Binuclear CpV, Cp*V, and Cp*Ta Complexes containing Organochalcogenolato Bridges, μ -ER (E = Sulfur, Selenium, Tellurium; R = Methyl, Phenyl, and Ferrocenyl)

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Dedicated to Professor Heinrich Vahrenkamp on the Occasion of his 60th Birthday

Abstract.¹⁾ Photolysis of the halfsandwich tetracarbonylmetal complexes $CpV(CO)_4$, $Cp*V(CO)_4$ and $Cp*Ta(CO)_4$ in solution in the presence of di(organyl)dichalcogenides E_2R_2 (E = S, Se, Te; R = Me, Ph, Fc) leads to diamagnetic doubly organochalcogenolato-bridged compounds, $[Cp^{()}M(CO)_2(\mu-ER)]_2$. According to the X-ray structure determinations carried out for $[CpV(CO)_2(\mu-TeMe)]_2$, $[Cp*V(CO)_2(\mu-TePh)]_2$ and $[Cp*Ta(CO)_2(\mu-SPh)]_2$, the molecular framework consists of a folded $M_2(\mu-ER)_2$ ring with the cyclopentadienyl ligands in *cis*-configuration and the organyl substituents R in a *syn*-equatorial arrangement, thus forming a bowl-shaped molecule with the four terminal CO ligands protruding into the inner sphere. The $M \cdots M$ distances (in the range between 305 and 330 pm) are not considered to indicate direct bonding interactions. The vanadium complexes $[Cp^{()}V(CO)_2(\mu-ER)]_2$ are completely decarbonylated in the presence of an excess of E_2R_2 in boiling toluene, and in many cases the paramagnetic quadruply-bridged products, $[CpV(\mu-ER)_2]_2$, can be isolated.

Keywords: Vanadium; Tantalum; Halfsandwich complexes; *Organo*chalcogenolato bridges; Crystal structure

Zweikernige CpV-, Cp*V- und Cp*Ta-Komplexe mit Organochalkogenolato-Brücken, μ -ER (E = Schwefel, Selen, Tellur; R = Methyl, Phenyl und Ferrocenyl)

Inhaltsübersicht.¹⁾ Die Photolyse der Halbsandwich-tetracarbonylmetall-Komplexe CpV(CO)₄, Cp*V(CO)₄ und Cp*Ta(CO)₄ in Lösung in Gegenwart von Di(organyl)dichalkogeniden E₂R₂ (E = S, Se, Te; R = Me, Ph, Fc) führt zu den diamagnetischen, zweifach organochalkogenolatverbrückten Verbindungen, [Cp⁰M(CO)₂(μ -ER)]₂. Nach den Röntgenstrukturanalysen, die für [CpV(CO)₂(μ -TeMe)]₂, [Cp*V(CO)₂(μ -TePh)]₂ und [Cp*Ta(CO)₂(μ -SPh)]₂ durchgeführt wurden, besteht das Molekülgerüst aus einem nichtebenen Vierring mit den Cyclopentadienyl-Liganden in

Introduction

Binuclear halfsandwich-type complexes with organochalcogenolato bridges can have various structural arrangements of the folded inner $M(\mu-ER)_2M$ core [1, 2, 3]. In principle, compounds of the group 6 metals with non-planar $M(\mu-ER)_2M$ center, such as *cis*-Konfiguration und den Organyl-Substituenten R in *syn*equatorialer Anordnung. So entsteht ein wannenförmiges Molekül, in dessen inneren Bereich die vier endständigen CO-Liganden hineinragen. Die Metall····Metall-Abstände (im Bereich von 305–330 pm) werden nicht als Hinweis auf direkte bindende Wechselwirkungen angesehen. Die Vanadiumkomplexe [Cp⁽⁾V(CO)₂(μ -ER)]₂ werden in Gegenwart von überschüssigem E₂R₂ in siedendem Toluol vollständig decarbonyliert, und in vielen Fällen lassen sich paramagnetische, vierfach verbrückte Produkte [CpV(μ -ER)₂]₂ isolieren.

 $[CpM(CO)_2(\mu-ER)]_2$ (M = Cr, Mo; E = S, Se, Te; R = Ph), may occur in 6 different geometrical forms [3] (A–F in Scheme 1) with Cp either in *trans* or *cis*, and the phenyl substituents either in *syn* or *anti* arrangements; in the case of *syn*, the two phenyl groups may be attached either in equatorial ("endo") or axial ("exo") positions. Each metal also carries two terminal carbonyl ligands. In the solid state, only the *trans*-Cp/*anti*-Ph arrangement (**D**) has been observed, e.g.

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¹⁾ Abbreviations: $Cp = \eta^5$ -cyclopentadienyl, η^5 -C₅H₅; $Cp^* = \eta^5$ -pentamethylcyclopentadienyl, η^5 -C₅Me₅; $Cp^{()} = Cp$ or Cp*. Fc = η^1 -ferrocenyl, CpFe(C₅H₄-)



Scheme 1 Possible geometrical isomers of $[CpM(CO)_2(\mu-ER)]_2$ complexes (M = transition metal; E = S, Se, Te; the carbonylligands are omitted for clarity)

in $[CpCr(CO)_2(\mu$ -EPh)]_2 (E = S [4], Te [5]) and in $[CpMo(CO)_2(\mu$ -EPh)]_2 (E = S [6, 7]), Se [8], Te [9]). However, several isomers appear to be present in solution [3] (s. Scheme 1).

On the other hand, the crystal structure determinations of the analogous complexes known so far with group 5 metals consistently indicate the *cis*-Cp/*syn*-R (eq.) arrangement (**B**), e.g. in $[Cp*V(CO)_2(\mu-SR)]_2$ (R = Me, Ph) [10] and in $[CpNb(CO)_2(\mu-SR)]_2$ (R = Me) [11].

In other binuclear bis(organochalcogenolato)bridged compounds, various other geometrical forms were confirmed by X-ray crystallography. Thus, the carbonyl-free rhodium complex $[CpRh(\mu-SPh)]_2$ is present in the crystal lattice in the *cis*-Cp/anti-Ph form (A) [12, 13], whereas $[CpRh(SePh)(\mu-SePh)]_2$ adopts the trans-Cp/anti-Ph (D) arrangement [14]. The complexes $[CpFe(CO)(\mu-SPh)]_2$ [15] iron and $[CpFe(CO)(\mu-SMe)]_{2}^{+}$ [16] are both present in the *cis*-Cp/syn-R (eq.) geometry (B). (In contrast, the formally analogous monocarbonyl molybdenum complex $[CpMo(CO)(\mu$ -SPh)]₂ has a planar M₂S₂ core; both trans-Cp/anti-Ph and trans-Cp/syn-Ph geometries have been observed [17]).

We had earlier investigated binuclear vanadium complexes, $[CpV(CO)_2(\mu-ER)]_2$ and $[Cp*V(CO)_2(\mu-ER)]_2$ (E = S, Se; R = Me, Ph) [10]. We now report on an extension of this work, including ferrocenyl-substituted chalcogenolato-bridges (EFc), tellurolato ligands (TeR; R = Me, Ph, Fc) and pentamethylcyclopentadienyl tantalum complexes.

Results and Discussion

Syntheses

The binuclear, organochalcogenolato-bridged vanadium complexes $[Cp^{()}V(CO)_2(\mu-ER)]_2$ were obtained by photolysis of the mononuclear tetracarbonylvanadium educts $CpV(CO)_4$ (1) and $Cp^*V(CO)_4$ (2) in tetrahydrofuran solution at 0 °C in the presence of the stoichiometric amount of di(organyl)dichalcogenide, REER. The corresponding Cp*Ta compounds were prepared similarly from Cp*Ta(CO)₄ (3) under irradiation in hexane solution. A survey of the products is given in Scheme 2 together with the numbering system. The complexes $[CpV(CO)_2(\mu-ER)]_2$ (4a–12a) (containing the unsubstituted cyclopentadienyl ring) and the Cp*V analogues (4b–12b) (containing the pentamethylcyclopentadienyl ring) are compared with the Cp*Ta complexes (4c–14c) (s. Scheme 2).

In boiling toluene (110 °C), the vanadium(II) complexes $[Cp^{()}V(CO)_2(\mu-ER)]_2$ lose all remaining CO ligands to give, in the presence of excess REER, paramagnetic vanadium(III) derivatives, $[Cp^{()}V(\mu-ER)_2]_2$. However, the tantalum(II) compounds could not be decarbonylated under comparable conditions, including boiling xylene (isomer mixture, b. p. ca. 140 °C).

paramagnetic vanadium(III) complexes The $[CpV(\mu-SR)_2]_2$ (4d, 7d, 10d) are the stable end products of the thermal reaction of $CpV(CO)_4$ (1) with organosulfur compounds. Following the initial report by Stone and coworkers [18] in 1963, some examples such as $[CpV(\mu-SMe)_2]_2$ (4d) [18, 19, 10] and $[CpV(\mu-SMe)_2]_2$ (4d) [18, 19, 10] and [CpV($\mu-SMe)_2$]_2 (4d) SPh_{2}_{2} (7d) [20, 21, 22, 10] had been described, and analogous ethane or ethene dithiolate complexes such as $[CpV(\mu_2-SCH_2CH(R)S)]_2$ (R = H, CH₃) [23] and $[CpV(\mu_2-SC(CF_3)=C(CF_3)S)]_2$ [24] have been studied with respect to the nature of their metal-metal interaction [20, 21, 23]. One organoselenido-bridged complex, $[CpV(\mu-SePh)_2]_2$ (8d), had also been characterized [20, 21]. The diamagnetic vanadium(II) dicarbonyl complexes, e. g. $[CpV(CO)_2(\mu$ -SPh)]_2 (7 a) [19, 10], are apparently intermediates on the route from 1 to the fully decarbonylated end product, e.g. $[CpV(\mu-SPh)_2]_2$ (7d), and can be isolated if the CO displacement is conducted photochemically [19, 10].



Scheme 2 Synthesis of the complexes and numbering system

Table 1 Characteristic spectroscopic data of the binuclear complexes $[CpV(CO)_2(\mu-ER)]_2$ (4a-12a), $[Cp^*V(CO)_2(\mu-ER)]_2$ (4b-12b) and $[Cp*Ta(CO)_2(\mu-ER)]_2$ (4c-14c)

Complex	ER	Yield	Infrared $v(CO)$, cm ^{-1 a)}		NMR (C_6D_6)			
						$\delta(^{1}\text{H})$ (Cp ⁽⁾)	$\delta(^{13}C) (Cp^{()})$	$\delta(^{51}V) (I_{1/2}[Hz])$
4 a	SMe ^{b)}	64%	1997 m,	1990 vs,	1933 s	4.60	93.7	-772 (610)
	• •					4.64	94.0	
5 a	SeMe ^{b)}	30%	1992 s,	1988 s,	1935 s	4.60	92.4	-803 (650)
	m b (b)	6604	10	0.6	1024	4.62	92.5	0(0(500)
6 a	TeMe ^o	66%	19	86 vs,	1934 s	4.567	89.7	-968 (500)
79	SPh	50%	1995 vs	1955 s	1916 m	4.370	95 3	-670 (750)
, u	5111	5070	1775 (6,	1955 8,	1910111	4.79	<i>90.0</i>	010 (150)
8 a	SePh	20%	1993 vs.	1948 s.	1917 sh	4.76	93.3	-695 (960)
			,	,		4.80	93.6	
9 a	TePh	55%	1987 vs,	1933 s,	1896 sh	4.71	90.1	-908 (1500)
						4.77	90.3	
10 a	SFc	26%	1991 vs,	1949 s		4.95	94.8	-642 (1000)
11 a	SeFc	12%	1989 s,	1942 m		4.91	93.0	-693 (1000)
						4.96	93.1	
12 a	TeFc	71%	1985 s,	1930 s		4.86	90.1	-906 (1550)
						4.89		
4 b	SMe ^{c)}	47%	1971 vs,	1910 s		1.65	11.2/103.7	-751 (870)
5 b	SeMe ^{c)}	35%	1969 vs,	1912 s		1.69	11.9/103.1	-757 (800)
6 b	TeMe ^{c)}	77%	1965 vs,	1913 s		1.80	13.3/102.0	-860 (1150)
7 b	SPh	51%	1971 vs,	1933 m,	1886 m	1.54	11.1/104.9	-686 (1270)
8 b	SePh	23%	1972 vs,	1933 s,	1887 m	1.62	11.8/104.1	-703 (1340)
9 b	TePh	76%	1969 vs,	1930 s,	1891 m	1.76	13.2/102.9	-804 (1600)
10 b	SFc	22%	1978 s,	1935 m		1.88	12.5/105.1	-495 (1400)
11 b	SeFc	21%	1976 s,	1934 m		1.90	12.7/104.0	-573 (1600)
12 b	TeFc	42%	1973 s,	1930 m		1.97	13.6/102.6	–750 (2000)
4 c	SMe ^{d)}	_		1934 s.	1880 s	2.00	11.6/102.8	
5c	SeMe d), e)	38%	1969 s.	· ·	1901 vs	1.91	11.9/101.3	
6 c	TeMe d), f)	29%	,	1934 vs.	1874 vs	1.80	12.6/102.3	
7 c	SPh	45%	1962 vs,	1915 s,	1862 m	1.74	11.1/102.3	
8 c	SePh ^{e)}	28%	1964 vs,	1917 s,	1863 m	1.83	11.8/101.5	
9 c	TePh ^{f)}	33%	1958 s.	· ·	1899 vs	1.73	12.7/103.1	
10 c	SFc	21%	1965 s,	1915 s,	1871 m	2.03	12.2/102.1	
11 c	SeFc ^{e)}	18%	1965 s,	1906 vs,	1870 w	2.07	12.5/101.2	
12 c	TeFc ^{f)}	16%	1968 s,	1917 w,	1897 m	2.09	13.5/100.3	
13 c	S <i>n</i> Bu	38%	1956 vs,	,	1880 s	1.91	11.6/101.8	
14 c	StBu	35%	1960 s,		1888 s	1.84	12.6/102.2	

a) IR solution spectra in hexane (4a-6a and 4b-12b); if the solubility in particular cases was insufficent, the series were measured either in toluene ⁵⁷ IR solution spectra in hexane (**4a-6a** and **4b-12b**); if the solubility in particular cases was insufficient, the series (**7a-12a**) or tetrahydrofuran (**4c-14c**). ^{b)} Methyl group NMR data (C_6D_6): $\delta(^{1}H)$: 1.99/2.03 (**4a**), 1.91/1.98 (**5a**); $\delta(^{13}C)$: 23.5/23.7 (**4a**), 6.5 (**5a**), -9.3/-12.3 (**6a**). ^{c)} Methyl group NMR data (C_6D_6): $\delta(^{1}H)$: 2.06 (**4b**), 2.01 (**5b**), 2.01 (**6b**); $\delta(^{13}C)$: 22.4 (**4b**), 4.7 (**5b**), -30.6 (**6b**). ^{d)} Methyl group NMR data (C_6D_6): $\delta(^{1}H)$: 1.65 (**4c**), 1.77 (**5c**), 1.84 (**6c**); $\delta(^{13}C)$: 10.8 (**4c**), 12.0 (**5c**). ^{e)} Selenium NMR data (C_6D_6): $\delta(^{77}Se)$: -220 (**5c**), +60 (**8c**), -55 (**11c**). ^{f)} Tellurium NMR data (C_6D_6): $\delta(^{125}Te)$: -593 (**6c**), -946 (**9c**), -213 (**12c**).

Spectroscopy

Some diagnostic IR and NMR spectra of the carbonyl-containing complexes are collected in Table 1. According to the v(CO) absorptions in the IR spectra, all CO ligands are terminal.

In the ¹H and ¹³C NMR spectra of the complexes $[CpV(CO)_2(\mu-ER)]_2$ (**4a–12a**), generally two signals are observed for the (unsubstituted) cyclopentadienyl ring ligand, indicating the presence of isomers (cf. [10, 19]). In a similar manner, two methyl signals are present in the methylchalcogenolato-bridged compounds **4a–6a**. However, the ⁵¹V NMR signals are apparently too broad to allow the identification of isomeric forms.

The NMR spectra of the Cp*-containing complexes $[Cp*V(CO)_2(\mu-ER)]_2$ (M = V, Ta) did not give any indications of the existence of isomers in solution; only one single signal was found for the Cp* ligands in the ¹Hand two signals in the ¹³C NMR spectra, and only one broad absorption appeared in the ⁵¹V NMR spectra.

The ⁵¹V NMR signals of the binuclear complexes 4a-12a and 4b-12b are observed between -500 and -1000 ppm (Table 1). Some trends are apparent: The ⁵¹V NMR signal is shifted to higher fields as the chal-



Fig. 1 Molecular geometry of $[CpV(CO)_2(\mu\text{-TeMe})]_2$ (**6a**) (the hydrogen atoms are omitted; Cp(1) and Cp(2) are the centers of the Cp rings attached to V(1) and V(2), respectively)

Selected distances/pm and angles/°:

$V(1) \cdots V(2)$	328.9(1)	V(1)-Te(1)	274.1(1)	V(1)-C(11)	194.2(5)
Te(1) \dots Te(2)	330.2	V(1)-Te(2)	272.0(1)	V(1)-C(12)	194.8(5)
$V(1) \cdots Cp(1)$	193.8	V(2)-Te(1)	272.3(1)	V(2)-C(13)	193.6(4)
$V(2) \cdots Cp(2)$	193.4	V(2)-Te(2)	272.4(1)	V(2)-C(14)	192.8(5)
V(1)-Te(1)-V(Te(1)-V(1)-Te C(11)-V(1)-C(V(1)-C(11)-O(V(2)-C(13)-O(Cp(1)-V(1)-Te Cp(1)-V(1)-Te Cp(2)-V(2)-Te Cp(2)-V(2)-Te	$\begin{array}{c} 2) \\ (2) \\ (12) \\ (1) \\ (3) \\ (1) \\$	74.0(1) 74.4(1) 84.2(2) 173.6(5) 173.3(4) 114.3 107.2 117.1	V(1)-Te(2) Te(1)-V(2) C(13)-V(2) V(1)-C(12) V(2)-C(14) Cp(1)-V(1) Cp(1)-V(1) Cp(2)-V(2) Cp(2)-V(2))-V(2))-Te(2))-C(14))-O(2))-O(4))-Te(2))-C(12))-Te(2)	74.3(1) 74.6(1) 82.7(2) 172.3(5) 173.5(5) 116.5 108.7 114.4

cogen is varied in the order S < Se < Te; a particularly large difference is always observed between the selenolato and the tellurolato compounds. Furthermore, the ⁵¹V NMR signal is moving to lower field, if the organyl group in ER changes from R = methyl via phenyl to ferrocenyl, and also if Cp is replaced by Cp*. According to the v(CO) frequencies which are decreasing in the same direction, the electron-donating character of the bridging ligands increases in the order EMe < EPh < EFc, and the Cp* ring ligand increases the charge density at the metal as compared to the unsubstituted Cp ligand.

X-Ray Crystallographic Structure Determinations

The molecular structures of $[CpV(CO)_2(\mu\text{-TeMe})]_2$ (6a), $[Cp^*V(CO)_2(\mu\text{-TePh})]_2$ (9b), and $[Cp^*Ta(CO)_2-(\mu\text{-SPh})]_2$ (7c) are presented in Figs. 1–3, together with selected distances and angles.

The basic structure of these 3 dinuclear complexes corresponds consistently to the *cis*-Cp/*syn*-R (eq.) arrangement (**B** in Scheme 1) and is therefore analogous to that of the Cp*V and CpNb compounds of this type which had been investigated earlier [10, 11]. A com-



Fig. 2 Molecular geometry of $[Cp*V(CO)_2(\mu-TePh)]_2$ (**9b**) (the hydrogen atoms are omitted; Cp*(1) and Cp*(2) are the centers of the Cp* rings attached to V(1) and V(2), respectively)

Selected distances/pm and angles/°:

$\begin{array}{lll} V(1) \cdots V(2) & 329 \\ Te(1) \cdots Te(2) & 319 \\ V(1) \cdots Cp^*(1) & 199 \\ V(2) \cdots Cp^*(2) & 199 \end{array}$	9.5(1)V(1)-Te(1)9.3V(1)-Te(2)5.9V(2)-Te(1)6.4V(2)-Te(2)	272.4(1)V(1)276.5(1)V(1)271.9(1)V(2)274.1(1)V(2)	$\begin{array}{ll} -C(11) & 193.9(6) \\ -C(12) & 194.5(7) \\ -C(25) & 193.5(6) \\ -C(26) & 192.8(7) \end{array}$
$\begin{array}{l} V(1)-Te(1)-V(2)\\ Te(1)-V(1)-Te(2)\\ C(11)-V(1)-C(12)\\ V(1)-C(11)-O(1)\\ V(2)-C(25)-O(3)\\ Cp^*(1)-V(1)-Te(1)\\ Cp^*(1)-V(1)-C(11)\\ Cp^*(2)-V(2)-Te(1)\\ Cp^*(2)-V(2)-Te(1)\\ Cp^*(2)-V(2)-C(25)\\ Cp^*(2)-V(2)-V(2)\\ Cp^*(2)-V(2)\\ Cp^*(2)-V(2)\\ Cp^*(2)-V(2)-V(2)\\ Cp^*(2)-V(2)\\ Cp^*(2)-V(2)-V(2)\\ Cp^*(2)-V(2)\\ C$	$\begin{array}{c} 74.5(1) \\ 71.2(1) \\ 81.0(3) \\ 170.2(6) \\ 171.1(6) \\ 112.9 \\ 106.7 \\ 116.3 \\ 5) 106.6 \end{array}$	$\begin{array}{c} V(1)-Te(2)-V(2)\\ Te(1)-V(2)-Te(2)-V(2)-C(2)\\ V(1)-C(12)-O(2)-V(2)-C(2)-O(2)\\ V(2)-C(26)-O(2)-O(2)-O(2)\\ Cp^*(1)-V(1)-Te(2)-V(2)-C(2)\\ Cp^*(2)-V(2)-Te(2)-V(2)-C(2)\\ Cp^*(2)-V(2)-C(2)-C(2)-C(2)\\ Cp^*(2)-V(2)-C(2)-C(2)-C(2)\\ Cp^*(2)-V(2)-C(2)-C(2)-C(2)\\ Cp^*(2)-V(2)-C(2)-C(2)\\ Cp^*(2)-V(2)-C(2)-C(2)\\ Cp^*(2)-V(2)-C(2)\\ Cp^*(2)-V(2)\\ Cp^*(2)-V($	$\begin{array}{cccc} 2) & 73.5(1) \\ 2) & 71.6(1) \\ 26) & 79.3(3) \\ 2) & 173.0(7) \\ 4) & 170.6(6) \\ e(2) & 120.6 \\ (12) & 108.5 \\ e(2) & 116.9 \\ e(2) & 116.9 \\ e(2) & 109.3 \end{array}$

parison of important structural data for all 6 complexes is given in Table 2. The methyl or phenyl substituents (R) occupy an equatorial ("endo") position with respect to the folded M_2E_2 ring.

Although the complexes are diamagnetic, as indicated by the NMR spectra, the presence of direct metal…metal interactions is a matter of debate [10].



Fig. 3 Molecular geometry of $[Cp*Ta(CO)_2(\mu-SPh)]_2$ (**7 c**) (the hydrogen atoms are omitted; Cp*(1) and Cp*(2) are the centers of the Cp* rings attached to Ta(1) and Ta(2), respectively)

Selected distances/pm and angles/°:

$\begin{array}{l} Ta(1) \cdots Ta(2) \\ S(1) \cdots S(2) \\ Ta(1) \cdots Cp^{*}(1) \\ Ta(2) \cdots Cp^{*}(2) \end{array}$	312.0(1) 281.4 207.6 208.0	$\begin{array}{l} Ta(1)-S(1) \\ Ta(1)-S(2) \\ Ta(2)-S(1) \\ Ta(2)-S(2) \end{array}$	253.4(2) 255.2(2) 252.0(2) 256.1(2)	$\begin{array}{l} Ta(1)-C(11)\\ Ta(1)-C(12)\\ Ta(2)-C(25)\\ Ta(2)-C(26) \end{array}$	205.1(7) 204.0(7) 201.7(9) 203.8(8)
$\begin{array}{l} Ta(1) - S(1) - Ta(2)\\ S(1) - Ta(1) - S(2)\\ C(11) - Ta(1) - C(1)\\ Ta(1) - C(11) - O(1)\\ Ta(2) - C(25) - O(3)\\ Cp^*(1) - Ta(1) - S(1)\\ Cp^*(1) - Ta(1) - S(1)\\ Cp^*(1) - Ta(1) - C(1)\\ Cp^*(2) - Ta(2) - S(1)\\ Cp^*(2) - Ta(2) - C(1)\\ Cp^*(2) - Ta(2) - $	76. 67. 2) 77.) 173.) 171. 1) 113. 1) 105. 1) 111. 25) 106.	3(1) 2(1) 6(3) 5(6) 5(6) 9 0 8 4	$\begin{array}{l} Ta(1) - S(2\\ S(1) - Ta(2\\ C(25) - Ta(1) - C(1\\ Ta(2) - C(2\\ Cp^*(1) - Ta\\ Cp^*(1) - Ta\\ Cp^*(2) - Ta\\ Cp^*(2) - Ta\\ Cp^*(2) - Ta\end{array}$)-Ta(2))-S(2) 2)-C(26) 2)-O(2) 6)-O(4) a(1)-S(2) a(1)-C(12) a(2)-S(2) a(2)-C(26)	75.2(1) 67.3(1) 79.1(3) 172.8(6) 174.9(6) 114.7 107.6 117.6 108.1

The $M \cdots M$ separations are found in the range between 305 and 330 pm and apparently depend mainly on the size of the chalcogen, - the long distances $(329 \pm 1 \text{ pm})$ being observed in the organotellurolatobridged molecules 6a and 9b. It is reasonable to assume that interaction and communication between the two metals is essentially transferred through the two ER bridges. The transannular distances between the two chalcogens $(280 \pm 2 \text{ pm in the sulfur, } 319.3 \text{ and}$ 330.2 pm in the tellurium compounds) can be considered as non-bonding. The angles at the metal $(E-M-E, 67-75^\circ)$ are generally more acute than those at the chalcogen (M-E-M, 73-79°), although they are comparable (74-75°) in the methyltellurolato complex, $[CpV(CO)_2(\mu\text{-TeMe})]_2$ (6a). The four carbonyl ligands are all protruding into the inner sphere of the bowl-shaped molecular framework which is formed by the $Cp_{2}^{()}M_{2}(\mu-ER)_{2}$ skeleton.

In contrast to the carbonyl-containing vanadium(II) complexes, $[Cp^{()}V(CO)_2(\mu-ER)]_2$, the fully decarbonylated vanadium(III) compounds $[Cp^{()}V(\mu-ER)_2]_2$ very probably contain direct metal-metal interactions. Although the (temperature-dependent) magnetic data, reported in the literature for the quadruply bridged dimers $[CpV(\mu-SMe)_2]_2$ (4d) [18], $[CpV(\mu-SPh)_2]_2$ (7d) [21, 22], $[CpV(\mu_2-SCH_2CH(R)S)]_2$ (R = H, Me) [23] and $[CpV(\mu_2-SC(CF_3)=C(CF_3)S)]_2$ [24], are somewhat confusing [cf. 23], they are definitely below the spin-only value of 2.83 $\mu_{\rm B}$ per vanadium which would indicate two uncoupled vanadium(III) centers. Therefore either a direct V-V bond and/or partial antiferromagnetic coupling through the organochalcogenolato bridges has to be assumed [23]. An X-ray structure analysis of $[CpV(\mu_2-SCH_2CH_2S)]_2$ [23] revealed a short V–V' contact of 254.2(1) pm and an acute V–S–V angle of $63.4(1)^\circ$, which are both consistent with a metal-metal bond. An attempt to obtain molecular parameters for $[CpV(\mu-SeMe)_2]_2$ (4b) was severely hampered by insufficient quality of the crystal and disorder of the selenium atoms; however, a short V-V contact of 263.6(4) pm and an acute V-Se-V angle of $61.4(1)^{\circ}$ could be firmly established [25].

Table 2 Characteristic structural data of the binuclear complexes $[Cp^{()}M(CO)_2(\mu-ER)]_2$ (M = V, Nb, Ta)

Complex	Distance, pm M⋯M	$\begin{array}{c} \text{Distance, pm} \\ E \cdots E \end{array}$	Angle, ° E–M–E	Angle, ° M–E–M	Angle, ° E–E–C	Dihedral An at E…E	gles, ° at M…M	Angle, ° Cp ⁰ M/MCp ⁰
6a [CpV(CO) ₂ (μ-TeMe)] ₂	328.9(1)	330.2	74.4(1) 74.6(1)	74.0(1) 74.3(1)	153.4 153.4	81.5	81.3	142.2°
4b [Cp*V(CO) ₂ (μ-SMe)] ₂ [10]	308.3(1)	281	71.2(1)	78.9(1)	161.7 161.7	77.2	97.8	140.6°
7b [Cp*V(CO) ₂ (μ-SPh)] ₂ [10]	307.0(1)	278	69.1(1) 69.1(1)	77.7(1) 77.7(1)	169.5 170.2	80.7	93.6	144.0°
9b [Cp*V(CO) ₂ (μ-TePh)] ₂	329.5(1)	319.3	71.2(1) 71.6(1)	74.5(1) 73.5(1)	162.2 162.8	84.3	86.1	150.8°
[CpNb(CO) ₂ (µ-SMe)] ₂ [11]	316.4(9)		70.9(5)	76.1(5) 76.5(3)			94.6	
7c [Cp*Ta(CO) ₂ (μ-SPh)] ₂	312.0(1)	281.4	67.2(1) 67.3(1)	76.3(1) 75.2(1)	172.4 170.4	85.0	91.0	169.7°

Apparently, the molecular geometry of the paramagnetic vanadium complex $[CpV(\mu-SeMe)_2]_2$ (**4b**) corresponds closely to that of the diamagnetic molybdenum analogue, $[CpMo(\mu-SMe)_2]_2$ (Mo–Mo 260.3(2) pm, angle Mo–S–Mo 64.0(2)°) and its paramagnetic cation in $[CpMo(\mu-SMe)_2]_2^+(PF_6^-)$ (Mo–Mo 261.7(4) pm, angle Mo–S–Mo 65.0(2)°), for both of which strong metal-metal interaction has been assumed [26].

Experimental

All synthetic work was carried out under an atmosphere of dry argon, using oven-dried glassware and Ar-saturated dry solvents. A high-pressure mercury arc (Heraeus, Original Hanau, TQ 718 (700 W)) was applied for the photo-induced reactions; the solutions were irradiated under stirring in water-cooled (10–16 °C) Schlenk tubes.

The NMR spectra were measured by using Jeol FX 90 Q, Bruker ARX 250 or AC 300 spectrometers. Chemical shifts are given with respect to Me₄Si [δ^{1} H (CHCl₃/CDCl₃) = 7.24, (C₆D₅H) = 7.15; δ^{13} C (CDCl₃) = 77.0, (C₆D₆) = 128.0]; Me₂Se [δ^{77} Se = 0 for Ξ (⁷⁷Se) = 19.071523 MHz]; Me₂Te [δ^{125} Te = 0 for Ξ (¹²⁵Te) = 31.549802 MHz]; VOCl₃ [δ^{51} V = 0]. For the IR-spectra, Perkin Elmer spectrometers 983G and FT-IR 2000 were available; the solution IR spectra were measured in the carbonyl region (2200–1600 cm⁻¹) in CaF₂ cuvettes (0.1 cm). Electron impact (EI) mass spectra (70 eV) were recorded using a Finnigan MAT 8500 spectrometer, and field desorption (FD) mass spectra using a Varian MAT 311 A spectrometer. Single crystal X-ray data were collected on a Siemens P4 diffractometer (MoK α , λ = 71.073 pm, graphite monochromator). Crystal and refinement data for **6a**, **9b**, and **7c** are listed in Table 3. All nonhydrogen atoms were refined with anisotropic temperature factors. The H-atoms were refined on calculated positions applying the riding model with fixed temperature factors (0.08 Å^2) .

Syntheses

The starting halfsandwich complexes (CpV(CO)₄ (1) [27], Cp*V(CO)₄ (2) [28], Cp*Ta(CO)₄ (3) [29]) and the di(ferrocenyl)dichalcogenides E_2Fc_2 (E = S, Se, Te) [30] were obtained according to literature procedures. The silica used for column chromatography (Merck Kieselgel 60, 0.06–0.2 mm) was heated under vacuum to 400 °C and saturated with argon.

Bis[(μ -organylchalcogenolato)-cyclopentadienyl-dicarbonyl-vanadium] (**4a–12a**): A THF solution (50 ml) containing 230 mg (1 mmol) CpV(CO)₄ (**1**) and either 1 mmol R₂E₂ (in the cases of **4a**, **5a**, **7a**, **8a**) or 0.5 mmol R₂E₂ (in the cases of **6a**, **9a–12a**) was irradiated for 20–150 min at 0 °C. The progress of the reaction was followed by IR spectroscopy in the ν (CO) region (2200–1600 cm⁻¹). The solutions were brought to dryness and the products purified by column chromatography over silica (elution of **1** together with R₂E₂ using hexane, elution of [CpV(CO)₂(μ -ER)]₂ (**4a–12a**) using hexane containing additional portions of CH₂Cl₂. The dimeric products were characterized by their ν (CO) frequencies, their ¹H/¹³C NMR data of the Cp ring ligands, and by the broad ⁵¹V NMR absorption (see Table 1).

Bis[(μ -organylchalcogenolato)-pentamethylcyclopentadienyl-dicarbonyl-vanadium] (**4b–12b**): In analogy to the pro-

Compound	$[CpV(CO)_2(\mu-TeMe)]_2$ (6 a)	$[Cp*V(CO)_2(\mu-TePh)]_2$ (9 b)	$[Cp*Ta(CO)_2(\mu-SPh)]_2 (7 c)$	
Formula	$C_{16}H_{16}O_4Te_2V_2$	$C_{36}H_{40}O_4Te_2V_2$	$C_{36}H_{40}O_4S_2Ta_2$	
М	629.4	893.8	962.7	
Space group	$P2_1/n$	$P2_1/n$	Pbca	
Crystal system	monoclinic	monoclinic	orthorhombic	
a/pm	851.8(2)	958.1(2)	1578.8(2)	
b/pm	1689.2(3)	2054.8(4)	2059.0(2)	
c/pm	1376.3(3)	1840.6(4)	2121.1(2)	
βĺ°	107.70(3)	99.97(3)	_	
$V (10^6 \text{ pm}^3)$	1886.6(7)	3568.9(13)	6895.0(13)	
Z	4	4	8	
$D_{calc} (g \cdot cm^{-3})$	2.216	1.663	1.855	
F(000)	1176	1752	3728	
Crystal size (mm)	$0.22 \times 0.25 \times 0.20$	$0.45 \times 0.20 \times 0.18$	$0.35 \times 0.18 \times 0.15$	
Crystal colour	dark red	dark red	red	
Crystal shape	isometric	prism	irregular	
Temperature/K	173	296	296	
Absorption correction		empirical (ψ -scans)		
$\mu(Mo\dot{K}\alpha)/mm^{-1}$	4.038	2.162	6.501	
Min./max. transmission factors	0.1235/0.1674	0.3097/0.3660	0.3078/0.6166	
2θ Range/°	2.0-50.0	3.0-50.0	3.0-60.0	
Collected reflections	4491	8124	12625	
Independent reflections	3321	6254	9947	
Observed reflections	3321	5147 (F > 2σ (F))	7442 (F > 2σ (F))	
Solution/Refinement		SHELXTL-PLUS V. 4.2		
$R/wR (w^{-1} = \sigma^2(F))$	0.032/0.023	0.043/0.035	0.051/0.029	
Max./min. residual electron density ($e \cdot 10^{-6} \text{ pm}^{-3}$)	1.13/-0.67	0.62/-0.47	1.02/-1.77	

Table 3Crystal and Refinement Data^{a)}

^{a)} Full details of the crystal structure determinations (except structure factors) have been deposited under the numbers CCDC 135372 (**6**a), -135373 (**9**b), and -135374 (**7**c) at the Cambridge Crystallographic Data Centre. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (Telefax: Int. + 12 23/3 36-0 33; E-mail: deposit@ccdc.cam.ac.uk)

cedure described for the syntheses of 4a-12a, a THF solution (50 ml) of 300 mg Cp*V(CO)₄ (2) was used for the photo-induced preparation of the Cp*V complexes 4b-12b. The products were eluted from the silica column in an orange to red zone. For spectroscopic data and yields see Table 1.

Bis[(μ -organylchalcogenolato)-pentamethylcyclopentadienyl-dicarbonyl-tantalum] (**4c–14c**): The complexes **7c–14c** were prepared in the usual way by irradiation of a solution containing 430 mg (1 mmol) Cp*Ta(CO)₄ (**3**) and the appropriate amount of E₂R₂ (1–2 mmol) in 100 ml hexane. The evolution of gas (CO) was followed until 1 mmol (25 ml) had been collected, then the solvent was removed under vacuum and the residue purified by column chromatography on silica. In general, the complexes were isolated as red solids.

The methylchalcogenolato complexes (4c-6c) could not be chromatographed due to their easy decomposition with concomitant reformation of E_2M_2 . 4c was only studied in the NMR tube, whereas 5c and 6c were synthesized as described above, but the precipitates were only washed repeatedly using hexane.

 $Bis[di(\mu - organyl chalcogenolato) - cyclopentadienylvanadium]$ (5d, 6d, 8d-11d) and bis[di(μ -organylchalcogenolato)-pentamethylcyclopentadienylvanadium] (4e-9e, 12e). The carbonyl-containing dimers described above were decarbonylated in the presence of an excess of E_2R_2 in boiling toluene solution. In general, 50–100 mg $[Cp^{()}V(CO)_2(\mu-ER)]_2$ and an excess of E_2R_2 in 15–20 ml toluene were held under reflux for 15-60 min. The gas evolution (CO) was accompanied by a colour change from red or violet to brown. The solvent was removed under vacuum and the excess of E_2R_2 removed by repeated washing with pentane. The black, paramagnetic products were identified by their EI mass spectra. The molecular ion (M^+) was observed in all cases, but its intensity decreased with increasing size of R, e.g. $[CpV(\mu-SeR)_2]_2$ $(\mathbf{R} = \mathbf{Me} \ (\mathbf{5d}), \ \mathbf{m/e} = 610 \ (\mathbf{M}^+), \ \mathbf{I}_{rel} = 90\%; \ \mathbf{R} = \mathbf{Ph} \ (\mathbf{8d}),$ $m/e = 858 (M^+), 10\%; R = Fc (11 d), m/e = 1288 (M^+), 5\%.$ The nature of the heaviest compound, $[Cp*V(\mu-TeFc)_2]_2$ (12 e) was confirmed by FD-MS, $m/e = 1622 (M^+, 100\%)$, to have the correct isotope pattern.

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