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LONG-CHAIN BI- AND TRI-DENTATE PHOSPHINES AS LIGANDS IN CARBONYLVANADIUM COMPLEXES

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Summary

The potentially tridentate ligands $PCy(CH_2CH_2PPh_2)_2$ ($pcy(pph_2)_2$) and $PPh(CH_2CH_2PCy_2)_2$ ($pph(pcy_2)_2$), p_3, react with $[Et_4N][V(CO)_6]$ and $CpV(CO)_4$ under UV irradiation to form the mononuclear chelate five-ring complexes *cis*-$[Et_4N][V(CO)_4p_3]$ and *cis*-$[CpV(CO)_2pcy(pph_2)_2]$, and the dinuclear $CpV(CO)_2\mu\text{-}p_3(CO)_3VCp$ (where the basic structure of the {*cis*-$CpV(CO)_2PP$} unit is a five-membered ring). Reaction between the carbonyl complexes and the bidentate ligands $Ph_2P(CH_2)_nPPh_2$ ($p_2(n)$; n =5, 6) affords $\{CpV(CO)_3\}_2\text{-}\mu\text{-}p_2(n)$ and $CpV(CO)_3\text{-}\mu\text{-}p_2(n)CpV(CO)_2p_2(n)$. There is also spectroscopic evidence for the formation of $[Et_4N][V(CO)_5p_3]$, *mer*-$[Et_4N][V(CO)_3p_3]$, $[Et_4N]_2[V(CO)_4\text{-}\mu\text{-}p_3V(CO)_5]$ and a species $\{CpV(CO)_2\}_n\{\mu\text{-}pph(pcy_2)_2\}_2$ (n = 2 or 3). Structural assignments are based on IR, ^{31}P and ^{51}V NMR data. The coordination behaviour of p_3 and $p_2(n)$ is compared with that of other bi- and tridentate phosphine ligands.

Introduction

In earlier reports on the coordinative properties of oligodentate phosphine and arsine ligands in carbonylvanadium compounds we considered the influence of electronic and steric factors on the product spectrum arising from the photo-induced replacement of CO for the weaker Group Va ligands.

Thus, while diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1—4) form mononuclear, cisoid chelate structures [1], $Ph_2P{-}PPh_2$, *trans*-$Ph_2PCH{=}CHPPh_2$, $Ph_2AsCH_2CH_2PPh_2$ and $Ph_2AsCH_2CH_2AsPh_2$ act as chelating and/or bridging ligands in mono- and di-nuclear complexes [2]. The tetradentate $[Ph_2PCH_2CH_2PPhCH_2]_2(p_4)$ affords $[\{V(CO)_4\}_{2n}(\mu\text{-}p_4)_n]^{2n-}$ and $\{HV(CO)_4\}_2\text{-}\mu\text{-}p_4$ [1,3], whereagainst the tetradentate $P(CH_2CH_2PPh_2)_3$ (pp_3) and the tridentate $CH_3C(CH_2PPh_2)_3$ (cp_3) and $PPh(CH_2CH_2PPh_2)_2$ (p_3'), p_m, form chelate complexes $[V(CO)_np_m]^-$ (n = 4, 3) and

$CpV(CO)_np_m$ (n = 2 and (p_3' only) 1 *) [4,5]. With cp_3, a complex $CpV(CO)_3$-μ-$cp_3(CO)_2VCp$ is obtained by reaction between $CpV(CO)_4$ and cp_3 in a sealed tube [7].

In the light of these investigations, we have now studied the ligands $Ph_2P(CH_2)_nPPh_2$ (n = 5: $p_2(5)$, n = 6: $p_2(6)$) and $RP(CH_2CH_2PR_2')_2$ (p_3; R = Cy, R' = Ph: $pcy(pph_2)_2$; R = Ph, R' = Cy: $pph(pcy_2)_2$) which, due to the spacing of the PPh_2 functions ($p_2(5)$, $p_2(6)$) or unfavourable steric interactions (cyclohexyl substituents on phosphorus) may be expected either to span *trans*-positions or to act as bridging ligands. No *trans*-disubstituted complexes have, however, been observed: $p_2(5)$ and $p_2(6)$ react to form dinuclear, ligand-bridged species, while the tridentate phosphines p_3 are more variable in their coordination behaviour, yielding chelates and bridged complexes.

Experimental

All reactions were carried out with UV irradiation under nitrogen and in oxygen-free, dried solvents. The general procedures and the irradiation apparatus employed were described previously [5]. $[Na(diglyme)_2][V(CO)_6]$ was purchased (Strem) and converted to $[Et_4N][V(CO)_6]$ as described in ref. 1. $CpV(CO)_4$ and the ligands $p_2(5)$ and $p_2(6)$ were obtained from commercial sources (Strem).

$pcy(pph_2)_2$ and $pph(pcy_2)_2$ were prepared as described for $PhP(CH_2CH_2PPh_2)_2$ [8] from $PPh_2CH{=}CH_2$ and PH_2Cy, or $PPh(CH{=}CH_2)_2$ and $PHCy_2$, respectively, using azobis(isobutyro)nitrile as a catalyst. The ligands were purified by passage of a methanol solution through a column filled with alumina (3 × 15 cm for ca. 5 g of the ligand), to yield, after removal of the solvent and treatment with n-heptane, white powders of the following ^{31}P NMR characteristics (THF solution):

	T (K)	δ (terminal P)	δ (central P)	$^3J(PP)$ (Hz)
$pcy(pph_2)_2$	295	−13.4 (d)	−10.0 (t)	21
	210	−14.5 (d)	−12.0 (t)	
$pph(pcy_2)_2$	295	−0.3 (d)	−16.5 (t)	23

Spectra

IR: ca 0.02 M THF solutions in 0.1 mm KBr cells; Perkin—Elmer spectrometer 337; absolute error ±1 cm^{-1}. $^{31}P\{^1H\}$ NMR: ca. 0.1 M THF solution in rotating 7.5 mm diameter vials; 36.44 MHz, Bruker WH 90 PFT spectrometer; absolute error ±0.1 (narrow signals) to ±2 ppm (broad signals). ^{51}V NMR; ca. 0.1 M THF solution in rotating 7.5 mm diameter vials fitted into 10 mm tubes containing $CDCl_3$ as external lock; standard (external) $VOCl_3$ neat; absolute error ±3 ppm at constant temperature (300 K).

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* The complex $CpV(CO)p_3'$ was formerly assigned the formula *trans*-$[CpV(CO)_2p_3']$ on the basis of IR and NMR spectroscopic arguments [4]. An X-ray structure shows, however, that p_3' is coordinated with all three P atoms [6].

Preparation of complexes

Analytical data and some of the properties and experimental details are listed in Tables 1a and 1b.

$\{\eta^5\text{-}C_5H_5V(CO)_3\}_2\text{-}\mu\text{-}Ph_2P(CH_2)_5PPh_2$ (I), $\{\eta^5\text{-}C_5H_5V(CO)_3\}_2\text{-}\mu\text{-}Ph_2P(CH_2)_6PPh_2$ (II), $\eta^5\text{-}C_5H_5V(CO)_3\text{-}\mu\text{-}Ph_2P(CH_2)_5PPh_2\{\eta^5\text{-}C_5H_5V(CO)_2\}Ph_2P(CH_2)_5PPh_2$ (III), and $\eta^5\text{-}C_5H_5V(CO)_3\text{-}\mu\text{-}Ph_2P(CH_2)_6PPh_2\{\eta^5\text{-}C_5H_5V(CO)_2\}Ph_2P(CH_2)_6PPh_2$ (IV).

A solution of 648 mg $CpV(CO)_4$ (2.84 mmol) and 625 mg of the ligand (1.4 mmol) in ca. 100 ml THF was irradiated for 2 h, during which time the colour changed from yellow-orange to a dark reddish brown. The solution was concentrated to 10 ml (room temperature, 1 Torr), and 50 ml n-heptane were added with vigorous stirring, affording a brown, powdery precipitate. Standing at 250 K over-night yielded additional product, which was filtered off, washed with 10 ml of heptane and dried under high vacuum (4 h). Complexes I and II (irradia-

TABLE 1a

EXPERIMENTAL DETAILS FOR ISOLATED COMPLEXES

Complex	*Molar* ratio [a]	*Irradia-*tion time (min)	*Colour*	*P/V* ratio	*Yield* (%)
$\{CpV(CO)_3\}_2\text{-}\mu\text{-}p_2(5)$ (I)	1/2	120	dark ochre	1.05/1	73
$\{CpV(CO)_3\}_2\text{-}\mu\text{-}p_2(6)$ (II)	1/2	30	ochre	1.08/1	95
II + $CpV(CO)_3\{\mu\text{-}p_2(6)\}CpV(CO)_2p_2(6)$ (IV)	1/1	20	red-brown	1.45/1	38
cis-$\{CpV(CO)_2pcy(pph_2)_2\}$ (V)	1/1	120	rusty brown	3.03/1	54
$CpV(CO)_2\{\mu\text{-}pcy(pph_2)_2\}CpV(CO)_3$ (VI)	1/2	75	curry	1.43/1	95
$CpV(CO)_2\{\mu\text{-}pph(pcy_2)_2\}CpV(CO)_3$ (VII)	1/2	30	brown	1.62/1	23
cis-$[Et_4N][V(CO)_4pcy(pph_2)_2]$ (IX)	1/1	240	dark red	2.88/1	85
cis-$[Et_4N][V(CO)_4pph(pcy_2)_2]$ (X)	1/1	60	red-brown	2.97/1	95

[a] Ligand: carbonyl complex.

TABLE 1b

ANALYTICAL DATA

Complex	Emperical formula	Molecular mass	Analysis (found (calcd.) (%))				
			C	H	N	P	V
I	$C_{45}H_{40}O_6P_2V_2$	840.64	64.3 (64.30)	5.2 (4.80)		7.2 (7.36)	11.5 (12.12)
II	$C_{46}H_{42}O_6P_2V_2$	854.66	64.7 (64.65)	5.7 (4.95)		6.9 (7.25)	10.6 (11.92)
II + IV [a]	$C_{60.5}H_{56}O_{5.5}P_3V_2$	1065.90	68.1 (68.17)	6.0 (5.30)		8.2 (8.72)	9.3 (9.56)
V	$C_{41}H_{44}O_2P_3V$	712.66	68.7 (69.10)	6.3 (6.22)		13.8 (13.04)	7.6 (7.15)
VI	$C_{49}H_{49}O_5P_3V_2$	912.73	64.1 (64.48)	5.7 (5.41)		10.0 (10.18)	11.3 (11.16)
VII	$C_{49}H_{67}O_5P_3V_2$	930.68	62.9 (63.23)	7.0 (7.26)		10.8 (9.98)	11.0 (10.95)
IX	$C_{46}H_{59}NO_4P_3V$	833.84	66.3 (66.26)	7.5 (7.13)	1.7 (1.68)	10.7 (11.14)	6.1 (6.12)
X	$C_{46}H_{77}NO_4P_3V$	851.98	64.7 (64.85)	9.6 (9.11)	1.7 (1.64)	11.2 (10.91)	6.2 (5.98)

[a] Calculated for a 1/1 mixture of II and IV.

tion time for II is 30 min) were obtained in this way as ochre powders.

If the molar ratio of the starting products is 1/1, red-brown products are isolated after 30 min of irradiation, and according to the spectroscopic data (vide infra) and analytical results they consist of equimolar amounts of III + I, and IV + II, respectively.

η^5-$C_5H_5\overline{V(CO)_2PPh_2CH_2CH_2P}(C_6H_{11})CH_2CH_2PPh_2$ (V),
η^5-$C_5H_5\overline{V(CO)_2PPh_2CH_2CH_2P}(C_6H_{11})CH_2CH_2PPh_2V(CO)_3$-$\eta^5$-$C_5H_5$ (VI), and
η^5-$C_5H_5\overline{V(CO)_2P(C_6H_{11})_2CH_2CH_2P}PhCH_2CH_2P(C_6H_{11})_2V(CO)_3$-$\eta^5$-$C_5H_5$ (VII)

516 mg $CpV(CO)_4$ (2.26 mmol) and 1165 mg $pcy(pph_2)_2$ (2.19 mmol) were dissolved in 100 ml THF and irradiated for 2 h. After concentration to ca. 10 ml, the solution was treated with 40 ml n-heptane. The slightly turbid solution was then set aside at 250 K for two days. After that time, red-brown V had precipitated. The complex was filtered off, washed with 10 ml heptane and dried under high vacuum (6 h).

For the preparation of VI and VII, 670 mg $CpV(CO)_4$ (2.9 mmol) and 880 mg of the ligand (1.4 mmol) were brought into reaction as described above. Irradiation times were 75 min ($pcy(pph_2)_2$) and 30 min ($pph(pcy_2)_2$).

cis-$[Et_4N][\overline{V(CO)_4PPh_2CH_2CH_2P}(C_6H_{11})CH_2CH_2PPh_2]$ (IX) and
cis-$[Et_4N][\overline{V(CO)_4P(C_6H_{11})_2CH_2CH_2P}PhCH_2CH_2P(C_6H_{11})_2]$ (X)

A solution of 417 mg $[Et_4N][V(CO)_6]$ (1.2 mmol) and 640 mg of the ligand (1.2 mmol) in ca. 100 ml THF was irradiated for 4 h ($pcy(pph_2)_2$) or 1 h ($pph(pcy_2)_2$), respectively. The initially yellow solution rapidly changed to dark-red. The CO absorption bands due to monosubstitution were absent after the irradiation times specified, and the trisubstituted complex was not formed in appriciable amounts. The solutions were concentrated at room temperature to ca. 10 ml, and 60 ml n-heptane was added with vigorous stirring to precipitate a deep red, pasty product which, after stirring for one day solidified to yield a red, powdery complex. The precipitate was then filtered off, washed twice with 10 ml portions of THF/heptane 1/3, and dried for 6 h under high vacuum. Complexes IX and X are thus obtained as orange-red to dark-red microcrystalline powders.

Results and discussion

The IR spectra of the complexes are listed in Table 2, ^{31}P and ^{51}V NMR spectra in Table 3. For comparison, published spectroscopic data of selected complexes, containing similar phosphorus functions, are listed in Table 4.

The reaction between $CpV(CO)_4$ and the ligands $p_2(5)$ and $p_2(6)$

The photo-induced reaction between $CpV(CO)_4$ and $p_2(n)$ ($n = 5, 6$) in a molar ratio of 2/1 yields red-brown solutions, from which the dinuclear, ligand-bridged complexes $\{CpV(CO)_3\}_2$-μ-$p_2(n)$ ($n = 5$: I, $n = 6$: II) can be precipitated.

With a 1/1 ratio, products with an approximate P/V ratio of 3/2 are obtained, which clearly differ in appearance and spectroscopic properties from I and II. The IR and ^{31}P NMR spectra show absorptions belonging to mono- and di-substituted units. The ^{31}P NMR spectrum also exhibits strong and narrow signals

TABLE 2

IR DATA (ν(CO) RANGE)

Complex	ν(CO) (cm^{-1}) [c]						
I	1950	1863	1846	(1768)[d]			
II	1950	1868	1855				
$CpV(CO)_3$-μ-$p_2(6)CpV(CO)_2p_2(6)$ (III) [a]	1951	(1909) [e]	1864	1848	(1828) [e]	1765 [d]	
IV [a]	1954	1868	1853	(1845) [e]	1767 [d]		
V	1878	1807	(1760) [f]				
VI	1953	1868	1845	(1800) [e]	1792 [d]		
VII	1953	1870 [d]	1866	1850	1789 [d]	(1730) [f]	
$\{CpV(CO)_2\}_3\{\mu\text{-}pph(pcy_2)_2\}_2$ (VIII) [b]	1865	1790	(1755) [f]				
$[V(CO)_5pcy(pph_2)_2]^-$	1963	1861	1815				
IX	(1915) [f]	1897	1793	1770	1745	(1725) [f]	
$[V(CO)_5pph(pcy_2)_2]^-$	1965	1865	1822				
X	(1920) [f]	1895	1820	1785	1770	1745	(1720) [f]
$[V(CO)_4\text{-}\mu\text{-}pph(pcy_2)_2V(CO)_5]^{2-}$ (XI) [b]	1965	1898	1865	1825	1790	1770	(1730) [f]

[a] Mixture of III + I and IV + II, respectively. [b] Tentative formulation; see text for discussion. [c] Absorptions in brackets are weak signals belonging to by-products. [d] Disubstitution. [e] Unassigned. [f] Trisubstitution.

around −18.5 ppm typical of uncoordinated PPh_2 groups. As shown by the ease of the formation of I and II, the overall reaction is probably represented by eq. 1 to 3 (see also ref. 11 for the first reaction step), where eq. 3 leads to the new products III and IV.

$$CpV(CO)_4 + p_2(n) \rightarrow CpV(CO)_3p_2(n) + CO \qquad (1)$$

$$CpV(CO)_3p_2(n) + CpV(CO)_4 \rightarrow \text{I, II} + CO \qquad (2)$$

$$\text{I, II} + p_2(n) \rightarrow CpV(CO)_3\text{-}\mu\text{-}p_2(n)CpV(CO)_2p_2(n) + CO \qquad (3)$$

$(n = 5\text{: III}, n = 6\text{: IV})$

Thus, dinuclear biligate complexes are formed having the IR absorption at ca. 1765 cm^{-1} characteristic of a *cis*-disubstituted, open complex such as *cis*-$[CpV(CO)_2(PPh_2Me)_2]$ (cf. Table 4). The reaction does not proceed to give quantitative formation of III and IV, which is probably due to competing photo-induced splitting of the vanadium—phosphorus bond. Elemental analysis of the isolated products indicate an approximate 1/1 mixture of I + III and II + IV, respectively.

The reaction between $CpV(CO)_4$ and the ligands $pcy(pph_2)_2$ and $pph(pcy_2)_2(p_3)$

For a 1/1 ratio of $CpV(CO)_4$: $pcy(pph_2)_2$ the reaction product is *cis*-$[CpV(CO)_2pcy(pph_2)_2]$ (V). The CO frequencies are at comparatively high wave numbers (1878 and 1807 cm^{-1}) and thus indicate a chelate five-ring structure (compare *cis*-$[CpV(CO)_2p_2(2)]$, *cis*-$[CpV(CO)_2p_2(4)]$ and *cis*-$[CpV(CO)_2p_3']$ in Table 4). The ^{51}V and ^{31}P NMR results are also consistent with this assumption: The ^{31}P NMR signal at −13.5 ppm shows that the only uncoordinated phosphorus function present is the PPh_2 group. The $^3J(PP)$ coupling (33 Hz) is somewhat enhanced as compared to the free ligand (21 Hz). The fine structure splitting (4.5 Hz) probably reflects $^5J(PCCPVP)$ coupling.

The analogous reaction between $CpV(CO)_4$ and $pph(pcy_2)_2$ yields a *cis*-disubstituted product in which, according to the ^{31}P NMR spectrum all the phos-

(Continued on p. 350)

TABLE 3

^{31}P (210 K) AND ^{51}V NMR DATA [a]

Complex	$\delta(^{31}P)_{uncoord.}$ (ppm)	$^3J(PP)$ (Hz)	$\delta(^{31}P)_{coord.}$ (ppm)	$\Delta\nu_{1/2}(^{31}P)_{coord.}$ (Hz) [c]	$\delta(^{51}V)$ (ppm)	$\Delta\nu_{1/2}(^{51}V)$ (Hz) [c]
I	[d]		[d]		−1357	420
II	(−18.5)	—	76	230	[d]	
III [b]	−18.1	—	87, 84, 74 [e]	70, 70, 160	−1360, −1140	460, v. br.
IV [b]	−18.7	—	86, 85, 74 [e]	50, 80, 160	−1360, [f]	500
V	−13.47 (dd) [g]	33 [g]	(121) [h]		(−895) [h]	(1050) [h]
			113, 99	320, 270	−1112	670
VI	(−14.0)	—	79, 99, 114 [i]	400, 400, 470	−1366, −1104	920, 1050
VII	—	—	(69), 72, 105	260, 440	−1372, −1040	1100, v. br.
VIII [b]	—	—	104	470	d	
IX	−14.6(d)	43	86, (78)	1600, (800)	−1824(t) [k]	
	(−14.0) [j]					
X	−2.4(d) [l]	34	95	1400	−1834	950
XI	−1.8(d)	33		v. br.	−1835, −1885(d) [m]	
	−17.5				(−1953) [n]	830

[a] Data in brackets correspond to weak signals representing by-products in negligeable amounts. [b] See footnotes *a* and *b* in Table 2. [c] Width of the NMR signals at half height; v. br. = very broad. [d] Not measured. [e] $CpV(CO)_3$—PPh_2. [f] Signal for disubstitution not observed. [g] Doublet of doublets; fine structure splitting $^5J(PP)$ 4.5 Hz. [h] CpV(CO)L. [i] 79: $CpV(CO)_3$—PPh_2, 99: $CpV(CO)_2$—PCy, 114: $CpV(CO)_2$—PPh_2. [j] Singlet; not assigned. [k] Triplet; $^1J(VP)$ ca. 220 Hz. [l] Fine structure indicated. [m] $[V(CO)_5pph(pcy_2)_2]^-$, doublet, $^1J(VP)$ 245 Hz. [n] $[V(CO)_6]^-$ (very narrow signal).

TABLE 4

IR AND NMR DATA FOR SELECTED CARBONYLPHOSPHINEVANADIUM COMPLEXES

Complex [a]	ν(CO) (cm^{-1})	$\delta(^{31}P)$ [b] (ppm)	$\delta(^{51}V)$ (ppm)	$\Delta\nu_{1/2}(^{51}V)$ (Hz)	$^{1}J(VP)$ (Hz)	Refs.
CpV(CO)$_3$PPh$_2$Me	1950 1863 1850	79	−1368		150	9
cis-[CpV(CO)$_2$(PPh$_2$Me)$_2$]	1856 1763	80	−1152		*c*	9
cis-[CpV(CO)$_2$p$_2$(2)]	1870 1799	112	−1110		*c*	1, 9
cis-[CpV(CO)$_2$p$_2$(4)]	1860 1774	72	−1360		*c*	1, 9
cis-[CpV(CO)$_2$p$_3$′]	1868 1795	102, 114	−1230	310	*c*	4
CpV(CO)p$_3$′ [d]	1798 1764	122	−970	380	*c*	4, 6
[V(CO)$_5$PCy$_3$]$^-$	1957 1849 1810		−1854	90	220	10
[V(CO)$_5$PPh$_2$Me]$^-$	1963 1859 1818		−1839	160	200	9
cis-[V(CO)$_4$(PPh$_2$Me)$_2$]$^-$	1898 1792 1772 1743		−1671	630	*c*	9
cis-[V(CO)$_4$p$_2$(2)]$^-$	1903 1799 1780 1742		−1790		225	1, 9
cis-[V(CO)$_4$p$_2$(4)]$^-$	1897 1795 1770 1746		−1699		*c*	1, 9
[V(CO)$_5$p$_3$′]$^-$	1965 1857 1818		−1820		*c*	4
cis-[V(CO)$_4$p$_3$′]$^-$	1903 1800 1770 1740		−1830	60	225	4, 5
mer-[V(CO)$_3$p$_3$′]$^-$	1910 1805 1714	62, 87	−1720	1900	*c*	4, 5

[a] Abbreviations for ligands: p$_2$(2) = Ph$_2$P(CH$_2$)$_2$PPh$_2$, p$_2$(4) = Ph$_2$P(CH$_2$)$_4$PPh$_2$, p$_3$′ = PPh(CH$_2$CH$_2$PPh$_2$)$_2$. [b] For coordinated P at 200—220 K. [c] Unresolved. [d] See footnote on p. 344.

phorus atoms are coordinated. Hence, the complex formed may be $\{CpV(CO)_2\}_2\{\mu\text{-}pph(pcy_2)_2\}_2$ (VIIIa) or $\{CpV(CO)_2\}_3\{\mu\text{-}pph(pcy_2)_2\}_2$ (VIIIb) or a mixture of VIIIa and VIIIb (the P/V ratio is 2.3/1) (see also the discussion of the overall reaction below). In VIIIb, the ligands act both as chelating and as bridging ligands in that two $\{Cp\overline{V(CO)_2PCy_2(CH_2)_2P}Ph(CH_2)_2PCy_2\}$ units are connected to each other via a $\{CpV(CO)_2\}$ moiety coordinated to the two free PCy_2 groups.

If the $CpV(CO)_4/p_3$ ratio is 2/1 to 3/1, the well defined complexes $Cp\overline{V(CO)_2PPh_2(CH_2)_2P}Cy(CH_2)_2PPh_2CpV(CO)_3$ (VI) and $Cp\overline{V(CO)_2PCy_2(CH_2)_2P}Ph(CH_2)_2PCy_2CpV(CO)_3$ (VII) are obtained, and in these the phosphine again has a chelating in addition to a bridging function. The structural assignments are based on the IR spectra (ν(CO) for $\{CpV(CO)_3\}$ and $\{cis\text{-}CpV(CO)_2\}$-chelate 5-rings), the ^{51}V NMR signals at −1370 ppm (monosubstitution) and −1100 ppm (disubstitution), and the ^{31}P NMR spectra (no uncoordinated phosphorus; $\delta(^{31}P)$ values for coordinated P: +79 ($\{CpV(CO)_3PPh_2\}$), +99 ($\{CpV(CO)_2PCy\}$), +114 ($\{CpV(CO)_2PPh_2\}$), +105 ($\{CpV(CO)_2PCy_2\}$ or $\{CpV(CO)_2PPh\}$)).

The overall reaction between $CpV(CO)_4$ and the tridentate phosphines p_3 can be summarized by the following scheme (eq. 4 to 7):

$$CpV(CO)_4 + p_3 \rightarrow CpV(CO)_3p_3 \tag{4}$$

$$CpV(CO)_3p_3 \rightarrow V + CO \tag{5}$$

$$V \rightarrow CpV(CO)p_3 + CO \text{ (incomplete reaction)} \tag{6a}$$

$$V + CpV(CO)_4 \rightarrow VI, VII + CO \tag{6b}$$

$$VII + p_3 + VII \rightarrow VIIIb + 2\ CO \tag{7}$$

with a possible side-chain

$$\begin{array}{l} CpV(CO)_3p_3 + p_3 \rightarrow cis\text{-}[CpV(CO)_2(p_3)_2] + CO \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow + CpV(CO)_4 \\ \qquad\qquad\qquad\qquad\qquad\quad VIIIa + 2\ CO \end{array} \tag{5'}$$

The reaction path represented by eq. 4 to 6a, which is the only one encountered with $PhP(CH_2CH_2PPh_2)_2$ (p_3') ([4] and footnote on page 344), appears to be hindered with p_3 due to the greater spatial requirement of the PCy and PCy_2 groups. The trisubstituted $CpV(CO)p_3$ can, however, be detected as a by-product by its IR absorption at 1760 cm^{-1} and, in the case of $CpV(CO)pcy(pph_2)_2$, the $\delta(^{51}V)$ (−895 ppm) and the $\delta(^{31}P)$ value (+121 ppm) (compare $CpV(CO)p_3'$ in Table 4).

The reaction between $[Et_4N][V(CO)_6]$ and p_3

The final products of reaction isolated from photosubstitution in the hexacarbonylvanadate (−I) anion are the *cis*-disubstituted complexes $[Et_4N][V(CO)_4p_3]$ ($p_3 = pcy(pph_2)_2$: IX, $p_3 = pph(pcy_2)_2$: X). The trisubstituted complexes *mer*-$[Et_4N][V(CO)_3p_3]$ are indicated only by a weak, but typical absorption at ca. 1920 cm^{-1}. In contrast, p_3' (and other tri- and tetra-dentate phosphines) has been shown to replace three CO groups to form *mer*-$[Et_4N][V(CO)_3p_3']$ [4,5] after sufficiently long irradiation times.

As shown by the IR spectra after about 10 min of UV irradiation, the first reaction step is the formation of $[Et_4N][V(CO)_5p_3]$ (cf. Table 3). The reaction proceeds rapidly to yield the disubstituted species, which exhibit a doublet of narrow lines in the ^{31}P NMR spectrum at —14.6 (IX) and —1.3 (X) ppm, indicating uncoordinated PPh_2 (IX) and PCy_2 (X), respectively, and thus a rigid chelate 5-ring structure. This is also evidenced by the rather high ^{51}V shielding ($\delta(^{51}V)$ ca. —1830 ppm; compare the analogous p_3' complexes in Table 4). The ^{51}V resonance of IX is resolved into a triplet ($^1J(^{51}V—^{31}P)$ 220 Hz). The ^{31}P absorptions of the coordinated phosphorus atoms are extremely broad, which is characteristic of depressed decoupling of the ^{31}P and ^{51}V nucleus and represents the unresolved eight-line pattern to be expected for the coupling of a spin 1/2 (^{31}P) to a spin 7/2 (^{51}V) nucleus. A similar effect has been observed for the $^1H—^{51}V$ coupling in $[CpV(H)(CO)_3]^-$ [3] and η^7-$C_7H_7V(CO)_3$ [12], and for the $^{19}F—^{51}V$ coupling in $[VOF_4]^-$ [13]. The $^{31}P—^{51}V$ coupling constant obtained indirectly from the overall width of the ^{31}P signals (ca. 1600/8) is in accord with those determined directly from the ^{51}V NMR spectra of comparable pentacarbonylphosphinevanadates (—I) [10].

An additional product is formed from $[V(CO)_6]^-$ and $pph(pcy_2)_2$ if the ratio of the reactants is 2/1. The red-brown powder isolated from this reaction (P/V 1.8/1) clearly differs from X in its IR (Table 2) and ^{51}V NMR (Table 3) spectra, which indicate that the complex contains $\{V(CO)_5^-\}$ (ν(CO) 1965 and 1865 cm^{-1}; $\delta(^{51}V)$ —1885 ppm, doublet: ^1J(VP) 245 Hz; compare $[V(CO)_5PCy_3]^-$ in Table 4) and $\{cis\text{-}V(CO)_4^-\}$ ($\delta(^{51}V)$ —1835 ppm) units. The compound must therefore contain $[V(CO)_4\text{-}\mu\text{-}p_3V(CO)_5]^{2-}$ (XI) moieties, linked to moieties in which the ligand is partly uncoordinated (cf. the ^{31}P NMR data in Table 3).

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