. The mirror plane is absent in complexes of the type $Cp'_2V_2E_5$ (**1′**), $Cp'_2V_2E_3O$ (**4′**) and in $Cp'_2V_2S_4O$ (**5a′**), for which four multiplets (partially overlapping in **1′** and **5′**) are found for the ring protons and six signals in the ^{13}C NMR spectra.

The IR spectra (KBr disks) of the binuclear oxo complexes **4** and **5** show an intense ν(V–O–V) stretching absorption between 790 and 720 cm^{-1}, characteristic of an oxo bridge [1–3]. The terminal oxo ligand in $Cp'VO(S_5)$ is monitored by a strong ν(V=O) band at 938 cm^{-1} (*cf.* $CpVO(S_5)$ and $Cp^*VO(S_5)$ 961 cm^{-1} [23]). The tetracarbonyl-dichalcogenide compounds **6** show two ν(CO) stretching bands, a very intense and sharp absorption between 2010 and 1960 cm^{-1}, and a strong and broad band near 1930 cm^{-1}.

The EI mass spectra of the binuclear chalcogenides **1–5** always contain the molecular ion, with a relative intensity in the range of 20–80% and a correct isotope pattern (in respect of the number of Se and/or Te atoms). The typical fragmentation involves loss of chalcogens, the heavier chalcogens being preferentially ejected, followed by elimination of one ring ligand. At higher heating rates, and especially in the case of complexes **2**, the molecular ion and the fragment ions of the corresponding pseudocubane clusters **7** can be observed. The molecular ions of **7c** and **7c′** were also present in the FD mass spectra of the oxo-tritellurides **4e** and **4e′**. The tetranuclear clusters are obviously generated in the mass spectrometer. Compared with the IR and NMR spectra of **4e** and **4e′** (Table 2), the clusters do not contain an oxo bridge, and are paramagnetic.

The EI mass spectra of the pseudocubane clusters **7** indicate stepwise loss of all four cyclopentadienyl ring ligands (Table 3). All expected tetranuclear fragment

Table 3

Mass spectra of the tetranuclear clusters

Complex	Fragment ions [a,b]					
	M^+ $Cp_4V_4E_4^+$	$(M-Cp)^+$ $Cp_3V_4E_4$	$(M-2Cp)^+$ $Cp_2V_4E_4^+$	$(M-3Cp)^+$ $CpV_4E_4^+$	$(M-4Cp)^+$ $V_4E_4^+$	$M^+/2$ $Cp_2V_2E_2^+$
$Cp_4V_4S_4$ (**7a**)	592(100)	527(50)	462(62)	397(21)	332(14)	296(18)
$Cp'_4V_4S_4$ (**7a′**)	648(100)	569(22)	490(32)	411(28)	332(17)	324(29)
$Cp^*_4V_4S_4$ (**7a***)	872(100)	737(14)	602(25)	467(23)	332(8)	436(44)
$Cp_4V_4Se_4$ (**7b**) [c]	782(87)	717(38)	652(31)	587(24)	522(20)	392(80)
$Cp'_4V_4Se_4$ (**7b′**)	838(83)	757(23)	680(28)	601(30)	522(29)	418(100)
$Cp'_4V_4Te_4$ (**7c′**) [c]	1032(78)	953(9)	874(16)	795(10)	716(12)	516(38)
$Cp^*_4V_4Te_4$ (**7c***) [c]	1256(2)					628(25)

[a] Cp denotes a cyclopentadienyl ring ligand such as η^5-C_5H_5 (Cp), η^5-$C_5H_4CH_3$ (Cp′) or η^5-$C_5(CH_3)_5$ (Cp*). [b] *m/e* (rel. intensity (%)), based on ^{51}V, ^{32}S, ^{80}Se and ^{128}Te. [c] The base peak (100%) in **7b** is *m/e* 116 (CpV^+), in **7c′** *m/e* 79 (Cp'^+) and in **7c*** *m/e* 884 ($Cp^*_2V_2Te_4^+$) (*cf.* [3]).

ions between the molecular ion and $V_4E_4^+$ can be observed, except for $Cp_4^*V_4Te_4$ (**7c***). In all cases the tetranuclear cluster also appears to be split into two moieties upon electron impact.

Experimental

The techniques, namely, the use of argon as inert gas, the details of the photo-induced reactions, the separation of reaction mixtures and the purification procedures by thin-layer and column chromatography on silica have been described previously [2,3]. The sources of the reagents and gases and details of the purification of the solvents have also been previously indicated.

The halfsandwich compounds $CpV(CO)_4$ [24] and $Cp'V(CO)_4$ [25] were prepared as previously described. The substituted derivatives $CpV(CO)_3L$ ($L = SMe_2$) [26] and $Cp'V(CO)_3L$ ($L = SMe_2$, MeCN) containing a labile two-electron donor ligand were generated *in situ* before use by photolysis of $Cp(')V(CO)_4$ in the presence of L [*cf.* 18]. The synthesis of the tetracarbonyl complexes $Cp_2^*V_2(CO)_4(\mu\text{-}S)_2$ (**6a***) [18] and $Cp_2^*V_2(CO)_4(\mu\text{-}Te)_2$ (**6c***) [3] was as described previously.

Decarbonylation of $Cp'V(CO)_4$ in the presence of sulfur

In boiling toluene. A solution of 400 mg (1.65 mmol) of $Cp'V(CO)_4$ in 20 ml of toluene containing 160 mg (5 mmol) of sulfur was refluxed for 18 h. After evaporation of the solvent, the black residue was extracted repeatedly with 5 ml portions of dichloromethane (CH_2Cl_2), and the solution concentrated then chromatographed on silica in a 20 cm column:

Zone	Eluent	Colour	Product and yield
I	Pentane/CH_2Cl_2 (10:1)	Yellow	$Cp'V(CO)_4 + S_8$
II	Pentane/CH_2Cl_2 (3:1)	Orange	$Cp'_2V_2S_4$ (**2a'**), 12 mg (4%)
III	Pentane/CH_2Cl_2 (2:1)	Black	$Cp'_2V_2S_5$ (**1a'**), 165 mg (48%)
IV	Pentane/CH_2Cl_2 (1:3)	Red-brown	$Cp'_2V_2S_3O$ (**4a'**) and $Cp'VO(S_5)$
V	Pentane/Et_2O (2:1)	Green	$Cp'_2V_2S_4O$ (**5a'**), 16 mg (5%)

Repetition of the chromatography of fraction IV led to separation of the two components:

Eluent	Colour	Product and yield
Pentane/Et_2O (5:1)	Orange	$Cp'_2V_2S_3O$ (**4a'**), 58 mg (19%)
Pentane/Et_2O (1:1)	Dark red	$Cp'VO(S_5)$, 20 mg (4%)

Under photolysis in THF solution. A solution containing 300 mg (1.24 mmol) of $Cp'V(CO)_4$ and 120 mg (3.75 mmol) of sulfur in 50 ml of THF was irradiated for 30 min at 0°C with light from a medium-pressure mercury arc (Heraeus, Original Hanau, TQ 718). Work-up by column chromatography gave $Cp'_2V_2S_4$ (**2a'**), 89 mg (37%), $Cp'_2V_2S_5$ (**1a'**), 137 mg (53%) and $Cp'_2V_2S_3O$ (**4a'**), 18 mg (7%).

Decarbonylation of Cp(′)V(CO)$_3$L (L = SMe$_2$, MeCN) in the presence of chalcogens

Reaction of Cp′V(CO)$_3$(MeCN) with selenium. A solution of 180 mg (0.74 mmol) of Cp′V(CO)$_4$ in 50 ml of THF/MeCN (4 : 1) was irradiated for 45 min at 0°C. Selenium (180 mg, 2.28 mmol) was added and the mixture stirred at room temperature for 16 h. The colour changed from red to green. The mixture was evaporated to dryness and the black residue extracted with CH$_2$Cl$_2$. Column chromatography on silica gave three zones:

Zone	Eluent	Colour	Product and yield
I	Pentane/CH$_2$Cl$_2$ (4 : 1)	Yellow	Cp′V(CO)$_4$
II	Pentane/CH$_2$Cl$_2$ (2 : 1)	Green	Cp$'_2$V$_2$Se$_5$ (**1b′**), 186 mg (77%)
III	CH$_2$Cl$_2$	Orange	Cp$'_2$V$_2$Se$_3$O (**4b′**), 40 mg (21%)

Reactions of CpV(CO)$_3$(SMe$_2$) with sulfur and selenium. Photolysis (45 min, 0°C) of a solution containing 240 mg (1.05 mmol) of CpV(CO)$_4$ and 0.7 ml (9.6 mmol) of SMe$_2$ in 50 ml of THF generated the reactive intermediate CpV(CO)$_3$(SMe$_2$). Following addition of 100 mg (3.13 mmol) S$_8$ the solution was stirred for 17 h at 25°C. The black mixture was evaporated to dryness and the residue extracted with CH$_2$Cl$_2$. The extract was filtered through a 5 × 2 cm^2 layer of silica, then concentrated and finally chromatographed rapidly on silica in a short column:

Zone	Eluent	Colour	Product and yield
I	Pentane/CH$_2$Cl$_2$ (4 : 1)	Yellow	CpV(CO)$_4$
II	Pentane/CH$_2$Cl$_2$ (2 : 1)	Orange	Cp$_2$V$_2$S$_4$ (**2a**), 25 mg (13%)
III	Pentane/CH$_2$Cl$_2$ (1 : 1)	Black	Cp$_2$V$_2$S$_5$ (**1a**), 75 mg (36%)

The analogous reaction (20 h) of CpV(CO)$_3$(SMe$_2$) (generated photolytically from 365 mg (1.60 mmol) CpV(CO)$_4$) with 380 mg (4.8 mmol) of selenium gave, after similar work-up, only Cp$_2$V$_2$Se$_5$ (**1b**):

Zone	Eluent	Colour	Product and yield
I	Pentane/CH$_2$Cl$_2$ (4 : 1)	Yellow	CpV(CO)$_4$
II	Pentane/CH$_2$Cl$_2$ (1 : 1)	Green	Cp$_2$V$_2$Se$_5$ (**1b**), 190 mg (38%)

Reactions of Cp(′)V(CO)$_3$(SMe$_2$) with tellurium. A solution of 310 mg (1.28 mmol) of Cp′V(CO)$_4$ and 0.7 ml (9.6 mmol) of SMe$_2$ in 50 ml of THF was irradiated for 45 min at 0°C. Tellurium powder (500 mg, 3.9 mmol) was added and the mixture stirred for 24 h. The colour gradually changed from red-brown to green. The solvent was evaporated and the residue extracted with CH$_2$Cl$_2$. The concentrated extract was chromatographed in the dark, on silica, and a brown-glass receiver was used in order to avoid photo-induced decomposition of the product.

Zone	Eluent	Colour	Product and yield
I	Pentane/CH$_2$Cl$_2$ (4 : 1)	Yellow	Cp′V(CO)$_4$
II	Pentane/CH$_2$Cl$_2$ (2 : 1)	Green	Cp$'_2$V$_2$Te$_3$O (**4c′**), 48 mg (11%)

The same procedure was used to isolate $Cp_2V_2Te_3O$ (**4e**). Only small amounts (3–5%) of the green compound **4e** were recovered from the column chromatography.

Dechalcogenation of pentachalcogenides $Cp(')_2V_2E_5$ by P^nBu_3

$Cp'_2V_2S_5$ (1a'). A solution of 69 mg (0.16 mmol) of **1a'** in 20 ml of CH_2Cl_2 was treated with 0.04 ml (0.16 mmol) of P^nBu_3 and stirred for 2 min. The colour changed from black to red. The mixture was taken to dryness, and a CH_2Cl_2 extract of the residue was purified by column chromatography on silica. Elution with pentane/CH_2Cl_2 (1:1) gave an orange-red band that contained 25 mg (40%) orange-red $Cp'_2V_2S_4$ (**2a'**).

$Cp'_2V_2Se_5$ (1b'). Treatment of a green solution of 138 mg (0.2 mmol) of **1b'** in 20 ml of CH_2Cl_2 with 0.05 ml (0.2 mmol) of P^nBu_3 produced a light-green solution. Upon chromatography on silica, a green fraction was eluted with pentane/CH_2Cl_2 (3:1) and contained 78 mg (65%) $Cp'_2V_2Se_4$ (**2b'**).

$Cp_2V_2S_5$ (1a). Sulfur abstraction from 70 mg (0.2 mmol) of **1a** with 0.05 ml (0.2 mmol) of P^nBu_3 in CH_2Cl_2 solution (20 ml) was accompanied by a rapid colour change from black to orange, indicating formation of **2a**. However, during chromatography on silica, the colour of the zone changed spontaneously to violet. With pentane/CH_2Cl_2 (1:1) for elution, 13 mg (22%) of $Cp_2V_2S_3$ (**3a**) were isolated.

Photo-induced preparation of tetracarbonyl-dichalcogenides $Cp(')_2V_2(CO)_4E_2$

$Cp'_2V_2(CO)_4S_2$ (6a'). A solution containing 242 mg (1 mmol) of $Cp'V(CO)_4$ and 1 ml (13.7 mmol) of SMe_2 in 30 ml of hexane was irradiated for 45 min at 0°C. The solution was taken to dryness (to remove excess SMe_2) and the residue redissolved in 20 ml hexane. The $Cp'V(CO)_3(SMe_2)$ solution was saturated with H_2S gas (1 min) and then stirred under an H_2S atmosphere for 3–4 h. Concentration to 10 ml and storage at −78°C overnight gave an orange-brown precipitate of **6a'** which was rinsed with a small amount of cold pentane and finally dried under high-vacuum. Yield 162 mg (74%).

$Cp_2V_2(CO)_4S_2$ (6a). A THF solution (35 ml) of 210 mg (0.92 mmol) of $CpV(CO)_4$ was saturated with H_2S gas and irradiated for 30 min at 0°C. The solvent was evaporated, the residue dissolved in 10 ml of hexane, and the solution kept at −78°C overnight. The orange-brown precipitate of **6a** was separated from the mother liquor, washed with cold pentane, and dried. Yield 170 mg (91%).

$Cp'_2V_2(CO)_4Te_2$ (6c'). The solution of 100 mg (0.41 mmol) of $Cp'V(CO)_4$ and 126 mg (0.38 mmol) of TeP^nBu_3 in 80 ml of hexane was irradiated for 1 h at 0°C. A dark-red precipitate of **6c'** was formed and the solution became colourless. The product **6c'** was washed twice with 30 ml portions of hexane and dried. The yield (127 mg) was almost quantitative.

The analogous procedure starting from $CpV(CO)_4$ gave $Cp_2V_2(CO)_4Te_2$ (**6c**), which was characterized by IR and ^{51}V NMR spectroscopy but decomposed within 15 min, leaving a THF-insoluble material.

Preparation of mixed-chalcogenide complexes $Cp'_2V_2E_2S_2$

$Cp'_2V_2Se_2S_2$ (2d'). A solution of $Cp'_2V_2(CO)_4S_2$ (**6a'**) (obtained from 210 mg (0.86 mmol) $Cp'V(CO)_4$ as described above, and 270 mg (0.6 mmol) of Na_2Se_5 in 30 ml of THF was stirred for 2 h. The solvent was removed, the residue extracted

with CH_2Cl_2, and the extract concentrated, then chromatographed on a column filled with silica in pentane.

Zone	Eluent	Colour	Product and yield
I	Pentane/CH_2Cl_2 (4:1)	Yellow	$Cp'V(CO)_4$
II	Pentane/CH_2Cl_2 (5:2)	Red-brown	$Cp'_2V_2Se_2S_2$ (**2d'**), 72 mg (35%)
III	Pentane/CH_2Cl_2 (1:1)	Green-brown	$Cp'_2V_2Se_nS_{5-n}$ (**1b'**–**1f'**), 34 mg

$Cp'_2V_2Te_2S_2$ (2f'). Starting from 228 mg (0.94 mmol) of $Cp'V(CO)_4$, the tetracarbonyl intermediate **6a'** was prepared and then treated with 480 mg (0.7 mmol) of Na_2Te_5 in THF (30 ml). After 3 h stirring the mixture was worked up in the usual way. Purification by chromatography on silica gave, upon elution with pentane/CH_2Cl_2 (2:1), 54 mg (20%) of **2f'**.

Preparation of pseudocubane clusters

By chalcogen abstraction. One millimole of a pentachalcogenide $Cp(')_2V_2E_5$ [or a tetrachalcogenide $Cp(')_2V_2E_4$] was dissolved in 20 ml of CH_2Cl_2 and treated with three [or two] equivalents of P^nBu_3. The solution turned dark. The consumption of the binuclear starting material (**1** or **2**) can be monitored by TLC, in which the binuclear complexes migrate if pentane/CH_2Cl_2 mixtures are used for elution, with the tetranuclear clusters remaining at the starting point. As soon as the binuclear starting compounds had disappeared (1–4 h), the solvent CH_2Cl_2 was removed, the residue taken up in 5 ml hexane, and the cluster precipitated by storing the solutions at dry-ice temperature. The supernatant liquid was discarded and the clusters crystallized from hexane/CH_2Cl_2.

Starting material	Reaction time	Colour	Product and yield
$Cp_2V_2Se_5$ (**1b**)	2 h	Brown	$Cp_4V_4Se_4$ (**7b**), 72%
$Cp'_2V_2Se_4$ (**2b'**)	4 h	Olive-brown	$Cp'_4V_4Se_4$ (**7b'**), 46%
$Cp'_2V_2Se_2S_2$ (**2d'**)	1 h	Black	$Cp'_4V_4S_4$ (**7a'**), quant.
$Cp'_2V_2Te_2S_2$ (**2f'**)	2 h	Black	$Cp'_4V_4S_4$ (**7a'**), quant.

Alternatively, **2d'** was treated with two equivalents of $NiCp_2$ in toluene for 16 h; $Cp'_4V_4S_4$ (**7a'**) was isolated in 70% yield.

By thermal decarbonylation. A solution of the tetracarbonyl-dichalcogenide $Cp'_2V_2(CO)_4E_2$ (**6'**) [or $Cp^*_2V_2(CO)_4E_2$ (**6***)] in toluene (20 ml) was stirred at 50–70°C until the CO evolution ceased. The progress of the reaction was monitored by IR spectroscopy. As soon as the ν(CO) absorptions of the tetracarbonyl precursor had disappeared, the solvent was removed, hexane (5 ml) added, and the cluster precipitated by cooling at −78°C. The solid was extracted with CH_2Cl_2, and recrystallized from hexane/CH_2Cl_2 mixtures.

Starting material	Reaction time	Colour	Product and yield
$Cp'_2V_2(CO)_4Te_2$ (**6c'**)	45 min (50°C)	Black	$Cp'_4V_4Te_4$ (**7c'**), quant.
$Cp^*_2V_2(CO)_4S_2$ (**6a***)	90 min (70°C)	Black	$Cp^*_4V_4S_4$ (**7a***), 70%
$Cp^*_2V_2(CO)_4Te_2$ (**6c***)	60 min (60°C)	Black	$Cp^*_4V_4Te_4$ (**7c***), 86%

Spectroscopic measurements

The NMR spectra were recorded with $CDCl_3$ solutions. ^{51}V NMR: Jeol FX 90Q (with neat $VOCl_3$ ($\delta(^{51}V)$ 0.0 ppm) as a reference) at 15°C. ^1H and ^{13}C NMR: Bruker AC 300 at room temperature. EI-MS: Finnigan MAT 8500 (ionization energy 70 eV, direct inlet). FD-MS: MAT 311 A. IR-spectra: Perkin–Elmer 983G, KBr disks.

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