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Preliminary communication

SYNTHESES WITH η^5-$C_5H_5V(CO)_3$THF: GENERATION, AND SUBSTITUTION REACTIONS. FIRST OBSERVATION OF ^{51}V—$^{117,119}Sn$ COUPLING

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Summary

The complex $CpV(CO)_3$THF has been prepared in THF solution (i) photochemically from $CpV(CO)_4$, and (ii) from $[CpV(H)(CO)_3]^-/[Ph_3C]^+$ at low temperatures. THF is replaced by $[CpV(H)(CO)_3]^-$ to form $[\{CpV(CO)_3\}_2\text{-}\mu\text{-H}]^-$, 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 $\delta(^{51}V)$ 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 $[CpV(SnCl_3)(CO)_3]^-$ (δ −1340 ppm rel. to $VOCl_3$), $^1J(^{51}V\text{—}^{117,119}Sn)$ is 900 Hz. The isotope effect on introducing ^{12}CO for ^{13}CO in $CpV(CO)_4$ is −0.48(2) ppm; $^1J(^{51}V\text{—}^{13}C)$ 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 = $SnCl_3^-$ and $GeCl_3^-$ [1], E^VR_3 [2,3], CNR [4]; n = 2: L = μ-SMe [5], $SnCl_3^-$ [1], alkyne [6,7], vinylketene [8]), or a precursor L′ of L (L = diene; L′ = cyclo-C_3Ph_3H [9], 2-oxonin [10], (ii) from $Cp_2V_2(CO)_5$ and L (L = CN^- and E^VR_3 [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], CH_3CN and CH_3^- [14], $E^{IV}R_3^-$ [15,16]). Special synthetic routes such as the preparation of $CpV(CO)_3CH(NH_2)$ from $[CpV(CO)_3]^{2-}$ and $[Me_2NCHCl]Cl$ [17], the preparation of $[CpV(CN)(CO)_3]^-$ by action of $K[N(SiMe_3)_2]$ on $CpV(CO)_4$ [18], the synthesis of $CpV(CO)_3PEt_3$ by the reduction of $CpVCl_2(PEt_3)_2$ 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 $CpV(CO)_4/PPh_3/CS_2$ [20] have also been noted. None of these previously described procedures is, however, generally applicable, and this prompted us to

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develop an alternative route to the complexes $CpV(CO)_3L$ (and, in a few cases, $CpV(CO)_2LL$) by the labile ligand method employing the still only partly characterized $CpV(CO)_3THF$.

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 $CpV(CO)_3PR_3$ and $Cp_2V_2(CO)_4PR_3$ from $CpV(CO)_4$ in the presence of phosphine ligands. Caulton also reported the IR spectrum of the (thermolabile) THF complex. The lability of $CpV(CO)_3THF$ contrasts with the stability of $CpNb(CO)_3THF$, at room temperature [23].

We have now obtained the vanadium complex by photolysis of THF solutions of $CpV(CO)_4$ at 190 to 230 K, or by abstraction of H^- from $[Et_4N][CpV(H)(CO)_3]$ suspended along with $[Ph_3C][BF_4]$ in THF at 195 K. The emerald green solutions of $CpV(CO)_3THF$, which can be prepared in concentrations up to 0.05 *M*, decompose above ca. 250 K to give $CpV(CO)_4$ and $Cp_2V_2(CO)_5$, suggesting that the electron-deficient fragment $CpV(CO)_3$ is formed as an intermediate, and that the photo-generation of $Cp_2V_2(CO)_5$ from $CpV(CO)_4$ in THF described by Herrmann et al. [24] proceeds via $CpV(CO)_3THF$. $CpV(CO)_3$ may either form $Cp_2V_2(CO)_5$ by loss of one CO, or recombine with CO to $CpV(CO)_4$. The formation of $CpV(CO)_2$ intermediates can be excluded since decomposition of $CpV(CO)_3THF$ in the presence of $Ph_2PCH_2PPh_2$ (dppm) yields $CpV(CO)_3dppm$ only. If $CpV(CO)_3THF$ is decomposed in the presence of ^{13}CO, $CpV(CO)_3(^{13}CO)$ and other species of the general composition $CpV(CO)_{4-n}(^{13}CO)_n$ are obtained, which can be distinguished by their ^{51}V NMR pattern. The doublet for $CpV(CO)_3(^{13}CO)$ ($^1J(^{51}V—^{13}C)$ 107 Hz) is shifted to high field (low frequency) relative to $CpV(CO)_4$. This isotope effect (−0.48(2) ppm) is of the same order of magnitude as that observed for $[V(CO)_5(^{13}CO)]^-$ [25]. Characteristic IR frequencies for $CpV(CO)_3THF$ are $\nu(CO)$ 1952 and 1850 cm^{-1}, which corresponds to the pattern reported by Caulton [22] and to that for $CpNb(CO)_3THF$ noted by Herrmann [23]. The vanadium chemical shift relative to $VOCl_3$ at 231 K is −217 ppm (compare $CpV(CO)_4$: −1534, $Cp_2V_2(CO)_5$: −1664, $[CpV(H)(CO)_3]^-$: −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):

$$[CpV(H)(CO)_3]^- + [Ph_3C]^+ \xrightarrow{\text{THF, 195 K}} CpV(CO)_3THF \xrightarrow{\text{L, 195 K}} CpV(CO)_3L \quad (1)$$

$$[CpV(H)(CO)_3]^- + [Ph_3C]^+ + L \xrightarrow{\text{195 K}} CpV(CO)_3L \quad (2)$$

$$CpV(CO)_4 \xrightarrow{\text{THF, } h\nu\text{, 230 K}} CpV(CO)_3THF \xrightarrow{\text{L, 230 K}} CpV(CO)_3L \quad (3)$$

$$CpV(CO)_4 + L \xrightarrow{h\nu\text{, 237 K}} CpV(CO)_3L \quad (4)$$

In the case where L is a bidentate nitrogen ligand NN (1,10-phenanthroline, 2,2′-bipyridyl), the disubstituted complexes *cis*-$[CpV(CO)_2NN]$ are formed, which are reminiscent of the Schiff base complex $CpV(CO)_2NC_6H_4(2\text{-}CH{=}NHCHMePh)$ [26]. C_2Ph_2 gives $CpV(CO)_2\text{-}\eta^2\text{-}C_2Ph_2$. The results are summarized in Table 1.

TABLE 1

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

L	$\delta(^{51}V)$[a] (ppm)	Temperature (K)	Spectrometer[c]	Colour[b]	Preparation[d]
n = 1					
Group VIIa					
Br^-	−578				
Group VIa					
THF	−217 (−136)	231	WL	green	2,4
SPh_2	−843 (−763)	232	WL	brown	1,3
SH(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
Group Va					
$2\text{-}NH_2\text{-}py$	−426	300	PFT	brown-red	1,3
NH_2Ph	−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]				
$Ph_2PCH_2PPh_2$	−1340 [195]				
PMe_2Ph	−1396 [171]				
$P(OMe)_3$	−1496 [311]				
PF_3	−1567 [434]				
$AsPh_3$	−1259				
$SbPh_3$	−1430				
$BiPh_2R$	−1260				
Group IVa					
CN^-	−1400				
$C\equiv CPh^-$	−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				
Other					
H^-	−1730 [20]				
$CpV(H)(CO)_3^-$	−1129	300	PFT	green	1,3
n = 2					
PhC≡CPh	−600	300	PFT	brown	1,3
o-phenanthroline	−21	300	WL	violet	1,3
1,10-bipyridyl	−63	300	WL	violet	1,3

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[a] Relative to $VOCl_3$ neat. In parentheses: $\delta(^{51}V)$ 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 wideline 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 ^{13}CO, 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 ν(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 $CpV(CO)_2$-η^2-C_2Ph_2 at 1992 and 1914 cm^{-1}, which are comparable to the values of ν(CO) reported by Nesmeyanov for the tolane complex in CS_2 solution [28].

The δ(^{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 δ(^{51}V) which can be allocated to distinct coordinating ligand functions. Thus, shielding decreases in the series $H^- \simeq \{Sn\} > \{Sb\} > \{C\} \simeq \{P\} > \{As\} > TePh_2 > \eta^2\text{-}PhC{\equiv}CPh > \{S\} > SePh_2 > \{N\} >$ THF.

Coordination of DMSO via S is evidenced by its shift value, which is close to those for other S-ligands, and by the ν(SO) of 1235 cm^{-1} (the ν(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 δ(^{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 -0.05×10^{-28} 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 $[Et_4N][CpV(H)(CO)_3]$ 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 $[Ph_3C][BF_4]$ were added dropwise during 10 min. Upon stirring for ca. 1 h, a dark green solution of $CpV(CO)_3THF$ 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 $CpV(CO)_3L$ was complete after ca. 10 h.

Alternatively, $CpV(CO)_3THF$ can be obtained by external irradiation (high pressure mercury lamp) for 10 min of a solution of 200 mg of $CpV(CO)_4$ 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 $[\{CpV(CO)_3\}_2\text{-}\mu\text{-H}]^-$, equimolar amounts of $CpV(CO)_3THF$ and $[Et_4N][CpV(H)(CO)_3]$ were used.

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