Tetracarbonyl(η^5-cyclopentadienyl)-vanadium Complexes with R_3E Substituents (E = Si, Ge, Sn) at the Cp-Ring**

Andreas Duch, Martin Hoch, and Dieter Rehder*

Abstract: The preparation and spectral properties (IR, ^{1}H- and ^{51}V-NMR, MS) of the complexes $[(\eta^5\text{-}R_3EC_5H_4)V(CO)_4]$, $R_3E = Me_3Si$, Et_3Ge, Et_3Sn and $n\text{-}Bu_3Sn$, are described. These compounds are obtained by direct reaction from $V(CO)_6$ and $R_3EC_5H_5$. The complexes $[R_3EV(CO)_6]$ are formed as by-products in the case of E = Sn and Ge. With $Ph_3PbC_5H_5$, the only metalated complex is $[Ph_3PbV(CO)_6]$.

Ring-substituted cyclopentadienyl-carbonylvanadium complexes $[Cp'V(CO)_4]$ have not been generally accessible until recently. We have now applied a newly developed route to this class of vanadium half-sandwich complexes (direct synthesis from hexacarbonylvanadium and the substituted cyclopentadienes Cp'H[1]) to the preparation of complexes with $Cp' = R_3EC_5H_4$, where $ER_3 = SiMe_3$ (**1**), $GeEt_3$ (**2**), $SnEt_3$ (**3**), and $SnBu_3$ (**4**). We have been interested in these compounds in view of (i) the potential stabilization of derivatives obtained by substitution of a CO ligand by a weak ligand such as tetrahydrofuran or hydrazine[2], and (ii) the impact of substituents in the Cp ring on the shielding of the ^{51}V nucleus.

The product spectrum for the reactions between $V(CO)_6$ and $R_3EC_5H_5$ in *n*-hexane (Equations (1) to (4)) largely depends upon the stability of the E–Cp bond. The reaction pattern for E = Si is similar to that of *alkyl*-substituted cyclopentadienes[1] in that the oxidation product **1** is formed along with the disproportionation product $[(Cp')_2V(CO)_2][V(CO)_6]$. With triorganogermyl- and -stannylcyclopentadienes, the neutral, 7-coordinated complexes $[R_3EV(CO)_6]$ are obtained as by-products, the preparation[3] and ^{51}V-NMR spectra[4] of which have been described previously for E = Sn. $Ph_3PbC_5H_5$ forms only the formerly unknown complex $[Ph_3PbV(CO)_6]$. In all cases, the formation of varying amounts of the parent compound $[C_5H_5V(CO)_4]$ is also observed along with the evolvement of H_2, CO, and finely distributed vanadium. The compounds are light-sensitive, especially in the case of the tin derivatives **3** and **4**. The vanadium complexes are considerably less stable than the isoelectronic half-sandwich complexes of manganese, $[(R_3EC_5H_4)Mn(CO)_3]$[5], which exist also for $R_3E = Ph_3Pb$.

$$C_5H_5SiMe_3 + V(CO)_6 \rightarrow \mathbf{1} + [(Me_3SiC_5H_4)_2V(CO)_2][V(CO)_6] \quad (1)$$
$$C_5H_5GeEt_3 + V(CO)_6 \rightarrow \mathbf{2} + [R_3GeV(CO)_6] \quad (2)$$
$$C_5H_5SnR_3 + V(CO)_6 \rightarrow \mathbf{3}\ (R = Et)/\mathbf{4}\ (R = n\text{-}Bu) + [R_3SnV(CO)_6] \quad (3)$$
$$C_5H_5PbPh_3 + V(CO)_6 \rightarrow [Ph_3PbV(CO)_6] \quad (4)$$

Spectroscopic data of the complexes **1**–**4**, together with the alkyl derivative $[(Ph_2HCC_5H_4)V(CO)_4]$ **5** are collated in Table 1. $\delta(^{51}V)$ values are in the expected range for $CpV(CO)_4$ complexes. Variations in ^{51}V shielding is governed by two effects[6]: An electronic effect, owing to the +I influence of the R_3E substituent, gives rise to an upfield shift with respect to $C_5H_5V(CO)_4$ as is observed in the case of **1** and **2**. This effect is counter-balanced or even overbalanced by a steric effect, which leads to a *de*shielding contribution due to diminished vanadium-3d/$R_3EC_5H_4$ interaction. The latter effect is responsible for the decrease of shielding where there are particularly bulky substituents, i.e. in the complexes **3**, **4**, and **5**.

The 70 eV mass spectra (see Scheme 1 for the fragmentation) all show the molecule ion peak. They are further characterized by successive CO loss to $Cp'V^{\oplus}$ typical of the parent compound[7], the pattern of which also dominates the region of $m/z < 115$. In the tin and germanium compounds, β-transfer of hydrogen occurs simultaneously and the trihydrostannyl- and -germyl-cyclopentadienyl-carbonylvanadium fragments are observed. Elimination of alkene and formation of the hydride are preferentially occurring processes in the MS fragmentation of $Et_nR_{4-n}E$[8], if E = Sn or Ge. In our complexes investigated here, all of the fragments $Et_nH_{3-n}E^{\oplus}$ are observed and further, by alkyne elimination, *cyclo*-$H_3EC_3H_2V^{\oplus}$. A third reaction path, which becomes increasingly important as the E–Cp bond becomes weaker with increasing size of E, starts with the one-step removal of the R_3E substituent. In the fragmentation of the silyl compound **1**, the ions $SiC_5H_4V^{\oplus}$, $SiME_3^{\oplus}$, $SiMe_2^{\oplus}$, and $SiMe^{\oplus}$ are also observed.

Preparation of $[(R_3EC_5H_4)V(CO_4]$ ($R_3E = Me_3Si$ **1**, *Et_3Ge* **2**, *Et_3Sn* **3**, *n-Bu_3Sn* **4**):

All operations were carried out under argon atmosphere and in brown glass ware. 655 mg (3.0 mmol) $V(CO)_6$ dissolved in 35 mL of *n*-hexane were treated with an equimolar amount of freshly prepared $R_3EC_5H_5$[9] and stirred, at 35°C ($Me_3SiC_5H_5$: under reflux), for 5 h. After filtration from metal flakes

Table 1. Spectroscopic data of the complexes **1**–**5**.

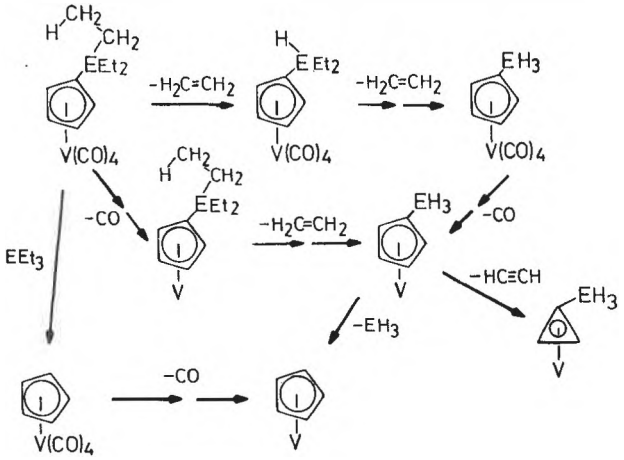
Complex	$\nu(CO)$[a] [cm^{-1}]				$\delta(^{51}V)$[b]	$W_{1/2}$ [Hz]	$\delta(^1H)$[c]		
							C_5H_4	CH_2	CH_3
1	2030		1935	1900[d]	−1542	40	5.41s, 5.27s		0.23s
2	2035	1947	1927	1895[d]	−1555	60	5.19t, 4.97t[e]	0.81q	0.20t
3	2035	1948[d]	1927	1895	−1524	110	5.25s, 5.12s	2.24q	1.67t
4	2033	1940[d]	1915	1895	−1522	140	[f]		
5[g]	2030	1949[d]	1928/1918[h]		−1518	250	5.25s[i]		

[a] In hexane. Assignments and relative intensities (from left to right): A_1, m; B_1, w; E, vs (broad); A', w (^{13}CO isotopomer). The observation of the IR-forbidden B_1 mode and the broadening of the E band indicate non-ideal C_{4v} symmetry.
[b] In [D$_6$]acetone relative to $VOCl_3$: $\delta(^{51}V)$ $[C_5H_5V(CO)_4] = -1534$. The spectra were obtained at 94.7 MHz on a Bruker AM 360 spectrometer in 10 mm vials at 298 K. $W_{1/2}$ is the line width at half-height.
[c] In $CDCl_3$ at 80 MHz. The resonances indicated with an s (singlet) are unresolved, relatively broad lines, the reason for the broadening being paramagnetic impurities present in the sample.
[d] Shoulder.
[e] $J = 1.8$ Hz.
[f] Unresolved, broad lines due to partial decomposition.
[g] Data for $[(Ph_2HCC_5H_4)V(CO)_4]$ from ref.[11].
[h] The E band is split.
[i] $\delta(^1H)$ for the hydrogen on C_{exo} is 5.08.

* *Correspondence:* Prof. Dr. D. Rehder
Institut für Anorganische und Angewandte Chemie
Universität Hamburg
Martin-Luther-King-Platz 6, D–2000 Hamburg 13
(Bundesrepublik Deutschland)

** *Acknowledgement:* This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Scheme 1



(and, in the case of the silyl compound, the ionic by-product), the intensely orange coloured solutions were concentrated (room temperature, vacuum) to ca. 5 mL and chromatographed on silicagel (Kieselgel 60, Merck, 70–230 mesh ASTM, conditioned by evacuation and treatment with argon; column dimensions 20 × 2.5 cm) with hexane as elutant. The orange fractions, containing the products **1**–**4** and $[C_5H_5V(CO)_4]$, were concentrated to 10 mL and kept at −25°C for several days. During this time, $[C_5H_5V(CO)_4]$ partly crystallized from the solution. The supernatant liquid was decanted and the compounds **1** to **4** obtained as orange coloured, crystalline powders after removal of the solvent. Mainly the tin derivatives **3** and **4** are exceedingly light-sensitive. Yields: **1** (contaminated with ca. 20% $C_5H_5V(CO)_4$) 640 mg (72%), **2** (+50% of $C_5H_5V(CO)_4$) 900 mg (60%), **3** (+10% of $C_5H_5V(CO)_4$) 590 mg (45%), **4** (free of $C_5H_5V(CO)_4$) 800 mg (51%). The amount of $[C_5H_5V(CO)_4]$ was determined by ^{51}V-NMR. Several recrystallizations allow for the isolation of **1**, **2**, and **3** practically free of $[C_5H_5V(CO)_4]$, at the expense, however, of the yield. $[Et_3GeV(CO)_6]$ and $[R_3SnV(CO)_6]$ can be washed off the column with hexane/tetrahydrofuran (5:1).

$[Ph_3PbV(CO)_6]$: 365 mg (1.67 mmol) of $V(CO)_6$ dissolved in 15 mL of *n*-hexane were treated with 840 mg (1.67 mmol) of $Ph_3PbC_5H_5$[10]. CO evolved and an orange solution was formed, which was stirred overnight (exclusion of light, argon atmosphere), filtered, concentrated to 5 mL, and chromatographed on silica gel (for the conditions, *vide supra*). The first fraction, which was eluted with hexane, was $[C_5H_5V(CO)_4]$. The second, red fraction, obtained upon elution with hexane/tetrahydrofuran (1:1), was evaporated to dryness (room temperature, vacuum) to yield 210 mg (19%) of $[Ph_3PbV(CO)_6]$. ν(CO) (tetrahydrofuran): 1850 and 1880 cm^{-1}; (hexane) 2066vs, 2019m, 1975s and 1950vs cm^{-1}. In tetrahydrofuran, the compound more likely is described by a contact ion pair $[Ph_3Pb][V(CO)_6]$ rather than in terms of a 7-coordinate $[Ph_3PbV(CO)_6]$.

Received: March 28, 1988 [FC 137]

[1] M. Hoch, A. Duch, D. Rehder, *Inorg. Chem. 25* (1986) 2907; D. Rehder, M. Hoch, M. Link, *Organometallics 7* (1988) 233; M. Hoch, D. Rehder, *Chem. Ber.*, in press. – This preparative route has first been employed for the synthesis of $[(C_5Me_5)V(CO)_4]$: W.A. Herrmann, W. Kalcher, *Chem. Ber. 115* (1982) 3886.

[2] C. Woitha, D. Rehder, *J. Organomet. Chem.*, in press.

[3] A. Davison, J.E. Ellis, *J. Organomet. Chem. 36* (1972) 113; J.E. Ellis, R.A. Faltynek, *Inorg. Chem. 15* (1976) 3169.

[4] R. Talay, D. Rehder, *J. Organomet. Chem. 262* (1984) 25.

[5] A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova, Y.V. Makarov, *Izv. Akad. Nauk SSSR Ser. Khim.* (1973) 2815.

[6] D. Rehder, *Chimia 40* (1986) 186; *Magn. Reson. Rev. 9* (1984) 125.

[7] R.B. King, *J. Am. Chem. Soc. 90* (1968) 1417.

[8] P.J. Barker, A.G. Davies, M.W. Tse, *J. Chem. Soc. Perkin Trans. 2* (1980) 941.

[9] The cyclopentadiene derivatives $R_3EC_5H_5$ were prepared from NaC_5H_5 and R_3EX (X = I for E = Ge, Cl for E = Si and Sn) as described in the literature: H.P. Fritz, C.G. Kreiter, *J. Organomet. Chem. 1* (1964) 323; M. Lesbre, R. Mazarolles, G. Manuel, *C.R. Acad. Sci. 255* (1962) 544.

[10] $Ph_3PbC_5H_5$ was prepared by a modified literature procedure (C. Gaffney, P.G. Harrison, *J. Chem. Soc. Dalton Trans.* (1962) 1055): 4 mL of a 1 M solution of NaC_5H_5 in tetrahydrofuran were added, at dry-ice temperature, to a suspension of 1.940 g (4.1 mmol) of Ph_3PbCl in 10 mL of diethyl ether. After 15 min of stirring, the mixture was allowed to warm up to room temperature. After 2 h of additional stirring and subsequent filtration, the solvent was removed. The residue was washed with a small amount of water, dried in vacuo and redissolved with toluene. After treatment with a little hexane, the solution was placed at −25°C for 1 day, after which time a yellow, crystalline precipitate had formed. This was collected, washed with hexane, and dried under high vacuum. Yield 1.065 g (51%) of light-yellow, light-sensitive crystals, *m.p.* 110°C.

[11] D. Rehder, D. Wenke, *J. Organomet. Chem.*, in press.