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THE COORDINATIVE PROPERTIES OF *cis/trans*-1,4-DIPHOSPHABUTENE AND 1,4-DIPHOSPHABUTYNE IN CARBONYLVANADIUM COMPOUNDS

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Summary

$[Et_4N][V(CO)_6]$ and η^5-$CpV(CO)_4$ react photochemically with *cis*-$Ph_2PCH{=}CHPPh_2$ (*c*-dppe) to form the mononuclear chelates *cis*-$[Et_4N][V(CO)_4$*c*-dppe] and *cis*-[η^5-$CpV(CO)_2$*c*-dppe]. With *trans*-$Ph_2PCH{=}CHPPh_2$ (*t*-dppe) and $Ph_2PC{\equiv}CPPh_2$ (dppa), the dinuclear complexes $[Et_4N]_2[\{V(CO)_5\}_2\mu$-*t*-dppe], $[Et_4N]_2[\{V(CO)_5\}_2\mu$-dppa], $\{\eta^5$-$CpV(CO)_3\}_2\mu$-*t*-dppe, *cis*-[$\{\eta^5$-$CpV(CO)_2\}_2(\mu$-*t*-dppe$)_2$], $\{\eta^5$-$CpV(CO)_3\}_2\mu$-dppa and $\{\eta^5$-$CpV(CO)_2\}_2(\mu$-dppa$)_2$ (which probably has a *trans*-configuration) are obtained. Spectroscopic evidence is given for several other complexes, including η^5-$CpV(CO)_2$ η^2-dppa with the ligand coordinated via the alkyne system. The complexes are discussed on the basis of their IR (CO-stretching region), ^{31}P and ^{51}V NMR spectra.

Introduction

In photoinduced reactions between carbonylvanadium compounds and oligo-tertiary phosphines and arsines, the products are commonly mononuclear chelate complexes [1—4]. If, however, for electronic or steric reasons, such structures are less favoured, dinuclear complexes may be formed. Thus, CO-substitution in $[V(CO)_6]^-$ for P_2Ph_4 [5], $Ph_2P(CH_2)_2AsPh_2$ and $Ph_2As(CH_2)_2AsPh_2$ [4] or $[Ph_2P(CH_2)_2PPhCH_2]_2$ [3] (LL) yields dinuclear complexes of the type $[\{V(CO)_5\}_2\mu\text{-LL}]^{2-}$ and *cis*-$[\{V(CO)_4\}_2(\mu\text{-LL})_2]^{2-}$. For derivatives of η^5-$CpV(CO)_4$, ligand-bridged, bimetallic structures are known with the tripod phosphine $MeC(CH_2PPh_2)_3$ [6] and the diphosphanes P_2Me_4, P_2Cy_4 and $P_2Me_2Ph_2$ [7].

Similarly, *trans*-$Ph_2PCH{=}CHPPh_2$ (*t*-dppe) and $Ph_2PC{\equiv}CPPh_2$ (dppa) can be expected to act as bridging ligands, whereas the coordinative properties of *cis*-$Ph_2PCH{=}CHPPh_2$ (*c*-dppe) towards η^5-$CpV(CO)_4$ and $[V(CO)_6]^-$ should parallel those of $Ph_2PCH_2CH_2PPh_2$ (dppe) [3] and *o*-$C_6H_4(PPh_2)_2$ (ppb) [8].

Typical examples of the different structural features encountered with the ligands *c*-dppe, *t*-dppe and dppa are the compounds M(CO)$_4$*c*-dppe (M = Cr, Mo, W) [9], [η^5-CpMn(NO)*c*-dppe]$^+$ [10], [η^5-CpMn(CO)(NO)*t*-dppe/dppa]$^+$ and [{η^5-CpMn(CO)NO}$_2\mu$-*t*-dppe/μ-dppa]$^{2+}$ [10]. A further interesting aspect of these ligands is the presence of an olefinic or acetylenic system which may compete with the PPh$_2$ groups for coordination to the metal.

Experimental

General method and materials

All operations were carried out under inert gas in oxygen-free solvents. For the preparation of monosubstituted products, a Duran vessel of about 30 ml capacity was placed close to the mercury source (Hanau TQ 150), protected by a quartz immersion well. The system was cooled from the outside with water. CO released during the reaction was partly retained by a mercury valve (20 mm excess pressure) and removed from time to time by a nitrogen flow. For disubstitution, an UV irradiation apparatus (Mangels 13/21) was used, which allows agitation of the reaction mixture and removal of carbon monoxide by passing a weak N$_2$-stream through a filter plate at the bottom of the vessel. The two types of apparatus will be referred to as *A* and *B*, respectively, in the preparative procedures described below. Starting materials were obtained from commercial sources (Strem); [Na(diglyme)$_2$][V(CO)$_6$] was converted to [Et$_4$N]-[V(CO)$_6$] [3].

Spectroscopic measurements

IR: ca. 0.02 *M* THF or CH$_3$CN solutions in 0.1 mm KBr cuvettes or as Nujol mulls; Perkin—Elmer 337; absolute error ±1 to ±3 cm^{-1}. ^{51}V NMR: ca. 0.2 *M* THF or CH$_3$CN solutions in rotating 7.5 mm diameter vials fitted into 10 mm vials containing CDCl$_3$ as external lock; Bruker WH 90, 23.66 MHz; external standard VOCl$_3$/CDCl$_3$; absolute error ca. ±1 ppm (limiting factor is the temperature constance). {^{1}H}^{31}P NMR: ca. 0.2 *M* THF or CH$_3$CN solutions in rotating 7.5 mm diameter vials at 202 ± 2 K; Bruker WH 90, 36.44 MHz; external standard H$_3$PO$_4$ 80%; external lock D$_2$O; absolute error less than 1 ppm for sharp signals and ca. ±3 ppm for broad resonances.

Analytical data and properties of isolated complexes are listed in Table 1.

cis-Tetraethylammonium tetracarbonyl(cis-1,1,4,4-tetraphenyl-1,4-diphosphabutene)vanadate(—I) cis-[Et$_4$N][V(CO)$_4$cis-Ph$_2$PCH=CHPPh$_2$] (Ib). 0.43 g (1.24 mmol) [Et$_4$N][V(CO)$_6$] and 0.49 g (1.24 mmol) *c*-dppe dissolved in 25 ml THF were irradiated for 125 min (*A*) with magnetic stirring. A red-brown solution was formed, from which Ib precipitated as a rust-coloured powdery substance which was filtered off, washed three times with 8 ml portions of n-heptane, and dried under high vacuum.

cis-Tricarbonyl-η^5-cyclopentadienyl(cis-1,1,4,4-tetraphenyl-1,4-diphosphabutene)vanadium(+I) cis-[η^5-CpV(CO)$_2$cis-Ph$_2$PCH=CHPPh$_2$] (IIb). A solution of 0.25 g (1.09 mmol) CpV(CO)$_4$ and 0.43 g (1.09 mmol) *c*-dppe in 110 ml THF was irradiated for 30 min (*B*) and evaporated to 10 ml. On addition of 60 ml n-heptane in small portions, IIb precipitated out as a copper-coloured powder, which was washed with heptane and, after two reprecipitations from

TABLE 1

ANALYTICAL DATA FOR ISOLATED COMPLEXES

Complex	Colour	Empirical formula (molecular mass)	Analysis (found (calcd.) (%))				
			C	H	N	P	V
Ib	rust-coloured	$C_{38}H_{42}NO_4P_2V$ (689.7)	65.6 (66.18)	6.2 (6.14)	2.1 (2.03)	8.5 (8.98)	7.7 (7.39)
IIb	copper-coloured	$C_{33}H_{27}O_2P_2V$ (568.5)	69.1 (69.73)	5.0 (4.78)	—	10.3 (10.90)	8.7 (8.96)
III	yellow	$C_{52}H_{62}N_2O_{10}P_2V_2$ (1038.9)	59.1 (60.12)	6.0 (6.02)	2.6 (2.70)	5.9 (5.96)	9.8 (9.81)
IVb	yellow-orange	$C_{42}H_{32}O_6P_2V_2$ (796.5)	63.6 (63.33)	4.1 (4.05)	—	7.7 (7.78)	12.4 (12.79)
IVc	brown	$C_{66}H_{54}O_4P_4V_2$ (1136.9)	69.2 (69.73)	5.2 (4.79)	—	11.0 (10.90)	8.8 (8.96)
V	yellow	$C_{52}H_{60}N_2O_{10}P_2V_2$ (1036.9)	59.5 (60.24)	5.9 (5.83)	2.9 (2.70)	5.9 (5.97)	9.6 (9.83)
VIb [a]	brown	$C_{42}H_{30}O_6P_2V_2$ (794.5)	63.0 (63.49)	4.7 (3.81)	—	8.6 (7.80)	13.0 (12.82)
VId	ochre	$C_{66}H_{50}O_4P_4V_2$ (1132.9)	67.5 (69.97)	4.4 (4.45)	—	9.1 (10.94)	8.4 (8.99)

[a] Contains mononuclear complex VIa.

THF/heptane, dried under high vacuum. Copper-red crystals of IIb can be obtained from a saturated THF solution treated with a small amount of heptane at 255 K.

Bis(tetraethylammonium)decacarbonyl-μ-(trans-1,1,4,4-tetraphenyl-1,4-diphosphabutene)divanadate(—I) $[Et_4N]_2[\{V(CO)_5\}_2\mu\text{-}(trans\text{-}Ph_2PCH{=}CHPPh_2)]$ *(III)*. 0.44 g (1.26 mmol) $[Et_4N][V(CO)_6]$ and 0.50 g (1.26 mmol) *t*-dppe were dissolved in 25 ml THF and irradiated for 240 min (*A*). During this time, yellow III precipitated out, and was filtered off, washed with heptane/THF, and dried.

From the supernatant liquid or the filtrate a red oil can be precipitated out with n-heptane; spectroscopic data indicate that it is a monosubstituted product.

If the reaction is carried out in apparatus *B* and with a molar ratio complex/ligand of 1/2, a micro-crystalline red product giving non-reproducible analyses suggests that it is a mixture of mono- and di-substitution product.

Hexacarbonyldi-η^5-cyclopentadienyl-μ-(trans-1,1,4,4-tetraphenyl-1,4-diphosphabutene)divanadium(+I) $\{\eta^5\text{-}CpV(CO)_3\}_2\mu\text{-}(trans\text{-}Ph_2PCH{=}CHPPh_2)$ *(IVb)*. A solution of 0.55 g (2.42 mmol) $CpV(CO)_4$ and 0.48 g (1.21 mmol) *t*-dppe in 30 ml THF was irradiated for 60 min (*A*). IVb precipitated out as an insoluble yellow-orange powder, which was washed with THF and dried under high vacuum.

cis-Tetracarbonyldi-η^5-cyclopentadienylbis[μ-(trans-1,1,4,4-tetraphenyl-1,4-diphosphabutene)]divanadium(+) cis-$\{\eta^5\text{-}CpV(CO)_2\}_2[\mu\text{-}(trans\text{-}Ph_2PCH{=}CHPPh_2)]_2$ *(IVc)*. 0.24 g (1.05 mmol) $CpV(CO)_4$ and 0.83 g (2.1 mmol) *t*-dppe were dissolved in 100 ml THF and irradiated for 40 min (*B*). The dark-brown solution was concentrated to 10 ml and brown IVc was precipitated with 60 ml n-heptane added in small portions and with vigorous stirring of the suspen-

TABLE 2

CO-STRETCHING FREQUENCIES AND FORCE CONSTANTS

Ligand LL Complex	Medium	ν(CO) (cm^{-1}) [a]				Force constants × 10^{-2} (Nm^{-1}) [b]				
cis-$Ph_2PCH{=}CHPPh_2$										
$[V(CO)_5LL]^-$ (Ia)	THF	1964	1864	1823		13,54	14,51	0,24		
cis-$[V(CO)_4LL]^-$ (Ib) [c]	CH_3CN	1904	1823	1790	1758	13,14	13,60	0,28	0,66	0,67
$CpV(CO)_3LL$ (IIa)	THF	1950	1865	1855		13,90	14.01	0,40	0,53	
cis-$CpV(CO)_2LL$ (IIb) [c]	THF	1874	1806			13,68	0,51			
trans-$Ph_2PCH{=}CHPPh_2$										
$[\{V(CO)_5\}_2\mu\text{-}LL]^{2-}$ (III) [c]	CH_3CN	1965	1830	(1830)		13,73	14,15	0,31		
$CpV(CO)_3LL$ (IVa)	THF	1950	(1865)	1852		13,85	14,05	0,40	0,53	
$\{CpV(CO)_3\}_2\mu\text{-}LL$ (IVb) [c, d]	Nujol	1951	1878	1834		13,59	14,24	0,36	0,48	
cis-$\{CpV(CO)_2\}_2(\mu\text{-}LL)_2$ (IVc) [c]	THF	1870	1803			13,62	0,50			
$Ph_2PC{\equiv}CPPh_2$										
$[\{V(CO)_5\}_2\mu\text{-}LL]^{2-}$ (V) [c]	CH_3CN	1970	1862	1835		13,74	14,52	0,26		
$CpV(CO)_3LL$ (VIa)/										
$\{CpV(CO)_3\}_2\mu\text{-}LL$ (VIb) [c]	THF	1955	1870	1855		13,90	14,12	0,40	0,53	
$\{$*cis*-$CpV(CO)_2LL\}$ (VIc) [e]	THF	1870	1804			13,63	0,49			
$\{CpV(CO)_2\}_2(\mu\text{-}LL)_2$ (VId) [c, d, f]	Nujol	1892	1864			14,24	0,21			
$CpV(CO)_2\eta^2\text{-}LL$ (VII)	THF	1995	1920			15,48	0,59			
$[V(CO)_5PPh_2Et]^-$ [g]	THF	1964	1858	1821		13,52	14,45	0,25		
$CpV(CO)_3PPh_2Et$ [g]	THF	1951	1863	1847		13,78	14,02	0,41	0,55	
cis-$[V(CO)_4Ph_2PCH_2CH_2PPh_2]^-$ [h]	THF	1903	1799	1780	1747	21,89	13,52	0,33	0,56	0,72
cis-$CpV(CO)_2Ph_2PCH_2CH_2PPh_2$ [h]	THF	1870	1799				13,60	0,53		
cis-$[V(CO)_4$*o*-$C_6H_4(PPh_2)_2]^-$ [g]	THF	1899	1857	1798	1776	13,46	13,68	0,16	0,72	0,63
cis-$CpV(CO)_2$*o*-$C_6H_4(PPh_2)_2$ [g]	THF	1876	1811			13,73	0,48			

[a] Assignments: $A_1^{(2)}$, E, $A_1^{(1)}$ (Ia, III and V); $A_1^{(2)}$, $A_1^{(1)}$, B_1, B_2 (Ib); $A'^{(1)}$, A'', $A'^{(2)}$ (IIa, IVa, IVb, VIa and VIb); A', A'' (IVc and VIc); A_1, B_1 (VId). Values in brackets were estimated for the calculation of force constants. [b] Assignment: k_1 (axial), k_2 (equatorial), k_i (interaction force constant) (Ia, III and V); k_1, k_2, k_c, k_c' (both for *cis* interaction), k_t (trans interaction) (Ib); k_1, k_2, k_c, k_t (IIa, IVa, IVb, VIa and VIb); k, k_i (IVc, VIc, and VId). [c] These complexes were isolated in substance. [d] In Nujol, the CO absorptions are shifted to smaller wave numbers for about 10 to 30 cm^{-1}; force constants therefore cannot be compared with those obtained from solution spectra. [e] Mono- or di-nuclear. [f] Probably *trans* configurated. [g] Unpublished. [h] From ref. 3.

sion. The complex was reprecipitated twice from THF/heptane, washed with heptane and dried under high vacuum.

Bis(tetraethylammonium)decacarbonyl-μ-(1,1,4,4-tetraphenyl-1,4-diphosphabutyne)divanadate(—I) $[Et_4N]_2[\{V(CO)_5\}_2\text{-}\mu\text{-}Ph_2PC{\equiv}CPPh_2]$ *(V).* The complex precipitated during irradiation (*A*, 100 min) of 25 ml of a THF solution containing 0.53 g (1.52 mmol) $[Et_4N][V(CO)_6]$ and 0.60 g (1.52 mmol) dppa. It was washed with THF and dried under high vacuum.

Hexacarbonyldi-η⁵-cyclopentadienyl-μ-(1,1,4,4-tetraphenyl-1,4-diphosphabutyne)divanadium(+I) $\{\eta^5\text{-}CpV(CO)_3\}_2\mu\text{-}Ph_2PC{\equiv}CPPh_2$ *(VIb).* A solution of 0.52 g (2.28 mmol) $CpV(CO)_4$ and 0.45 g (1.14 mmol) dppa dissolved in 30 ml THF was irradiated for 30 min (*A*). The dark-brown solution was evaporated to 10 ml and treated with 70 ml n-heptane. A brown precipitate of VIb (containing small amounts of VIa; see following section) was thus obtained which, after standing for three days at 255 K, was filtered off, washed with heptane, and dried under high vacuum.

Tetracarbonyldi-η⁵-cyclopentadienylbis[μ-(1,1,4,4-tetraphenyl-1,4-diphosphabutyne)]divanadium(+I) $\{\eta^5\text{-}CpV(CO)_2\}_2(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2$ *(VId).* 30 ml of a THF solution containing 0.32 g (1.39 mmol) $CpV(CO)_4$ and 0.55 g (1.39 mmol) dppa were irradiated for 165 min (*A*). During this time an ocherous powder of VId precipitated out, and was washed with two 5 ml portions of THF and dried under high vacuum. VId is only slightly soluble in CH_3CN and so could not be purified by recrystallization.

Dicarbonyl-η⁵-cyclopentadienyl-η²-(1,1,4,4-tetraphenyl-1,4-diphosphabutyne)-vanadium(+I) $\eta^5\text{-}CpV(CO)_2\eta^2\text{-}Ph_2PC{\equiv}CPPh_2$ *(VII).* An optimum amount of VII is formed after 135 min irradiation time (*A*) of a solution containing 0.59 g (2.59 mmol) $CpV(CO)_4$ and 1.02 g (2.95 mmol) dppa in 10 ml THF. After irradiation, the dark-brown solution also contains the compounds VIa, VIc and VId (see the following section). VII cannot be isolated by gel- or adsorption chromatography or by fractionated precipitation. It decomposes when the solution is evaporated.

Results

Spectra

IR, ^{31}P NMR and ^{51}V NMR spectral data of the complexes (including those which were not isolated but spectroscopically identified) are listed in Tables 2 and 3. For comparison, data for complexes containing the ligands PPh_2Et, dppe and ppb are included.

The IR pattern in the CO-stretching region is consistent with the local C_{4v} $(2A_1 + E)$, C_{2v} $(2A_1 + B_1 + B_2)$ and C_s symmetry $(2A' + A''$ and $A' + A'')$, respectively). For allocation of the stretching modes of ionic complexes we follow published procedures (C_{4v} [11], C_{2v} [12]); force constants were calculated according to the Cotton—Kraihanzel approximation (C_{4v} [13]) and a procedure recently proposed by Jernigan and Brown (C_{2v} [12]). Band assignment for derivatives of $CpV(CO)_4$ was carried out on the basis of the CK-assumption $k_1 < k_2$, although this approach, derived for pseudo-octahedral complexes, may not hold strictly in our tetragonally pyramidal complexes. For the computation of force constants, the secular equations given by Durig et al. [14] were

TABLE 3

^{31}P AND ^{51}V NMR DATA

Complex	$\delta(^{31}P)$ [a] (ppm)	$\Delta\delta(P)$ [b] (ppm)	$\delta(^{51}V)$ [c] (ppm)	$^1J(VP)$ (Hz)
Ia			—1835	214
Ib			—1830	—
IIa	—25			
IIb	+120	143	—1143	—
III			—1836	214
IVa	+9	103	—1362	—
IVc	+120	128	—1143	—
V			—1823	232
VIa	—35, +69	104	—1344	—
VIb	+73	108	—1281	—
VIc	+91	126	—1139	—
VII	+13		—517	
$[V(CO)_5PPh_2Et]^-$ [d]			—1842	225
$CpV(CO)_3PPh_2Et$ [d]	+90	104	—1361	171
cis-$[V(CO)_4dppe]^-$ [e]			—1790	225
cis-$CpV(CO)_2dppe$ [e]	+112	127	—1110	—
cis-$[V(CO)_4ppb]^-$ [d]			—1755	230
cis-$CpV(CO)_2ppb$ [d]	+117	132	—1125	—

[a] Relative to H_3PO_4 at 200 K. The ^{31}P NMR shift values for the ligands are: *c*-dppe —23.1, *t*-dppe —8.2, dppa —32.6 ppm. [b] Coordination shift. [c] Relative to $VOCl_3$ at room temperature. [d] Unpublished. [e] From ref. 3.

used. Employing the additional relation $k_{trans} = 1.33\ k_{cis}$ *, all four force constants can be calculated.

At room temperature, evaluable ^{31}P NMR spectra cannot be obtained due to quadrupole interaction between the ^{51}V ($I = 7/2\ \hbar$) and ^{31}P nuclei. For neutral complexes, however, molecular correlation times increase considerably with decreasing temperature [8]. At about 220 to 200 K, relaxation times become sufficiently short to cause ^{51}V—^{31}P decoupling. The signals obtained (to low field for coordinated phosphorus), though distinct, are still broadened through interference with the field gradient tensor of the neighbouring quadrupolar nucleus. Sharp singlets upfield of the standard, in contrast, are indicative for non-ligated PPh_2 groups.

The ^{51}V NMR spectra of most of the monosubstituted complexes show doublets. The chemical shift values are similar to those of known carbonylphosphinevanadium compounds (see Table 3 and ref. 16). No triplet splitting is observed in disubstituted compounds which again is due to quadrupole broadening of the resonance lines.

Preparation and properties

The complexes are formed by photo-induced reaction between the starting products dissolved in THF. For monosubstitution, the reaction is conveniently

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* This assumption is based on an interpolation between the two relations $k_t = k_c$ [$(CO)_t$—M—$(CO)_t$ angle = 90°] and $k_t = 2k_c$ [CK-approximation; $(CO)_t$—M—$(CO)_t$ angle = 180°], employing an angle of 120° as obtained from structural data on $CpV(CO)_2dppe$ [15].

carried out in Duran vessels, thus filtering out shortwave UV light. Ib, III, IVb, V and VId, which are only sparingly soluble in THF, precipitate in the course of reaction and can be reprecipitated from CH_3CN/THF if soluble in CH_3CN (Ib, III). IIb, III, IVc and IVb are precipitated from the concentrated THF solution by addition of n-heptane. Derivatives of $[Et_4N][V(CO)_6]$ are yellow (monosubstitution) to red (disubstitution), the neutral cyclopentadienyl complexes form red-brown, microcrystalline powders. All compounds are sensitive to oxygen, especially when dissolved in THF or CH_3CN. They decompose on heating.

Discussion

Complexes with cis-$Ph_2PCH{=}CHPPh_2$

King and Eggers [9] describe an extremely air-sensitive, brown product obtained by refluxing $CpV(CO)_4$ and *c*-dppe in Bu_2O, which they assume to be a mixture of $CpV(CO)_2$*c*-dppe ($\nu(CO)$ = 1866 and 1790 cm^{-1}) and CpV(*c*-dppe)$_2$. Photochemically, *c*-dppe readily forms the expected mononuclear complexes Ib and IIb. The intermediates Ia and IIa, very likely mononuclear as well, are characterized by their spectra.

If the CO-stretching force constants k_1 (Ib) and k (IIb), respectively, are taken as a measure for the π-acceptor ability of the ligands [12,13,17], *c*-dppe is intermediate between dppe and ppb. On the other hand, by the ^{51}V NMR scale [18], *c*-dppe is the ligand exhibiting the stronger integral ($\pi + \sigma$) ligand strength, if we omit considerations concerning variations of NMR parameters with the ring size. In chelate ring systems $M\{Ph_2P(CH_2)_nPPh_2\}$ ($n = 1$, dppm; $n = 2$, dppe; $n = 3$, dppp), chemical shifts have been shown to be primarily governed by ring strains, causing variations in the σ and π overlap between the metal and phosphorus, the five-membered M-dppe system being less strained than M-dppm and M-dppp [3,19]. In this view, the high-field shift of the ^{51}V signal and the high ^{31}P coordination shift for Ib and IIb as compared to V-dppe and V-ppb indicate a diminished angle distortion in the V-*c*-dppe species.

Complexes with trans-$Ph_2PCH{=}CHPPh_2$

The reaction between *t*-dppe and $CpV(CO)_4$ produces three products, depending on the molar ratio of the reactants. The analytically confirmed, insoluble complex IVb can be isolated from a mixture containing the reactants $CpV(CO)_4$ and *t*-dppe in a molar ratio of 2/1. The soluble compound IVa (ratio of starting products 1/1) is presumably mononuclear; spectral data are practically identical to those for $CpV(CO)_3PPh_2Et$ (cf. Tables 2 and 3). If the ratio is 1/2, the disubstituted dinuclear complex IVc is obtained, the phosphorus atoms occupying *cis* positions. The CO-stretching frequencies of IVc are similar to those of $CpV(CO)_2$dppe and $CpV(CO)_2$ppb. The ^{51}V nucleus is, however, less shielded in these two compounds than in the ten-membered ring structure of IVc, which can be interpreted in terms of a more strained structure in the dppe- and ppb-complexes. An analogous effect has been observed for the shielding of the ^{51}V nucleus in *cis*-$[V(CO)_4dpae]^-$ and *cis*-$[\{V(CO)_4\}_2(\mu\text{-dpae})_2]^{2-}$ (dpae = $Ph_2AsCH_2CH_2AsPh_2$) [4]. Finally, there is evidence for a complex η^5-$CpV(CO)_2$-η^2(*t*-dppe) (sharp ^{31}P NMR signals at +1 and +31 ppm, $\delta(^{51}V) = -660$ ppm) with a 'side-on' coordination of the ligand (vide infra).

A bimetallic species with a bridging *t*-dppe substituting one CO-group in each carbonylvanadium moiety is also formed with $[Et_4N][V(CO)_6]$. The complex III tends to decompose in CH_3CN solution to form $[V(CO)_6]^-$ and a compound which, following its IR spectrum (1896, 1793, 1781 and 1772 cm^{-1}), is a complex containing a *cis*-$\{V(CO)_4\}^-$ moiety. The same complex is formed, when the irradiation is carried out with a molar ratio complex/ligand of 1/2. No final conclusion can yet be drawn as to its structure.

Complexes with $Ph_2PC{\equiv}CPPh_2$

The reaction between $[Et_4N][V(CO)_6]$ and dppa yields the complex V. The slightly higher CO absorptions and smaller ^{51}V shift of V as compared to III or $[V(CO)_5PPh_2Et]^-$ may account for improved d_π electron delocalization from vanadium into the antibonding π type orbitals of the C≡C triple bond.

$CpV(CO)_4$ and dppa react to yield the biligate dimetallic species VId, which is insoluble in all solvents. The supernatant solution contains several additional products which, according to IR, ^{31}P NMR and ^{51}V NMR spectra, may be identified as monosubstituted compound (mono- and di-nuclear, VIa and VIb) and soluble disubstituted product VIc. The pattern of the IR spectrum of VId is strikingly different from that of VIc and other known $CpV(CO)_2L_2$ complexes in that the stretching frequencies are shifted to high wave numbers and the second band in VId (1864 cm^{-1}) is vanishingly weak. We therefore suggest a *trans*-position for the ligating groups in VId (and a *cis* position in VIc) with the two CO groups of each $\{CpV(CO)_2P_2\}$ moiety lying almost exactly opposite to each other, the A'-mode thus having almost zero intensity [20]. This structural assignment is, however, somewhat contradictory to formerly published results on *cis*- and *trans*-$CpV(CO)_2PhP(CH_2CH_2PPh_2)_2$ [2].

The ^{31}P NMR spectrum of the reaction mixture shows, along with broad signals corresponding to coordinated phosphorus (+69, +73, +91 ppm; see Table 3) and a sharp signal at −35 ppm corresponding to the uncoordinated P atom of VIa (and possibly VIc) another sharp resonance at +13 ppm. This signal again has to be assigned to unligated phosphorus, with a downfield shift of 48 ppm, though. An extreme lowfield shift of the ^{51}V resonance signal (the lowest shielding for carbonylvanadium compounds measured until now), and unusually high CO absorptions in the IR spectrum are two additional factors which lead us to propose a structure with the ligand coordinated via the acetylene system, hence η^5-$CpV(CO)_2\eta^2$-dppa (VII). The IR data of VII are in accord with those of the formerly described acetylene complexes η^5-$CpV(CO)_2C_2R_2$ [21], for which a 'side-on' coordination of the ligand is postulated.

The direct interaction between the π^*-acceptor orbitals of dppa and the $CpV(CO)_2$ system may well account for the observed spectroscopic properties: Enhanced π electron delocalization from vanadium into the π^*(dppa) orbitals results in diminished electron population of the π^*(CO) orbitals. A loss of diamagnetic anisotropy in the triple bond will add to the paramagnetic term of the shielding constant, thus shifting the ^{51}V resonance downfield. This effect may be responsible for the lowfield shift of the ^{31}P NMR signal as well, although the shielding of the ^{31}P nuclei should also be subject to changes of the C—P—C angle and the electron density in the neighbouring C≡C bond.

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