

VANADIUM–METAL BONDS IN CARBONYLVANADIUM COMPLEXES: A ^{51}V NMR SPECTROSCOPIC INVESTIGATION

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Summary

The complexes $[\text{V}(\text{ER}_m)(\text{CO})_6]$ ($\text{ER}_m = \text{SnPh}_3, \text{SnEt}_3, \text{PbPh}_3, \text{AuPPh}_3$), $[\text{V}(\text{EPh}_3)(\text{CO})_5\text{PPh}_3]$ and $[\text{Et}_4\text{N}]_2[\text{V}(\text{EPh}_3)(\text{CO})_5]$ ($\text{E} = \text{Sn}, \text{Pb}$), and $[\text{Et}_4\text{N}][\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)(\text{CO})_3]$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) have been prepared and investigated by ^{51}V NMR spectroscopy. Shielding of the vanadium nucleus decreases in the order $\text{Sn} > \text{Ge} > \text{Si} > \text{Pb}$ as a result of counteracting effects upon the paramagnetic deshielding term. The trends are discussed in the general context of molecular parameters (polarizability, covalency, electronegativity, and ligand strength) influencing metal shielding in transition metal carbonyl derivatives. In the case of $[\text{V}(\text{SnR}_3)(\text{CO})_6]$, ion pair formation ($[\text{R}_3\text{Sn}]^+[\text{V}(\text{CO})_6]^-$) rather than seven-coordination is predicted. $[\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{SnPh}_3)(\text{CO})_3]^-$ extends the low-frequency region of the $\delta(^{51}\text{V})$ scale to -2054 ppm relative to VOCl_3 .

Introduction

During the past decade, various carbonylvanadium complexes containing a vanadium–metal bond have been described. The metal attached to vanadium usually is an organo-derivative of a member of the Group IVA family, but gold, mercury and copper compounds have also been prepared. The complexes may be allocated to one of the following classes:

(a) Seven-coordinate, neutral complexes $[\text{V}(\text{ER}_m)(\text{CO})_{6-n}(\text{p})_n]$, where $n = 0-2$ and (p) e.g. $\text{PPh}_3, \text{PBu}_3$ or $0.5\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. ER_m may be SnPh_3 [1,2], SiH_3 ($n = 0$) [3], AuPPh_3 [1,4,5], HgEt [1], and $\text{Cu}(\text{triars})$ ($\text{triars} = \text{MeAs}(\text{C}_6\text{H}_4\text{AsMe}_2)_2$) [4].

(b) Eight-coordinate, neutral complexes: e.g. $[\text{V}(\text{AuPPh}_3)_3(\text{CO})_5]$ [6].

(c) Seven-coordinate, anionic complexes $[\text{V}(\text{ER}_3)_2(\text{CO})_5]^-$, where $\text{ER}_3 = \text{SnPh}_3, \text{SnCy}_3$ (Cy is cyclohexyl) and PbPh_3 [7–9].

(d) Six-coordinate, anionic complexes $[\text{V}(\text{ER}_3)(\text{CO})_5]^{2-}$, where $\text{ER}_3 = \text{SnPh}_3, \text{SnMe}_3$ and PbPh_3 [7,8].

(e) Seven-coordinate, anionic half-sandwich complexes $[\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{EZ}_3)(\text{CO})_3]^-$, $\text{EZ}_3 = \text{SnPh}_3$ [10], SnCl_3 and GeCl_3 [11,12].

The preparation of the complexes usually involves the reaction between a carbonylvanadate ($[\text{V}(\text{CO})_6]^-$, $[\text{V}(\text{CO})_5\text{PPh}_3]^-$ or $[\text{V}(\text{CO})_5]^{3-}$) and a cationic ligand $[\text{ER}_m]^+$ (in the form of $[\text{ER}_m]\text{Cl}$). Once coordinated to vanadium, the organometal ligand should rather be considered ER_m^- ; the formal oxidation state of vanadium in classes **a**, **c** and **e** is then +I. Similarly, the formal oxidation state of vanadium in $[\text{V}(\text{AuPPh}_3)_3(\text{CO})_5]$ is +III instead of -III as in its precursor, the super-reduced anion $[\text{V}(\text{CO})_5]^{3-}$. These compounds are therefore closely related to the hydrido complexes $[\text{V}(\text{H})(\text{CO})_{6-n}(\text{p})_n]$ [13], “[$\text{V}(\text{H})_3(\text{CO})_5$]” [14] and $[\text{V}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{CO})_3]^-$ [13,15], a fact which has some implications to their vanadium-51 NMR spectroscopic characteristics (vide infra). The situation is somewhat different with the pseudo-octahedral complexes of class **d**. Again, the organo-tin and -lead ligands are counted negative (and hence considered iso-electronic with SbPh_3 and BiPh_3), leaving the vanadium center in the oxidation state -I. This class of complexes therefore belongs to the large family of $[\text{V}(\text{CO})_6]^-$ derivatives and may be compared directly with other pentacarbonylvanadates (-I) of the general composition $[\text{V}(\text{CO})_5\text{L}]^-$, where L is a group VA [16,17] or VIA ligand [17].

In this contribution, we have undertaken the first ^{51}V NMR study of complexes belonging to the classes **a**, **d** and **e**, including some compounds which have not yet been reported (lead derivatives of class **a**, silicon, germanium and lead derivatives of class **e**). The aim in this study is to elucidate the influence of molecular parameters, such as the ligand strength, covalency and nephelauxetic effects upon the metal shielding, and to estimate the weight of non-local diamagnetic contributions as one goes down Group IVA. Further, the problem of seven-coordination vs. contact-ion pair formation is discussed.

To evaluate the observed shieldings of the ^{51}V nucleus, we employ the mean energy approximation of the paramagnetic deshielding term σ_{para} of the overall shielding σ' :

$$\sigma_{para} = \text{const } \overline{\Delta E}^{-1} \langle r^{-3} \rangle C^2$$

Here, $\overline{\Delta E}$ is the mean energy separation between HOMOs and LUMOs taking part in electronic transitions or (for complexes of local C_{4v} symmetry such as $[\text{V}(\text{ER}_3)(\text{CO})_5]^{2-}$) the main allowed transition ($e \rightarrow a_1$ [18]). r is the distance of the V-3d electrons from the ^{51}V nucleus, and C is the V-3d LCAO coefficient. These three quantities correlate with the molecular parameters mentioned above. The overall shielding σ' is usually expressed as a sum of three terms:

$$\sigma' = \sigma_{para} + \sigma_{dia}^{local} + \sigma_{dia}^{non-local}$$

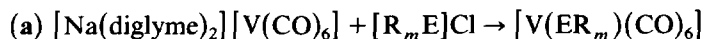
The local diamagnetic term is dominated by the core electrons ($\sigma_{dia} = \text{const. } \sum_i \langle r^{-1} \rangle_i P_i$, P_i = electron population of the i -th orbital) and practically constant for a given nucleus. For ^{51}V , σ_{dia} amounts to 1710 ± 10 ppm [18–20].

Metal NMR studies on low-valent transition metal complexes containing Group IVA triorganyls as ligands have previously been carried out on $^{55}\text{Mn}(\text{ER}_3)(\text{CO})_5$ [21], $^{59}\text{Co}(\text{ER}_3)(\text{CO})_4$ [22], and $^{93}\text{Nb}(\eta^5\text{-C}_5\text{H}_5)(\text{ER}_3)(\text{CO})_3$ [23].

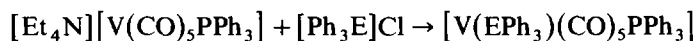
Results and discussion

^{51}V NMR data are collated in Table 1 which, for new complexes, also contains characteristic IR data for the CO stretching region.

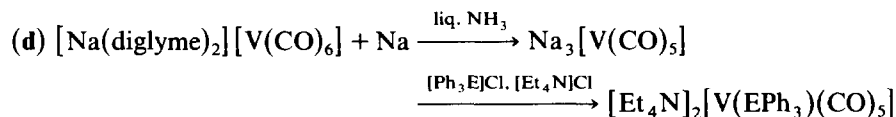
The complexes belonging to classes **a** and **d** were prepared by an analogous method to that described by Ellis et al. [1,2,6–9], and class **e** complexes by reaction of $[\text{V}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{CO})_3]^-$ with $[\text{ER}_3]\text{Cl}$:



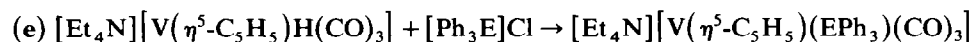
$[\text{Ph}_3\text{Ge}]\text{Cl}$ also reacted to give a short-lived compound with a characteristic $\nu(\text{CO})$ at 2020 cm^{-1} . The complex readily decomposed and could not be isolated.



The lead compound forms a red powder which slowly decomposes above -5°C .



$[\text{Ph}_3\text{Ge}]\text{Cl}$ did not react to give a well defined product.



In the case of $\text{E} = \text{Si}, \text{Ge}$ and Pb , a second ^{51}V NMR signal, possibly due to a disubstituted species $[\text{Et}_4\text{N}]_2[\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)_2(\text{CO})_2]$, is also observed; for $\text{E} = \text{Si}$, this is the main component in the reaction mixture.

Shielding variations are presented graphically in Figs. 1 and 2. In Fig. 1, $\delta(^{51}\text{V})$ values are compared with $\delta(^{55}\text{Mn})$, $\delta(^{59}\text{Co})$ and $\delta(^{93}\text{Nb})$ of the corresponding manganese, cobalt and niobium complexes; in Fig. 2, shielding trends of $[\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)(\text{CO})_3]^-$ are compared with those of halogen and pnictogen derivatives containing the $\{\eta^5\text{-C}_5\text{H}_5\text{V}(\text{CO})_3\}$ moiety.

In all the complexes containing a Group IVA triorganyl, the common feature is a maximum shielding for the tin derivative and a minimum shielding for the lead derivative; germanium occupies a medium position. This consistent trend (shielding decreases in the order $\text{SnPh}_3 > \text{GePh}_3 > \text{PbPh}_3$) clearly shows that non-local diamagnetic contributions to the overall shielding are negligibly small (there may be a small contribution to the ordering $\text{SnPh}_3 > \text{GePh}_3$ and, in the case of $[\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)(\text{CO})_3]$, also to the low-field position of the silicon derivative). This is also apparent from the high field position of the hydrido species in all but the vanadium complexes and is further documented by the ordering of AsEt_3 and BiEt_3 in $[\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{E}^{\text{V}}\text{Et}_3]$ and other vanadium species containing phosphine, arsine, stibine and bismuthine ligands [16,24,25].

Further, throughout the vanadium series, the ligand function belonging to the 5th period of the Periodic Table (i.e. SnPh_3 , SbEt_3 , I) imposes the highest shielding,

TABLE 1
 ^{51}V NMR AND IR a DATA

Class ^b	Complex	$\delta(^{51}\text{V})$ (ppm)	$\Delta\nu_{1/2}^c$ (Hz)	$\nu(\text{CO})$ (cm^{-1})
a	$[\text{V}(\text{CO})_6]^-$	-1954 ^d	<1.2 ^d	
	$[\text{V}(\text{ER}_m)(\text{CO})_6]$			
	1, $\text{ER}_m = \text{SnPh}_3^e$	-1953	45	2060vs 1980m 1910s 1830m ^f (CH_2Cl_2)
	2, $\text{ER}_m = \text{SnEt}_3^e$	-1954	48	2065vs 2020m 1985s 1955vs
	3, $\text{ER}_m = \text{PbPh}_3$	-1750	3700	1940sh 1903m ^f (KBr)
	4, $\text{ER}_m = \text{AuPPh}_3$	-1836	<100	
a	$[\text{V}(\text{CO})_5\text{PPh}_3]^-$	-1813 ^f	220	
	$[\text{V}(\text{EPH}_3)(\text{CO})_5\text{PPh}_3]$			
	5, E = Sn	-1651	700	
	6, E = Pb	-1565 (265 K) ^g	1500	2013s 1875m 1910vs 1890sh 1855s (KBr)
d	$[\text{V}(\text{EPH}_3)(\text{CO})_5]^{2-}$			
	7, E = Sn	-1994	69	
e	8, E = Pb	-1967	41	
	$[\text{V}(\eta^5\text{-C}_3\text{H}_5)_2\text{H}(\text{CO})_3]^-$	-1730 ^h	60 ⁱ	
	$[\text{V}(\eta^5\text{-C}_3\text{H}_5)\text{EPH}_3(\text{CO})_3]^-$			
	9, E = Si	-1860 -650 ^j	<100	1945s 1840s 1810sh (CH_2Cl_2)
	10, E = Ge	-2026 -645 ^j	<1000	1947s 1875m 1830vs 1785s (CH_2Cl_2)
	11, E = Sn	-2054	110	1969w 1880s 1790sh 1775vs ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$) ⁱ
	12, E = Pb	-1789 -648 ^j	<1000	1968, 1892s 1868vs 1800vs ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$)

^a For new complexes only. ^b See text. ^c Width of the resonance signal at half height. ^d From ref. 24. ^e The tin complexes should probably be described as ion pairs $[\text{R}_3\text{Sn}][\text{V}(\text{CO})_6]$; see text for discussion. ^f Doublet, $J(^{51}\text{V}-^{31}\text{P})$ 204 Hz. ^g -1547 ppm extrapolated to 300 K, assuming a temperature gradient for δ of 0.5 ppm/deg [24]. ^h From ref. 13. ⁱ ^1H decoupled. ^j Tentatively assigned to $[\text{V}(\eta^5\text{-C}_3\text{H}_5)(\text{EPH}_3)_2(\text{CO})_2]^{2-}$. ^k Undefined by-product or decomposition band. ^l Data from ref. 10 (hmpa): 1891s, 1795s,br.

calling for an explanation based on a common origin for the high metal shielding.

Since the local diamagnetic term is about constant, and the non-local term can be ruled out as an effective factor, variations in shielding will have to be accounted for in terms of variations of the paramagnetic term. In σ_{para} , two counteracting parameters, ΔE and $\langle r^{-3} \rangle C^2$, will affect the ^{51}V shielding. In the low-valent vanadium complexes under consideration, the $\text{V} \rightarrow \text{L} \pi$ -interaction will be the main factor to bring about alterations in ΔE : a strongly π withdrawing ligand will lead to a decrease of σ_{para} and an increase of σ (increase of $|\delta|$). This effect places phosphines, which are good π acceptors, at the high-field (low-frequency) side of the shielding scale (Fig. 2), and the extremely weakly interacting bismuthines and triorganyllead ligands at the low-field (high-frequency) side. $\langle r^{-3} \rangle C^2$ decreases as the nephelauxetic effect of the ligand and the covalency of the vanadium–ligand bond increases. The overall effect imparted by this parameter is a decrease of σ_{para} and an increase of σ' as one goes down the groups, passing through a maximum with the donor functions of the 5th period, being over-powered again by ΔE as one passes to PbR_3 and BiR_3 .

The increase of $\delta(^{51}\text{V})$ in the sequence $\text{SiR}_3 < \text{GeR}_3 < \text{SnR}_3$ (and also in the sequence $\text{F} < \text{Cl} < \text{Br} < \text{I} < \text{H}$ [26] and $\text{AsR}_3 < \text{SbR}_3$ [16,24,25]) parallels the decrease of the electronegativities of L (increase of the ionicity of the V–L bond), and further parallels the increase of the polarizability and Pearson basicity of L. In Fig. 2, values for the electronegativities (Allred–Rochow, and taken from a recent recalculation by Zhang [27]), polarizabilities [28] and $\text{p}K_s(\text{CH}_3\text{Hg}^+)$ [29] are indicated. The trends down the groups which, in the case of the halide ligands, have been termed “normal halogen dependence” of the metal shielding by Kidd [30], are also observed across the periods ($\text{Cl} < \text{PEt}_3 < \text{SiPh}_3$, $\text{Br} < \text{AsEt}_3 < \text{GePh}_3$, $\text{I} < \text{SbEt}_3 < \text{SnPh}_3$) and are quite a common feature in metal shielding of low-valent transition metal complexes [31].

For the class **a** complexes, an additional interesting feature is that the triorganyl tin derivatives exhibit exactly the same $\delta(^{51}\text{V})$ as $[\text{V}(\text{CO})_6]^-$, while the lead and gold complexes show a low-field (high-frequency) shift of the ^{51}V resonance which is to be expected as one passes from six-coordinated to the less symmetrical seven-coordinated complexes. In the solid state, seven-coordination has been established for $[\text{V}(\text{AuPPh}_3)(\text{CO})_6]$ [5] and $[\text{V}(\text{SnPh}_3)_2(\text{CO})_5]^-$ [7]. In solutions of $[\text{V}(\text{SnR}_3)(\text{CO})_6]$, however, the anion $[\text{V}(\text{CO})_6]^-$, as shown by the invariant resonance position of -1954 ppm, appears to be present. The signal is considerably broadened, though, suggesting a non-vanishing nuclear electric field gradient caused by distortion of the ideal O_h symmetry through contact-ion pair formation; hence $[\text{R}_3\text{Sn}]^+ [\text{V}(\text{CO})_6]^-$. Since the ^{51}V nucleus has a nuclear quadrupole moment ($Q = -0.05 \cdot 10^{-28} \text{ m}^2$; nuclear spin $I = 7/2$), a loss of symmetry will substantially influence line widths. Ion pair formation in the carbonylvanadate system has formerly been reported for phosphine derivatives by Darensbourg [32] based on IR evidence.

Experimental

Spectroscopic measurements

IR spectra were scanned on a Perkin–Elmer 577 spectrometer under the conditions indicated in Table 1. ^{51}V NMR spectra: complexes **1**, **2**, **5** to **8**: Bruker WH 90 PFT spectrometer at 23.66 MHz, 300 K, in 7.5 mm vials; complexes **3**, **4**, **9** to **12**:

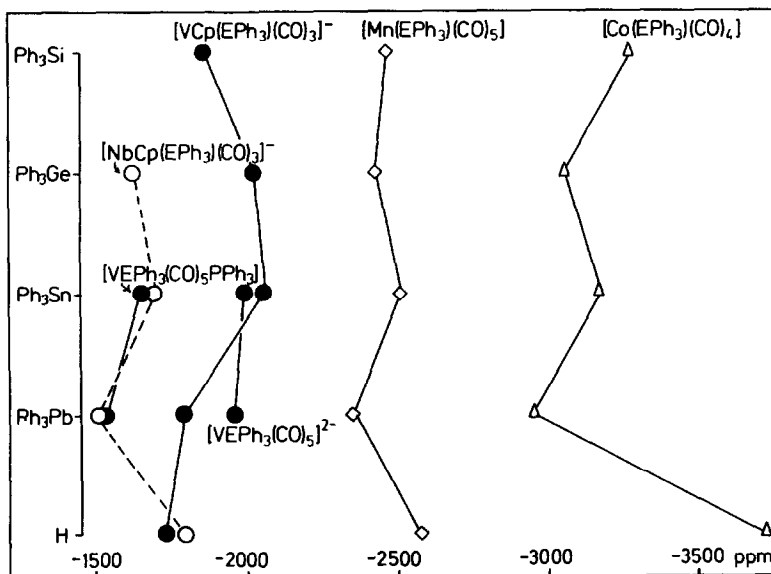


Fig. 1. $\delta(M)$ of carbonyl complexes containing the ligands ER_3 (where E is a Group IVA metal or metalloid) and H. ●, $\delta(^{51}\text{V})$ relative to VOCl_3 , this work; ○, $\delta(^{93}\text{Nb})$ relative to NbOCl_3 , ref. 23; ◇, $\delta(^{55}\text{Mn})$ relative to MnO_4^- , ref. 21; △, $\delta(^{59}\text{Co})$ relative to $\text{Co}(\text{CN})_6^{3-}$, ref. 22.

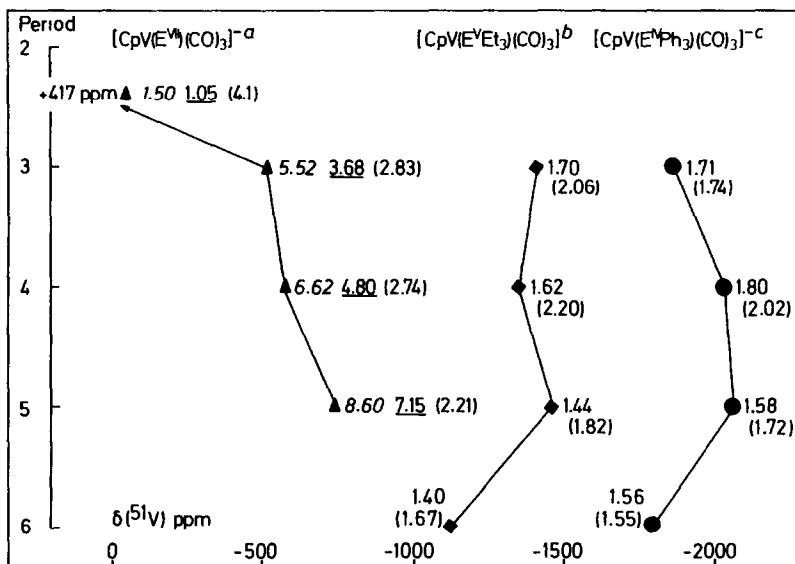


Fig. 2. Variations of $\delta(^{51}\text{V})$ of $[\text{V}(\eta^5\text{-C}_5\text{H}_5)\text{X}(\text{CO})_3\text{L}]$ complexes with Group VIIA (Δ), VA (\blacklozenge) and IVA (\bullet) ligands. ^a $\text{E}^{\text{VII}} = \text{F, Cl, Br, I}$, from ref. 26; the numerals are the pK_a (italics), polarizabilities (10^{-24} cm^{-3}) (underlined) and Allred-Rochow electronegativities $\chi(\text{AR})$ (in parentheses). ^b $\text{E}^{\text{V}} = \text{P, As, Sb, Bi}$, from ref. 16; the numerals indicate the $\chi(\text{Z})$ given by Zhang [27] for the +III state, and the $\chi(\text{AR})$ (in parentheses). ^c $\text{E}^{\text{IV}} = \text{Si, Ge, Sn, Pb}$, this work; numerals are $\chi(\text{Z})$ for the +IV state, and $\chi(\text{AR})$.

Bruker SWL 3-100 wide-line spectrometer at 0.984 T (central field) and 11.0 MHz, 300 K, modulation amplitude 0.1 mT and (**4**, **9**, **11**) 5 μ T, sweep width 3 mT, in 15 mm vials. All measurements were carried out in ca. 0.05 M thf under an inert gas atmosphere. Absolute error for $\delta(^{51}\text{V})$: ± 2 ppm (WH 90) and ± 10 ppm (SWL 3-100). The absolute error for the half-width is < 5 Hz (**1**, **2**, **7**, **8**), ca. 0.2 kHz (**3**, **5**, **6**), and ± 30 Hz (**11**).

Preparative procedures

Starting materials were purchased (Strem, Alfa) or prepared as described elsewhere ($[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{PPh}_3]$ [16], $[\text{Et}_4\text{N}][\text{V}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{CO})_3]$ [13]). The complexes **1**, **4**, **5**, **7** and **8** were prepared by routes similar to literature procedures, following the preparative schemes given below for **3** and **6**. All operations were carried out under nitrogen. Silica gel (70–230 mesh ASTM, Merck) was dried under vacuum for one h and stored under nitrogen.

$[\text{V}(\text{PbPh}_3)(\text{CO})_6]$, **3**. 970 mg $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$ (1.9 mmol) and 925 mg $[\text{Ph}_3\text{Pb}]\text{Cl}$ (2 mmol) were jointly dissolved in 40 ml CH_2Cl_2 and treated with 30 ml of O_2 -free water. After one h of stirring, the originally yellow solution had turned to dark red. The organic layer was separated and passed through a silica gel column (8×2.5 cm). The dark red fraction, drawn from the column, was concentrated to 5 ml. On addition of ca. 25 ml heptane, the ruby-red, fine crystals which separated were filtered off and dried under high vacuum for 4 h. Analysis: found: C, 42.6; H, 2.42; V, 7.9. $\text{C}_{24}\text{H}_{15}\text{O}_6\text{PbV}$ (657.5) calcd.: C, 43.84; H, 2.30; V, 7.75%.

$[\text{V}(\text{SnEt}_3)(\text{CO})_6]$ (**2**) was prepared similarly, to yield a yellow product.

$[\text{V}(\text{PbPh}_3)(\text{CO})_5(\text{PPh}_3)]$, **6**. This compound was prepared similarly, using the procedure given for **3**, from $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{PPh}_3]$ and $[\text{Ph}_3\text{Pb}]\text{Cl}$. The reaction was carried out at room temperature, but concentration of the eluant was undertaken at -5°C and the product (a red, micro-crystalline powder) was stored in the cold. Found: C, 54.6; H, 3.3; P, 3.2; V, 6.0. $\text{C}_{41}\text{H}_{30}\text{O}_5\text{PPbV}$ (891.8) calcd.: C, 55.22; H, 3.39; P, 3.41; V, 5.71%.

$[\text{Et}_4\text{N}][\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)_n(\text{CO})_{4-n}]$ ($n = 1$: **9–12**; $n = 2$). 255 mg $[\text{Et}_4\text{N}][\text{V}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{CO})_3]$ (0.8 mmol) and an equimolar amount of $[\text{Ph}_3\text{E}]\text{Cl}$ were dissolved in 40 ml CH_2Cl_2 (E = Si) or 1/1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (E = Ge, Sn, Pb) and stirred until the evolution of gas had ceased (ca. 30 min). The gray precipitate was filtered off, the filtrate concentrated to 5 ml and treated with heptane until the solution became slightly turbid. The complexes precipitated while standing several days at -15°C , to yield red-brown (**9**, E = Si; **10**, E = Ge), wine-red (**11**, E = Sn) and dark red (**12**, E = Pb) powders, respectively. Except of the tin compound, which has been described previously [10], the complexes could not be obtained in an analytically defined form (cf. Table 1).

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