

Preliminary communication

**SYNTHESES WITH η^5 -C₅H₅V(CO)₃THF: GENERATION, AND
 SUBSTITUTION REACTIONS. FIRST OBSERVATION OF ^{51}V — $^{117,119}\text{Sn}$
 COUPLING**

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(Received February 2nd, 1985)

Summary

The complex CpV(CO)₃THF has been prepared in THF solution (i) photochemically from CpV(CO)₄, and (ii) from [CpV(H)(CO)₃]⁻/[Ph₃C]⁺ at low temperatures. THF is replaced by [CpV(H)(CO)₃]⁻ to form [{CpV(CO)₃]₂-μ-H]⁻, and by various ligands L with C, η^2 -C≡C, Sn, N, O, S, Se or Te functionality to yield CpV(CO)₃L and *cis*-[CpV(CO)₂LL] (LL = bipy, *o*-phen, tolane). The δ (^{51}V) values range over ca. 1400 ppm and allow the assignment of distinct coordination modes for ambidentate ligands. The temperature gradient is ca. +1.2 ppm/deg. For [CpV(SnCl₃)(CO)₃]⁻ (δ -1340 ppm rel. to VOCl₃), $^1J(^{51}\text{V}$ — $^{117,119}\text{Sn})$ is 900 Hz. The isotope effect on introducing ^{12}C for ^{13}C in CpV(CO)₄ is -0.48(2) ppm; $^1J(^{51}\text{V}$ — $^{13}\text{C})$ 107 Hz.

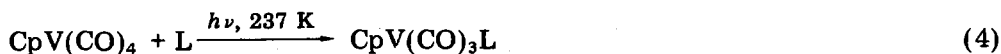
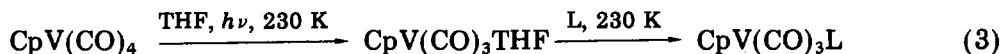
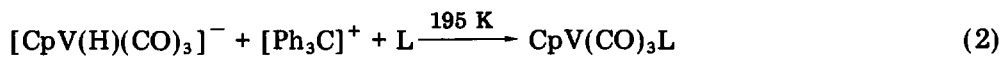
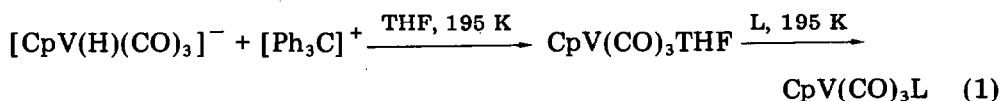
Various derivatives of CpV(CO)₄ of the general formula CpV(CO)_{4-n}L_n have been prepared by (i) photo-induced CO-substitution in CpV(CO)₄ in the presence of L ($n = 1$: L = SnCl₃⁻ and GeCl₃⁻ [1], E^VR₃ [2,3], CNR [4]; $n = 2$: L = μ -SMe [5], SnCl₃⁻ [1], alkyne [6,7], vinylketene [8]), or a precursor L' of L (L = diene; L' = cyclo-C₃Ph₃H [9], 2-oxonin [10]), (ii) from Cp₂V₂(CO)₅ and L (L = CN⁻ and E^VR₃ [11], alkyne and cyclobutadiene [12]), or (iii) from [CpV(CO)₃]²⁻ (or [CpV(H)(CO)₃]⁻) and L ($n = 1$: L = Hal⁻ [13,14], CH₃CN and CH₃⁻ [14], E^{IV}R₃⁻ [15,16]). Special synthetic routes such as the preparation of CpV(CO)₃CH(NH₂) from [CpV(CO)₃]²⁻ and [Me₂NCHCl]Cl [17], the preparation of [CpV(CN)(CO)₃]⁻ by action of K[N(SiMe₃)₂] on CpV(CO)₄ [18], the synthesis of CpV(CO)₃PET₃ by the reduction of CpVCl₂(PET₃)₂ with Zn/Al under 1 bar of CO [19], or the formation of CpV(CO)_{4-n}(CS)_n ($n = 1, 2$) in the system CpV(CO)₄/PPh₃/CS₂ [20] have also been noted. None of these previously described procedures is, however, generally applicable, and this prompted us to

develop an alternative route to the complexes $\text{CpV}(\text{CO})_3\text{L}$ (and, in a few cases, $\text{CpV}(\text{CO})_2\text{LL}$) by the labile ligand method employing the still only partly characterized $\text{CpV}(\text{CO})_3\text{THF}$.

This compound was suggested by Barnett et al. [21] and by Caulton et al. [22] to be an intermediate in the photo-induced generation of $\text{CpV}(\text{CO})_3\text{PR}_3$ and $\text{Cp}_2\text{V}_2(\text{CO})_4\text{PR}_3$ from $\text{CpV}(\text{CO})_4$ in the presence of phosphine ligands. Caulton also reported the IR spectrum of the (thermolabile) THF complex. The lability of $\text{CpV}(\text{CO})_3\text{THF}$ contrasts with the stability of $\text{CpNb}(\text{CO})_3\text{THF}$, at room temperature [23].

We have now obtained the vanadium complex by photolysis of THF solutions of $\text{CpV}(\text{CO})_4$ at 190 to 230 K, or by abstraction of H^- from $[\text{Et}_4\text{N}][\text{CpV}(\text{H})(\text{CO})_3]$ suspended along with $[\text{Ph}_3\text{C}][\text{BF}_4]$ in THF at 195 K. The emerald green solutions of $\text{CpV}(\text{CO})_3\text{THF}$, which can be prepared in concentrations up to 0.05 M, decompose above ca. 250 K to give $\text{CpV}(\text{CO})_4$ and $\text{Cp}_2\text{V}_2(\text{CO})_5$, suggesting that the electron-deficient fragment $\text{CpV}(\text{CO})_3$ is formed as an intermediate, and that the photo-generation of $\text{Cp}_2\text{V}_2(\text{CO})_5$ from $\text{CpV}(\text{CO})_4$ in THF described by Herrmann et al. [24] proceeds via $\text{CpV}(\text{CO})_3\text{THF}$. $\text{CpV}(\text{CO})_3$ may either form $\text{Cp}_2\text{V}_2(\text{CO})_5$ by loss of one CO, or recombine with CO to $\text{CpV}(\text{CO})_4$. The formation of $\text{CpV}(\text{CO})_2$ intermediates can be excluded since decomposition of $\text{CpV}(\text{CO})_3\text{THF}$ in the presence of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) yields $\text{CpV}(\text{CO})_3\text{dppm}$ only. If $\text{CpV}(\text{CO})_3\text{THF}$ is decomposed in the presence of ^{13}CO , $\text{CpV}(\text{CO})_3(^{13}\text{CO})$ and other species of the general composition $\text{CpV}(\text{CO})_{4-n}(^{13}\text{CO})_n$ are obtained, which can be distinguished by their ^{51}V NMR pattern. The doublet for $\text{CpV}(\text{CO})_3(^{13}\text{CO})$ ($^1J(^{51}\text{V}-^{13}\text{C})$ 107 Hz) is shifted to high field (low frequency) relative to $\text{CpV}(\text{CO})_4$. This isotope effect ($-0.48(2)$ ppm) is of the same order of magnitude as that observed for $[\text{V}(\text{CO})_5(^{13}\text{CO})]^-$ [25]. Characteristic IR frequencies for $\text{CpV}(\text{CO})_3\text{THF}$ are $\nu(\text{CO})$ 1952 and 1850 cm^{-1} , which corresponds to the pattern reported by Caulton [22] and to that for $\text{CpNb}(\text{CO})_3\text{THF}$ noted by Herrmann [23]. The vanadium chemical shift relative to VOCl_3 at 231 K is -217 ppm (compare $\text{CpV}(\text{CO})_4$: -1534 , $\text{Cp}_2\text{V}_2(\text{CO})_5$: -1664 , $[\text{CpV}(\text{H})(\text{CO})_3]^-$: -1730 ppm; all at 300 K in THF).

The replacement of THF by L can be carried out by the following methods (eq. 1 to 4):



In the case where L is a bidentate nitrogen ligand NN (1,10-phenanthroline, 2,2'-bipyridyl), the disubstituted complexes *cis*- $[\text{CpV}(\text{CO})_2\text{NN}]$ are formed, which are reminiscent of the Schiff base complex $\text{CpV}(\text{CO})_2\text{NC}_6\text{H}_4(2\text{-CH}=\text{NHCHMePh})$ [26]. C_2Ph_2 gives $\text{CpV}(\text{CO})_2\text{-}\eta^2\text{-C}_2\text{Ph}_2$. The results are summarized in Table 1.

TABLE 1

⁵¹V CHEMICAL SHIFTS AND SELECTED EXPERIMENTAL DETAILS FOR CpV(CO)_{4-n}L_n COMPLEXES

L	$\delta(^{51}\text{V})^a$ (ppm)	Temperature (K)	Spectrometer ^c	Colour ^b	Preparation ^d
<i>n</i> = 1					
<i>Group VIIa</i>					
Br ⁻	-578				
<i>Group VIa</i>					
THF	-217 (-136)	231	WL	green	2,4
SPh ₂	-843 (-763)	232	WL	brown	1,3
SH(<i>i</i> -Pr)	-906 (-826)	232	WL	brown	1,3
SC(NH ₂) ₂	-854	300	PFT	brown-red	1,3
SC(Me)NH ₂	-947	300	PFT	brown-red	1,3
S(O)Me ₂ (DMSO)	-977	300	PFT	red-brown	1-4
SePh ₂	-906 (-836)	232	WL	red-brown	1,3
TePh ₂	-1145	300	WL	red-brown	1,3
<i>Group Va</i>					
2-NH ₂ -py	-426	300	PFT	brown-red	1,3
NH ₂ Ph	-496	300	PFT	brownish	1,3
PhN=CHPh	-491	300	PFT	red	1,3
4-CN-py	-492	300	PFT	red-brown	1,3
pyridine	-519	300	PFT	red	1-4
1-Methylimidazole	-650	300	PFT	red	1,3
Imidazole	-659	300	PFT	red	1,3
NCS ⁻	-699	300	PFT	red	3
NCMe	-719	300	PFT	red	1-4
NCPH	-732	300	PFT	red	1-4
phthalodinitrile	-740	300	PFT	red	2,4
PPh ₃	-1316 [157]				
Ph ₂ PCH ₂ PPh ₂	-1340 [195]				
PMe ₂ Ph	-1396 [171]				
P(OMe) ₃	-1496 [311]				
PF ₃	-1567 [434]				
AsPh ₃	-1259				
SbPh ₃	-1430				
BiPh ₂ R	-1260				
<i>Group IVa</i>					
CN ⁻	-1400				
C≡CPh ⁻	-1414	300	PFT	brown	1,3
CNCy	-1401				
¹³ CO	-1535 [107]	300	PFT	orange	^e
SnCl ₃ ⁻	-1340 [900]	300	PFT	red-brown	1,3
SnPh ₃ ⁻	-2054				
<i>Other</i>					
H ⁻	-1730 [20]				
CpV(H)(CO) ₃ ⁻	-1129	300	PFT	green	1,3
<i>n</i> = 2					
PhC≡CPh	-600	300	PFT	brown	1,3
<i>o</i> -phenanthroline	-21	300	WL	violet	1,3
1,10-bipyridyl	-63	300	WL	violet	1,3

^a Relative to VOCl₃ neat. In parentheses: $\delta(^{51}\text{V})$ extrapolated to 300 K, using a temperature gradient of +1.17 ppm/deg (which is the gradient found for CpV(CO)₃py in the temperature range of 229 to 302 K).

^b In THF solution (except for L = DMSO, NCMe, NCPH and py, where the ligand itself has been employed as the solvent). ^c WL = Bruker SWL 3-100 wide-line spectrometer, PFT = Bruker WH-90 PFT spectrometer.

^d 1, 2, 3 and 4 refer to eq. 1-4 see text. ^e Prepared by UV irradiation of a THF solution of CpV(CO)₄, saturated with ¹³CO, at 195 K, warming up to 250 K and vigorous shaking.

For comparison, some data on known complexes ($L = PR_3, AsR_3, SbR_3, BiR_3$ [2,3,27,32], $CNCy$ [4], $SnPh_3^-$ [15], Br^- [13] and CN^- [27,32] are included.

The complexes $CpV(CO)_3L$ are thermolabile ($L = SPh_2, SePh_2, SH(i-Pr)$) or stable at room temperature as long as they are solvent-stabilized. Except for $L = NCS^-$, $TePh_2$ and $CNCy$, the compounds cannot be isolated as solids even at low temperatures. In solution, they exhibit the characteristic CO stretching patterns, i.e. a sharp band of weak to medium intensity around 1950 cm^{-1} ($A'(cis)$) and a broad, very strong absorption at ca. 1860 cm^{-1} ($A'(trans) + E$), which sometimes shows an asymmetry to higher wave numbers ($A'(trans)$). The $\nu(CO)$ bands of the complexes $CpV(CO)_2NN$, which can be isolated as solids, are at 1870 and 1808 cm^{-1} (THF solution), those of $CpV(CO)_2\eta^2-C_2Ph_2$ at 1992 and 1914 cm^{-1} , which are comparable to the values of $\nu(CO)$ reported by Nesmeyanov for the tolane complex in CS_2 solution [28].

The $\delta(^{51}V)$ values of the complexes show a differentiation which resembles the trends for the ^{51}V shieldings observed in the systems $[V(CO)_5L]^-$ [29], $[V(NO)_2L_4]^+$ [30] and $CpV(NO)_2L$ [31]: increasing CO substitution decreases the shielding of the metal nucleus ($CpV(CO)_4$ (-1534) $>$ $CpV(CO)_3L$ (-217 to ca. -1400) $>$ $CpV(CO)_2NN$ (-21 to -63 ppm)) except where L is a very strong π acceptor (PF_3) or an extremely "soft" ligand (H^- , SnR_3^-). Within the class of $CpV(CO)_3L$ compounds, there are specific ranges for $\delta(^{51}V)$ which can be allocated to distinct coordinating ligand functions. Thus, shielding decreases in the series $H^- \approx \{Sn\} > \{Sb\} > \{C\} \approx \{P\} > \{As\} > TePh_2 > \eta^2-PhC\equiv CPh > \{S\} > SePh_2 > \{N\} > THF$.

Coordination of DMSO via S is evidenced by its shift value, which is close to those for other S-ligands, and by the $\nu(SO)$ of 1235 cm^{-1} (the $\nu(SO)$ of uncoordinated DMSO is 1055 cm^{-1} ; compare also $[V(CO)_5DMSO]^-$: 1288 cm^{-1} [29]). Thiurea (-854) and thioacetamide (-947 ppm) also ligate through sulfur, while SCN^- (-699 ppm) appears to prefer N-coordination. $2-NH_2$ -py, according to its $\delta(^{51}V)$ shift, coordinates via NH_2 , $4-NC$ -py via the pyridine-N (as do these pyridine derivatives in the anionic complexes $[V(CO)_5py]^-$).

The ^{51}V NMR signals are singlets, broadened by the effective quadrupole relaxation (nuclear spin of ^{51}V $7/2$, quadrupole moment $-0.05 \times 10^{-28}\text{ m}^2$). An exception is the complex $[CpV(SnCl_3)(CO)_3]^-$ for which, along with the central line (85% intensity) there is a flanking doublet (15% of the overall intensity) due to $^1J(^{51}V-^{117,119}Sn)$ coupling. The couplings to the ^{117}Sn and ^{119}Sn nuclei, respectively, are not resolved because of the very similar magnetogyric ratios of the two magnetically active tin nuclei and the line broadening caused by the ^{51}V nucleus. The experimental overall coupling is 900 Hz , which can be related to $J(V-^{117}Sn)$ 880 and $J(V-^{119}Sn)$ 920 Hz and a half-width of the resonance lines of 190 Hz . The coupling constant is larger by a factor of 4 to 5 than those commonly observed between ^{51}V and ^{31}P in $CpV(CO)_3PR_3$ complexes [27,32] (cf. also Table 1).

Experimental

All operations were carried out under N_2 and in absolute, O_2 -free solvents. $[Et_4N][CpV(H)(CO)_3]$ was prepared from $Na_2[CpV(CO)_3]$ and $[Et_4N]Cl$ in CH_3CN as described previously [34]. The ligands SCN^- and $SnCl_3^-$ were employed as the tetraethylammonium, $PPhC\equiv C^-$ as the potassium salts.

In a typical experiment, 165 mg (0.5 mmol) of $[\text{Et}_4\text{N}][\text{CpV}(\text{H})(\text{CO})_3]$ were treated with 60 ml of THF and cooled to 195 K. To this suspension/solution, 5 ml of a CHCl_3 solution of 165 mg (0.5 mmol) of $[\text{Ph}_3\text{C}][\text{BF}_4]$ were added dropwise during 10 min. Upon stirring for ca. 1 h, a dark green solution of $\text{CpV}(\text{CO})_3\text{THF}$ was formed. This solution was treated at 195 K with a 5-fold molar excess of L (dissolved in a few ml of THF if solid at room temperature) and, with continuous stirring, warmed to 243 K. The formation of $\text{CpV}(\text{CO})_3\text{L}$ was complete after ca. 10 h.

Alternatively, $\text{CpV}(\text{CO})_3\text{THF}$ can be obtained by external irradiation (high pressure mercury lamp) for 10 min of a solution of 200 mg of $\text{CpV}(\text{CO})_4$ in 50 ml THF (saturation) contained in a borosilicates vessel at ca. 200 K. During the irradiation, a weak N_2 stream is passed through the solution. For the synthesis of $[\{\text{CpV}(\text{CO})_3\}_2-\mu\text{-H}]^-$, equimolar amounts of $\text{CpV}(\text{CO})_3\text{THF}$ and $[\text{Et}_4\text{N}][\text{CpV}(\text{H})(\text{CO})_3]$ were used.

References

- 1 T. Kruck and W. Molls, *Z. Anorg. Allgem. Chem.*, **420** (1976) 158.
- 2 R. Talay and D. Rehder, *Chem. Ber.*, **111** (1978) 1978.
- 3 R. Borowski, D. Rehder and K. von Deuten, *J. Organomet. Chem.*, **220** (1981) 45.
- 4 N. Coville, personal communication.
- 5 F. Y. Petillon, J. L. Le Quere and J. E. Guerschais, *Inorg. Chim. Acta*, **37** (1979) L453.
- 6 R. Tsumura and N. Hagihara, *Bull. Chem. Soc. Japan*, **38** (1965) 1901.
- 7 D. F. Foust and M. D. Rausch, *J. Organomet. Chem.*, **239** (1982) 321.
- 8 R. B. King and C. D. Hoff, *J. Organomet. Chem.*, **225** (1982) 245.
- 9 K.-J. Jens and E. Weiss, *Chem. Ber.*, **117** (1984) 2469.
- 10 M. D. Rausch and A. V. Grossi, *J. Chem. Soc., Chem. Commun.*, (1978) 401.
- 11 E. O. Fischer and R. J. J. Schneider, *Chem. Ber.*, **103** (1970) 11.
- 12 L. N. Lewis and K. G. Caulton, *J. Organomet. Chem.*, **252** (1983) 57.
- 13 R. Talay and D. Rehder, *Inorg. Chim. Acta*, **77** (1983) L175.
- 14 R. J. Kinney, W. D. Jones and R. G. Bergman, *J. Am. Chem. Soc.*, **100** (1978) 7902.
- 15 R. Talay and D. Rehder, *J. Organomet. Chem.*, **262** (1984) 25.
- 16 K. M. Pfahl and J. E. Ellis, *Organometallics*, **3** (1984) 230; J. E. Ellis, R. A. Faltynek and S. C. Hentges, *J. Organomet. Chem.*, **120** (1976) 389.
- 17 A. J. Hawthorn, M. F. Lappert and K. Turner, *J. Chem. Soc. Dalton Trans.*, (1978) 348.
- 18 D. Rehder, *Z. Naturforsch. B*, **31** (1976) 273.
- 19 J. Nieman, J. H. Teuben, J. C. Huffman and K. G. Caulton, *J. Organomet. Chem.*, **255** (1983) 193.
- 20 S. S. Rajan, *Ind. J. Chem. A*, **15** (1977) 520.
- 21 L. N. Lewis and K. G. Caulton, *Inorg. Chem.*, **19** (1980) 1840.
- 22 G. Alway and K. W. Barnett, *Inorg. Chem.*, **19** (1980) 779.
- 23 W. A. Herrmann, W. Kalcher, H. Biersack, I. Bernal and M. Creswick, *Chem. Ber.*, **114** (1981) 3558.
- 24 W. A. Herrmann and J. Plank, *Chem. Ber.*, **112** (1979) 392.
- 25 K. Ihmels and D. Rehder, *Inorg. Chim. Acta*, **96** (1985) L69.
- 26 H. Brunner and W. A. Herrmann, *Z. Naturforsch. B*, **28** (1973) 606.
- 27 D. Rehder, H.-Ch. Bechthold, A. Kececi, H. Schmidt and M. Siewing, *Z. Naturforsch. B*, **37** (1982) 631.
- 28 A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova and A. A. Pasynskii, *Dokl. Chem.*, **182** (1968) 789.
- 29 K. Ihmels and D. Rehder, *Chem. Ber.*, in press; *Organometallics*, in press.
- 30 F. Näumann and D. Rehder, *Z. Naturforsch. B*, **39** (1984) 1647 and 1654.
- 31 M. Herberhold and H. Trampisch, *Z. Naturforsch. B*, **37** (1982) 614.
- 32 D. Rehder, *Magn. Reson. Rev.*, **9** (1984) 125.
- 33 D. Wenke, K. Ihmels, P. Oltmanns and D. Rehder, *Inorg. Chim. Acta*, in press.
- 34 U. Puttfarcken and D. Rehder, *J. Organomet. Chem.*, **185** (1980) 219.