APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 519–526 (2000)

REVIEW

Sandwich and half-sandwich complexes derived from pentamethylcyclopentadienyl tetracarbonyl vanadium, Cp*V(CO)$_4$†

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A survey is presented on various reactions of Cp*V(CO)$_4$, including CO ligand substitution and/or oxidative decarbonylation, to give complexes in which the formal oxidation state of vanadium may vary from 0 to V. Diamagnetic Cp*V complexes can be rapidly and conveniently characterized by ^{51}V NMR spectroscopy.

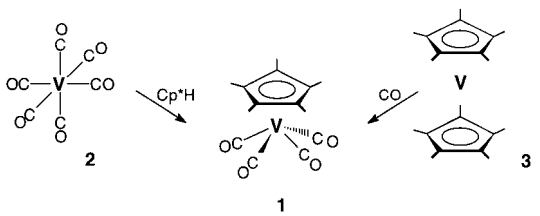
Keywords: vanadium; metal carbonyl compounds; oxidative addition; ligand substitution; ^{51}V NMR

INTRODUCTION

The half-sandwich fragment (η^5-pentamethylcyclopentadienyl)vanadium, [VCp*], has become a favoured building block in mono-, di- and oligonuclear vanadium complexes, mainly for two reasons:

(a) the metal is well protected sterically by the voluminous and firmly bound Cp* ring ligand, and
(b) the use of ^{51}V NMR spectroscopy can provide additional information on both the structure and the intramolecular interactions, particularly in the case of diamagnetic complexes.

A versatile educt for the synthesis of Cp*V complexes is the diamagnetic, four-legged piano-stool half-sandwich compound Cp*V(CO)$_4$ (**1**)[1,2] which formally takes an intermediate position between the paramagnetic precursors, V(CO)$_6$ (**2**) and VCp*$_2$ (**3**)[3,4] (Scheme 1).



Scheme 1

The permethylated half-sandwich Cp*V(CO)$_4$ (**1**), first described[1] in 1982, is conveniently prepared[1,2] by the reaction of V(CO)$_6$ (**2**) with pentamethylcyclopentadiene (Eqn [1]). It forms orange, volatile crystals (m.p. 144 °C)[2] and is photosensitive both in the solid state and, especially, in solution.

$$\underset{\mathbf{2}}{V(CO)_6} + Cp^*H \longrightarrow \underset{\mathbf{1}}{Cp^*V(CO)_4} + 2CO + \tfrac{1}{2}H_2 \quad [1]$$

REACTIVITY OF Cp*V(CO)$_4$

The complexes derived from Cp*V(CO)$_4$ (**1**) can be classified according to the oxidation state of the metal.

Compounds containing vanadium in low oxidation states (0,I)

The formal oxidation state vanadium(I) in

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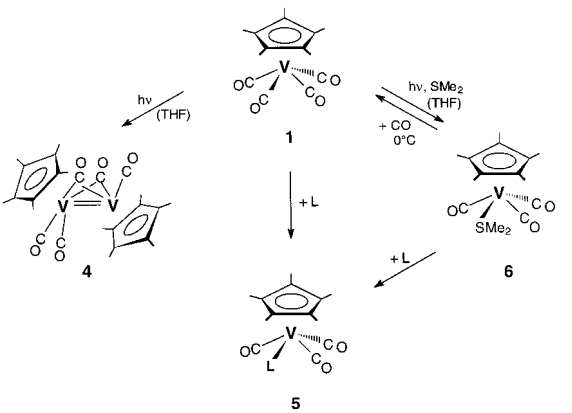
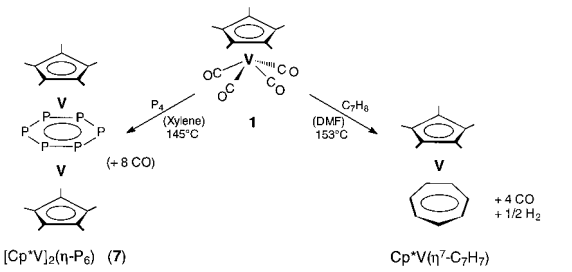
† Presented at the XIIIth FECHEM Conference on Organometallic Chemistry, held 29 August–3 September 1999, Lisbon, Portugal.



Scheme 2 L = C≡N—R (R = tBu, Cy) (Ref. 8), N_2H_4 (Ref. 9), N_2H_3Me, NH_2NMe_2 (Ref. 9), NC_5H_4-Z(4) (Z = H, Me, Et, Ph) (Ref. 8) PMe_3, $P(C_7H_7)_3$, P_4S_3, P_4Se_3 (Ref. 8) $P_4(CO)_2VCp^*$ (Ref. 13), SR_2(R = Me, Et) (Ref. 8), $S(CH_2)_n$ (n = 3,4,5) (Ref. 8).



Scheme 3

$Cp^*V(CO)_4$ (**1**) generally remains unchanged in photo-induced carbonyl substitution processes. Thus, the decarbonylation of **1** leads to the binuclear complex $Cp^*_2V_2(CO)_5$ (**4**),[1] for which two semibridging carbonyl ligands supporting a metal–metal multiple bond can be assumed (Scheme 2) — in agreement with the structure of the unsubstituted analogue, $Cp_2V_2(CO)_5$.[5,6]

A limited number of monosubstituted derivatives, $Cp^*V(CO)_3L$ (**5**), have been obtained either by direct irradiation of **1** in the presence of a two-electron ligand (**L**) in THF or hexane solution, or in a two-step sequence using a photochemically generated intermediate such as the dimethyl sulfide complex $Cp^*V(CO)_3(SMe_2)$ (**6**),[7] from which the labile ligand SMe_2 may be displaced in a dark reaction by various other ligands **L** (Scheme 2). This indirect method[7] involving temporary stabilization of the fragment [$Cp^*V(CO)_3$] in solution avoids exposure of the newly formed product to UV light. Some complexes **5** could only be characterized by ^1H and ^{51}V NMR spectroscopy in solution, e.g. several derivatives of the 4-substituted pyridines, $Cp^*V(CO)_3(NC_5H_4–Z)$ (Z = H, Me, Et, Ph).[8] It is interesting that π-olefinic ligands **L** did not give stable derivatives, nor could disubstituted products be isolated, although CpV derivatives of the type $CpV(CO)_2L_2$ (**L** = two-electron ligand) are known (for references see Ref. 10 and literature cited therein) and acetylene complexes $Cp^*V(CO)(L)C_2H_2$ (**L** = CO, PMe_3) have been prepared.[11]

The co-thermolysis of $Cp^*V(CO)_4$ (**1**) with white phosphorus (P_4) in boiling xylene (145 °C) leads to complete decarbonylation and formation of the green triple-decker $Cp^*V(\mu\text{-}P_6)VCp^*$ (**7**) (Scheme 3).[12] Under photochemical conditions at room temperature, carbonyl-containing precursors of **7** — such as $Cp^*V(CO)_2(P_4)$, $Cp^*_2V_2(CO)_2(\mu\text{-}P_2)_2$ and $Cp^*V(CO)_2(\mu\text{-}P_4)V(CO)_3Cp^*$ — can be isolated and characterized.[13]

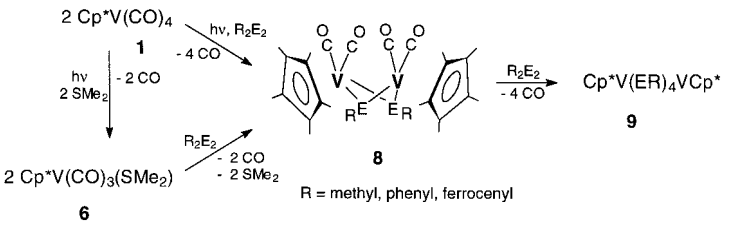
A reductive decarbonylation of $Cp^*V(CO)_4$ (**1**) is formally involved in the reaction with cyclohepta-1,3,5-triene which leads to the paramagnetic mixed-sandwich $(\eta^5\text{-}C_5Me_5)V(\eta^7\text{-}C_7H_7)$.[14]

Experiments directed towards the reduction of $Cp^*V(CO)_4$ (**1**) have not been described, although ample results on the reduction of the unsubstituted analogue $CpV(CO)_4$ to give $[CpV(CO)_3]^{2-}$ and/or $[CpV(CO)_3H]^-$ are available.[15–17] Reduction with sodium amalgam in THF[15] or with sodium in liquid ammonia, THF[17] or DMF[16] uniformly leads to the dianion $[CpV(CO)_3]^{2-}$ which, after protonation by water, can be converted to the yellow salt $[(Ph_3P)_2N^+][CpV(CO)_3H^-]$.[17]

Compounds containing vanadium(II) and vanadium(III)

The reaction of $Cp^*V(CO)_4$ (**1**) with diorganodichalcogenides, R_2E_2 (R = Me, Ph, Fc; E = S, Se, Te), results in stepwise oxidative decarbonylation[7,18] (Scheme 4). Both the diamagnetic vanadium(II) complexes **8** and the carbonyl-free paramagnetic vanadium(III) products **9** contain organosulfido, organoselenido or organotellurido bridges exclusively[7,18] without appreciable direct metal–metal interaction. The four terminal CO ligands in **8** protrude into the bowl-shaped cave formed by the $[Cp^*_2V_2(\mu\text{-}ER)_2]$ framework.

The dinuclear tetra-bridged vanadium(III) complexes $Cp^*V(\mu\text{-}ER)_4VCp^*$ (**9**)[18] are structurally related to the purple tetrakis(benzoato)-bridged compounds $Cp^*V(\mu\text{-}PhCOO)_4VCp^*$, which were



Scheme 4

obtained from the reaction of VCp^*_2 (**3**) with benzoic acid.[19] The half-sandwich **1** might also be used as educt, as deduced from the reactions of the unsubstituted analogue $CpV(CO)_4$ with a variety of carboxylic acids in boiling toluene to give $CpV(\mu\text{-}RCOO)_4VCp$ (R = H, CCl_3, CF_3, Ph, C_6H_4-F(3), C_6H_4-OMe(3), 2-furanyl and 2-thienyl).[20]

The tetranuclear complexes containing triply-bridging chalcogenido ligands, e.g. $[Cp^*V(\mu_3\text{-}O)]_4$,[23] $[Cp^*V(\mu_3\text{-}S)]_4$[30] and $[Cp^*V(\mu_3\text{-}Te)]_4$,[30] are paramagnetic pseudocubane clusters of vanadium(III).

Compounds containing vanadium(IV)

If an orange solution of $Cp^*V(CO)_4$ (**1**) in pentane or hexane is brought into contact with elemental halogens ($X_2 = Cl_2$, Br_2, I_2), a quantitative conversion into the trihalides takes place (Scheme 5).[21] The very air-sensitive paramagnetic products Cp^*VX_3 (**10**) are insoluble in the saturated hydrocarbon solvent and therefore efficiently protected against traces of air by the supernatant liquid.

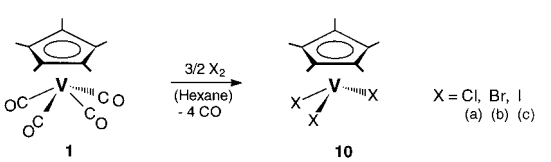
The reaction of Cp^*VCl_3 (**10a**) with an excess of trimethylsilyl azide (1:10) results in a stepwise substitution of the chlorine atoms by azido ligands to give dinuclear, paramagnetic bis(azido)-bridged complexes (Scheme 6).[22] The two azido bridges are formed first, followed by introduction of the terminal azido ligands.

The azide-rich dimer **11** (Fig. 1) is obtained directly as the final product from the slow reaction of **1** with an excess of trimethylsilyl azide in pentane solution in an open vessel (under air).[22] The long V…V distance (344.0 pm) points to weak or negligible direct metal–metal interactions.

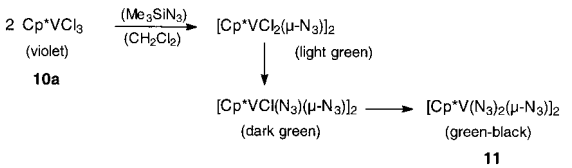
Cp*V complexes of vanadium(IV) containing bridging oxo ligands have been obtained by reduction of various vanadium(V) oxo compounds. Examples are the tetramer $[Cp^*VCl(\mu\text{-}O)]_4$,[23] with an essentially planar $[V(\mu\text{-}O)]_4$ cyclic framework,[24] and the cage $Cp^*_4V_4(\mu\text{-}O)_6$,[23] with an adamantane-like skeleton.[25,26] The latter is also prepared in reasonable yields (60%) by oxidation of VCp^*_2 (**3**) with N_2O gas.[25,26]

A series of dinuclear Cp*V complexes containing vanadium in the formal oxidation state IV is accessible via oxidative decarbonylation of **1** with a large excess of sulfur or selenium, either in boiling toluene or by UV irradiation in THF solution.[27] These reactions lead initially to pentachalcogenides, $Cp_2V_2E_5$ [E = S (**12a**), Se (**12b**)], which can undergo stepwise desulfurization or deselenization by tributylphosphane (Scheme 7) to give tetrachalcogenides, $Cp^*_2V_2E_4$ (**13a, 13b**), and then trichalcogenides $Cp^*_2V_2E_3$ (**14a, 14b**). The reverse reaction, i.e. addition of chalcogen to reconvert **14a**, **14b** back to **13a**, **13b** and **12a**, **12b** sequentially, has been used to prepare dinuclear products with mixed sets of bridging chalcogens.[28,29] Thus, many compounds of the types $Cp^*_2V_2E_n\cdot[n = 5$ (**12**), 4 (**13**) and 3 (**14**)] have been synthesized which may contain different chalcogens (E, E′ = O, S, Se, Te).[28,29]

In the dinuclear vanadium(IV) complexes **12–14** the chalcogens are all involved in either chalcogenido or dichalcogenido bridges. The compounds



Scheme 5



Scheme 6

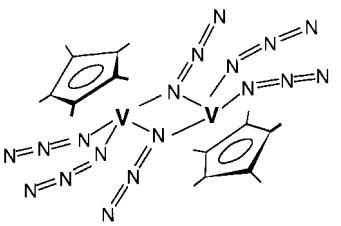
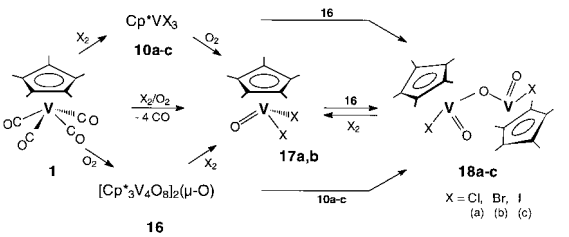


Figure 1 $[Cp^*V(N_3)_2(\mu\text{-}N_3)]_2$ (**11**). From Ref 22.



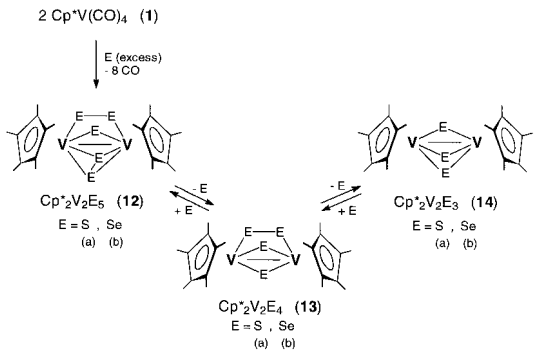
Scheme 8

are diamagnetic and are therefore assumed to contain a metal–metal bond; this assumption is supported by the V–V distances found in $Cp^*_2V_2Se_3O$ [250.2(2) pm] and $Cp^*_2V_2S_2Se_2$ [264.1(2) pm].[28] The single oxo bridges in $Cp^*_2V_2(O)S_4$[27] and $Cp^*_2V_2(O)E_3$ (E = S, Se, Te)[28,29] probably stem from a former carbonyl ligand of the educt $Cp^*V(CO)_4$ (**1**).

It is difficult to isolate carbonyl-containing intermediates along the route from **1** to the dinuclear Cp*V–chalcogenide complexes **12–14**, although careful photolysis of **1** in solution in the presence of either H_2S or $Bu_3P(Te)$ gave labile vanadium(III) products of the composition $[Cp^*V(CO)_2(\mu\text{-}E)]_2$ [E = S (**15a**),[7] Te (**15c**)[29]]. These carbonyl-containing dimers **15a** and **15c** could be characterized spectroscopically but lost CO easily to give the pseudocubane clusters $[Cp^*V(\mu_3\text{-}E)]_4$ (E = S or Te),[30] which contain the metal in the formal oxidation state III.

Compounds containing vanadium(V)

The highest possible oxidation state is reached in the oxidative decarbonylation of $Cp^*V(CO)_4$ (**1**) by molecular oxygen, e.g. in toluene or THF solution.[21] However, the molecular structure of the dark red product, $[Cp^*_6V_8O_{17}]$ (**16**), remains obscure. According to Bottomley and co-workers,[26] who obtained an analogous product[23,26] by oxidation of either VCp^*_2 (**3**), $Cp^*_4V_4(\mu\text{-}O)_6$ or $[Cp^*V(\mu_3\text{-}O)]_4$ with dioxygen gas, an oxo bridge appears to exist between two tetranuclear $[Cp^*_3V_4O_8]$ units, corresponding to the structure $[Cp^*_3V_4O_8]_2(\mu\text{-}O)$ (**16**).



Scheme 7

The most versatile educt for the synthesis of Cp*V–oxo complexes is the green half-sandwich complex $Cp^*V(O)Cl_2$ (**17a**), which is conveniently prepared (yield >80%) in one step by the simultaneous treatment of $Cp^*V(CO)_4$ (**1**) with Cl_2 and O_2 in CCl_4 solution (Scheme 8).[31] Other high-yield routes to **17a** have recently been explored.[32,33] Its half-sandwich structure has been confirmed.[24]

An equilibrium exists between the mononuclear **17a** and the oxo-bridged dinuclear complex, $[Cp^*V(O)Cl]_2(\mu\text{-}O)$ (**18a**), depending on the availability of chloro and oxo ligands (Scheme 8).[21] The exact concentration of chloro and oxo ligands can be simply controlled by addition of either **10a**, **17a** or **16** to the reaction mixture. The binuclear complexes $[Cp^*V(O)X]_2(\mu\text{-}O)$ [X = Cl (**18a**), Br (**18b**)] are also formed when O_2 gas is bubbled through solutions of $Cp^*V(CO)_4$ (**1**) in chloroform or bromoform.[21]

The mononuclear half-sandwich $Cp^*V(O)Cl_2$ (**17a**) opens the route to more highly aggregated Cp*V–oxo complexes by halogen abstraction, as studied in detail by Bottomley and co-workers.[23,34] The reactions with silver carbonate, Ag_2CO_3, can be conducted stepwise to give either dinuclear $[Cp^*V(O)Cl]_2(\mu\text{-}O)$ (**18a**)[23] or trinuclear $[Cp^*V(O)(\mu\text{-}O)]_3$ (containing a six-membered ring in the chair conformation).[34] Strong reductants such as the *s*-block metals Na, K, Mg, Ca or their amalgams lead to a mixture of three products:[23] the black cubane-like cluster $[Cp^*V(\mu_3\text{-}O)]_4$, the green–black adamantane-like cage $(Cp^*V)_4(\mu_2\text{-}O)_6$ and

Table 1 ^{51}V NMR spectra of carbonyl-containing Cp*V complexes[a]

Complex	$\delta^{51}V$	($\Delta\nu_{1/2}$)	Solvent	Ref.
$Cp^*V(CO)_4$ (**1**)	−1525		THF	9
	−1512	(37)	$CDCl_3$	7
	−1472		C_6D_6	8
	−1478		Hexane	9
$Cp^*_2V_2(CO)_5$ (**4**)	−1826		THF	9
	−1797		Hexane	9
$Cp^*V(CO)_3L$ (**5**)				
L = SMe_2 (**6**)	−886	(140)	$CDCl_3$	7
$S(CH_2)_3$	−927		C_6D_6	8
$S(CH_2)_4$	−864		C_6D_6	8
$S(CH_2)_5$	−897		C_6D_6	8
C≡N—Cy	−869		C_6D_6	8
N_2H_4	−680	(160)	THF	9
NH_2NHMe	−687	(170)	THF	9
NH_2NMe_2	−623	(185)	THF	9
NHMeNHMe	−570	(170)	THF	9
pyridine	−571	(170)	THF	8
	−573	(165)	C_6D_6	8
$NC_5H_4Z(4)$				
Z = CH_3[b]	−579	(210)	THF	8
Ph	−586	(330)	C_6D_6	8
CN	−775	(210)	C_6D_6	8
pyrazole	−659	(170)	THF	8
imidazole	−686	(190)	THF	8
N≡C—Me	−759		MeCN	7
$Cp^*V(CO)_3L$ (**5**)				
L = PMe_3	−1348[c]		C_6D_6	8
P_4S_3	−1313[c]	(210)	C_6D_6	8
P_4Se_3	−1266[c]	(190)	C_6D_6	8
$P(C_7H_7)_3$	−1268[c]	(260)	C_6D_6	
$Cp^*V(CO)_2L$				
L = C_2H_2	−560		$(CD_3)_2CO$, −20 °C	11
C_2Me_2	−648		$(CD_3)_2CO$, −20 °C	11
PhC_2H	−557		$(CD_3)_2CO$, −20 °C	11
$Cp^*V(CO)(PMe_3)L$				
L = C_2H_2	−296[c]		$(CD_3)_2CO$, −20 °C	11
PhC_2H	−333		$(CD_3)_2CO$, −20 °C	11
$Cp^*V(CO)_2(\eta^4\text{-}P_4)$	−1034	(90)	C_6D_6	13
$[Cp^*V(CO)_2(\mu\text{-}P_2)]_2$	+625	(250)	C_6D_6	13
$[Cp^*V(CO)_2(\mu\text{-}ER)]_2$ (**8**)				18
ER = SMe[b]	−751	(870)	C_6D_6	
SeMe	−757	(800)	C_6D_6	
TeMe	−860	(1150)	C_6D_6	
ER = SPh[b]	−686	(1270)	C_6D_6	
SePh	−703	(1370)	C_6D_6	
TePh[b]	−804	(1600)	C_6D_6	
ER = SFc	−495	(1400)	C_6D_6	
SeFc	−573	(1600)	C_6D_6	
TeFc	−750	(2000)	C_6D_6	
$[Cp^*V(CO)_2(\mu\text{-}S)]_2$ (**15a**)	−721	(1200)	C_6D_6	29
$[Cp^*V(CO)_2(\mu\text{-}Te)]_2$ (**15c**)	−853	(1500)	C_6D_6	29

[a] Chemical shift, $\delta^{51}V$, relative to external $VOCl_3$ (linewidths at half height, $\Delta\nu_{1/2}$ [Hz], in parentheses). The data reported in Refs. 8 and 13 were obtained at 25 °C; data in Ref. 11 at −20 °C.
[b] X-ray structure analysis available.
[c] Coupling constants, $^1J(^{51}V,^{31}P)$, for $Cp^*V(CO)_3L$ complexes: L = PMe_3 164 Hz, $P(C_7H_7)_3$ 158 Hz, P_4S_3 211 Hz, P_4Se_3 187 Hz; for $Cp^*V(CO)(PMe_3)C_2H_2$ 322 Hz.

Table 2 ^{51}V NMR spectra of carbonyl-free Cp*V complexes[a]

Complex	$\delta^{51}V$	($\Delta\nu_{1/2}$)	Solvent	Ref.
$Cp^*V(O)X_2$				
X = F	−404[c]		$CDCl_3$	21
Cl[b] (**17a**)	−25	(66)	$CDCl_3$	21, cf. 24
	−14.5	(85)	CH_2Cl_2/CD_2Cl_2	31
Br (**17b**)	+119	(83)	$CDCl_3$	21
	+127	(97)	CH_2Cl_2/CD_2Cl_2	31
OMe	−404	(93)	CH_2Cl_2/CD_2Cl_2	31, 35
OPh	−362	(180)	CH_2Cl_2/CD_2Cl_2	31
OC_6H_4-Me(4)	−534		$CH_2Cl_2/CDCl_3$	35
SPh[b]	−38		$CH_2Cl_2/CDCl_3$	35, 36
$X_2 = S_5$[b]	+44	(140)	$CDCl_3$	37
$(SC_5H_4)_2Fe$	−117	(172)	$CDCl_3$	38
$(SeC_5H_4)_2Fe$[b]	−338	(174)	$CDCl_3$	38
$[Cp^*V(O)X]_2(\mu\text{-}O)$				
X = F	−509[c]		$CDCl_3$	21
Cl[b] (**18a**)	−360	(250)	$CDCl_3$	21
Br (**18b**)	−309	(293)	$CDCl_3$	21
I	−238	(333)	$CDCl_3$	21
N_3	−480	(466)	$CDCl_3$	cf. 22
$[Cp^*V(O)(\mu\text{-}O)]_3$	−530 −545	(Ratio 2:1)	$CDCl_3$	34
$[Cp^*{}_3V_4O_8]_2(\mu\text{-}O)$ (**16**)	−573 −472	(Ratio 3:1)	C_6D_6	21
	−578 −481	(850) (1650)	C_6H_5Me	26
$[Cp^*V]_2(\mu\text{-}P_6)$[b] (**7**)	79[c]		C_6D_6	13, cf. 12
$Cp^*{}_2V_2S_5$ (**12a**)	596	(395)	$CDCl_3$	28
$Cp^*{}_2V_2Se_5$ (**12b**)	1119	(270)	$CDCl_3$	28
$Cp^*{}_2V_2S_4$ (**13a**)	1541	(635)	$CDCl_3$	28, 29
$Cp^*{}_2V_2Se_4$ (**13b**)	2139	(510)	$CDCl_3$	28, 29
$Cp^*{}_2V_2S_3$ (**14a**)	1630	(1550)	$CDCl_3$	28, 29
$Cp^*{}_2V_2Se_3$ (**14b**)	2205	(1200)	$CDCl_3$	28, 29
$Cp^*{}_2V_2S_3O$	1266	(570)	$CDCl_3$	28, 29
$Cp^*{}_2V_2Se_3O$[b]	1647	(720)	$CDCl_3$	28, 29
$Cp^*{}_2V_2Te_3O$	2240	(680)	$CDCl_3$	29
$Cp^*{}_2V_2S_2Se_2$[b]	1704	(690)	$CDCl_3$	28, 29
$Cp^*{}_2V_2Se_2Te_2$	2375	(660)	$CDCl_3$	29

[a] Chemical shift, $\delta^{51}V$, relative to external $VOCl_3$ (linewidths at half height, $\Delta\nu_{1/2}$ [Hz], in parentheses). The data reported in Refs. 21, 28 and 29 were obtained at 15 °C.
[b] X-ray structure analysis available.
[c] Coupling constants, $^1J(^{51}V,^{19}F)$, for $Cp^*V(O)F_2$ 234 Hz and $[Cp^*V(O)F]_2(\mu\text{-}O)$ 190 Hz. Coupling constant $^1J(^{51}V,^{31}P)$ for $[Cp^*V]_2(\mu\text{-}P_6)$ 57 Hz.

the purple ring $[Cp^*VCl_2]_3$. The key intermediate is assumed[23] to be a dimer, $[Cp^*V(O)Cl]_2$.

The half-sandwich $Cp^*V(O)Cl_2$ (**17a**) is also the parent compound of several diamagnetic derivatives of the type $Cp^*V(O)R_2$ (R = Ph,[31] OMe,[31] OPh,[35] $OC_6H_4Me(4)$,[35] SPh[35,36]), which all contain vanadium(V). Dianionic chelate ligands (R_2 = pentasulfide(S_5)[37] and ferrocene dichalcogenolate ($Fe(C_5H_4E)_2$; E = S, Se)[38] have been used in an analogous manner.

It is remarkable that the oxidative decarbonylation of $Cp^*V(CO)_4$ (**1**) by molecular oxygen leads to oligonuclear aggregates such as $[Cp^*{}_3V_4O_8]_2(\mu\text{-}O)$ (**16**) which contain terminal oxo ligands, whereas the corresponding reaction with a large excess of sulfur or selenium consistently gives dinuclear

products, $Cp^*_2V_2E_5$ [E = S (**12a**), Se (**12b**)],[27] where all five chalcogen atoms are involved in chalcogenido or dichalcogenido bridges.

NMR STUDIES

Three groups of Cp*V complexes are diamagnetic:

(a) all carbonyl-containing derivatives of the parent half-sandwich $Cp^*V(CO)_4$ (**1**) (cf. Table 1)
(b) complexes containing vanadium(V) (d^0) (cf. Table 2);
(c) dinuclear Cp*V compounds containing vanadium(IV) (d^1) with a metal–metal bond supported by a bridging chalcogenido system (cf. Table 2).

In these cases the [Cp*V] units can conveniently be identified by NMR spectroscopy. The η^5-pentamethylcyclopentadienyl ring [$Cp^* = C_5(CH_3)_5$] is easily recognized by an intense methyl singlet in the ^{1}H NMR and two signals in the ^{13}C NMR spectra. More important is the fact that the ^{51}V NMR spectroscopy provides a most sensitive probe for the detection and identification of new Cp*V complexes. Due to the favorable NMR properties of the ^{51}V nucleus ($I = 7/2$) such as high receptivity (0.381 relative to ^{1}H), high natural abundance (99.76%) and low quadrupole moment ($Q = 0.052 \times 10^{-28}$ m^2), rapid accumulation is possible. The ^{51}V NMR spectroscopy related to organometallic compounds has been studied in particular by Rehder.[39–41]

The range of δ^{51}V chemical shifts (relative to $VOCl_3 = 0$) at present extends from those of $[CpV(CO)_3(SnPh_3)]^-$ (−2054)[42] to those of $Cp^*_2V_2Se_2Te_2$ (+2375).[29] Characteristic δ^{51}V data are collected in Tables 1 and 2, together with the linewidths, $\Delta\nu_{1/2}$, where available. It should be pointed out, however, that both δ^{51}V and $\Delta\nu_{1/2}$ values depend on the temperature and the solvent,[40,41] and that comparisons should be based on data obtained under the same conditions.

It is clear from Tables 1 and 2 that the oxidation state of the metal is not correlated with the chemical shift, δ^{51}V.[41,43] The carbonyl-containing complexes (Table 1) have their ^{51}V signal at very high field (with a notable exception of the cluster-type compound $[Cp^*V(CO)(\mu\text{-}P_2)]_2$, and they show normal electronegativity/polarizability dependence, i.e. the signal moves upfield if a chalcogen (E = S, Se, Te) is replaced by the heavier congener, e.g. in the series $[Cp^*V(CO)_2(\mu\text{-}ER)]_2$ (**8**)[18] and $[Cp^*V(CO)_2(\mu\text{-}E)]_2$ (**15**).[29]

On the other hand, the (carbonyl-free) vanadium(V) complexes (Table 2) consistently show inverse electronegativity/polarizability dependence of ^{51}V shielding,[41] e.g. in the halide (X = F, Cl, Br, I) complexes $Cp^*V(O)X_2$ (**17**)[21,31] and $[Cp^*V(O)X]_2(\mu\text{-}O)$ (**18**).[21] A particularly strong 'inverse chalcogen effect' is found in the dinuclear chalcogenide vanadium(IV) complexes $Cp^*_2V_2E_n$ [$n = 5$ (**12**), 4 (**13**) and 3 (**14**)].[28,29]

The ^{51}V signals are much broader in the case of the dinuclear carbonyl–vanadium complexes $[Cp^*V(CO)_2(\mu\text{-}ER)]_2$ (**8**) as compared with mononuclear compounds. It is also remarkable that the half-linewidth increases dramatically if the number of chalcogen atoms in the carbonyl-free complexes $Cp^*_2V_2E_n$ ($n = 5$, 4, 3) is reduced. The increasing linewidth can be taken to indicate reduced symmetry around the ^{51}V nucleus.

CONCLUSIONS

Although various precursors (such as VCp^*_2 (**3**),[3,4] $[Cp^*VCl_2]_3$,[32,33] $Cp^*_2V(CO)$ and $Cp^*_2VCl_2$) are available to introduce the building block [VCp*] into metal complexes, the educt $Cp^*V(CO)_4$ (**1**) is particularly suitable in this respect because the carbonyl ligands are conveniently eliminated from the reaction mixture as CO gas. The formal oxidation state of vanadium in the [VCp*] unit may vary between 0 and V, depending on the coligands.

Oligonuclear aggregates containing [VCp*] units are well known in the chemistry of oxo complexes,[23] and a limited number of pseudocubane clusters such as $[Cp^*V(\mu_3\text{-}N)]_4$,[44] $[Cp^*V(\mu_3\text{-}O)]_4$,[23] $[Cp^*V(\mu_3\text{-}S)]_4$[30] and $[Cp^*V(\mu_3\text{-}Te)]_4$[30] have been described. In general, however, the Cp*V units tend to stabilize dinuclear structures, as in $[Cp^*V(CO)_2(\mu\text{-}ER)]_2$ (**8**) and $Cp^*_2V_2E_n$ [$n = 5$ (**12**), 4 (**13**), 3 (**14**)]; E = S, Se, Te.

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