Journal of Organometallic Chemistry, 139 (1977) 293—304

PHOTO-INDUCED INTRODUCTION OF $PhP(CH_2CH_2PPh_2)_2$ INTO $[Et_4N][V(CO)_6]$ AND $[\eta^5\text{-}CpV(CO)_4]$

IRENE MÜLLER and DIETER REHDER *
Institut für Anorganische und Angewandte Chemie der Universität, 6 Martin-Luther-King-Platz, D-2000 Hamburg 13 (B.R.D.)

(Received May 16th, 1977)

Summary

The complexes *cis*-$[Et_4N][V(CO)_4\text{triphos}]$ (I) (triphos = $PhP(CH_2CH_2PPh_2)_2$), *mer*-$[Et_4N][V(CO)_3\text{triphos}]$ (II), *cis*-$[\eta^5\text{-}CpV(CO)_2\text{triphos}]$ (III), and *trans*-$[\eta^5\text{-}CpV(CO)_2\text{triphos}]$ (IV) were isolated from the photolytic reaction between the potentially triligate triphos and $[Et_4N][V(CO)_6]$ or $[\eta^5\text{-}CpV(CO)_4]$, respectively. IV is formed by photo-induced configurational rearrangement of III, and is an isomeric mixture of two species with uncoordinated PPh_2 and PPh groups. Further reaction of I on silica gel yields a neutral, probably binuclear, complex $\{fac\text{-}[V(CO)_3\text{triphos}]\}_2$ (V) with the triphos ligands probably occupying *facial* positions in the $V(CO)_3P_3$ moieties. Spectroscopic evidence is given for the monoligate species $[V(CO)_5\text{triphos}]^-$ and $[\eta^5\text{-}CpV(CO)_3\text{triphos}]$. Structural assignments of the complexes are based on IR, ^{31}P NMR, and ^{51}V NMR parameters.

Introduction

Recent development in carbonylvanadium chemistry includes new species of unsubstituted carbonylvanadium compounds isolated in low temperature matrices [1,2], vanadium—copper carbonyls [3], and substitution products derived from the $[V(CO)_6]^-$ anion with vanadium in the formal oxidation states —I [4—6] and (possibly) —III [7]. Further, carbonylcyclopentadienylvanadium compounds were investigated with respect to CO substitution [5,8,9], introduction of carbon monoxide [10], oxidation reactions [11], and reduction reactions [12]. The complexes were subject to condiserations concerning unusual coordination numbers of the central vanadium atom such as 7 and 8 [4,7,13] and to a variety of physical and physiochemical parameters: kinetic studies were carried out to elucidate the CO substitution mechanism [14]. Protonation reactions [15], studies on the electrochemical behaviour [16], and X-ray investigations [1,17,18] were discussed in terms of chemical behaviour as correlated with structural principles. Attempts to interpret the interelectronic vanadium—ligand interaction were made via ^{51}V NMR [5,9,19], ^{13}C NMR [20], ESR [21], IR [22], and electron absorption spectra [23,24]. Allyl-, allyl-biphosphine [18] and oligophosphine substituted species derived from $[V(CO)_6]^-$ [4,6,25], $V(CO)_6$ [26], and $[\eta^5\text{-}CpV(CO)_4]$ [6,27,28], exhibiting comparatively high thermal stability and relatively low air-sensibility, have attracted considerable interest regarding structural and bonding properties in the vanadium—ligand interaction sphere.

Extending former work on substitution products of $[\eta^5\text{-}CpV(CO)_4]$ and $[V(CO)_6]^-$ with bidentate and tetradentate phosphine ligands [6], we now describe new compounds with the potentially triligate $PhP(CH_2CH_2PPh_2)_2$ which present some new structural principles and provide new preparative pathways to carbonylvanadium complexes. We have used IR and ^{31}P NMR spectroscopic investigations for characterization of products, and also the recently developed ^{51}V NMR spectroscopy [5,9,19].

Experimental

General method and materials

All operations were carried out under nitrogen in anhydrous solvents. The irradiation apparatus was a glass vessel of about 120 ml capacity (Mangles, Bonn) equipped with a cooling mantle and a quartz immersion well. The irradiation source was a high pressure mercury lamp (Hanau). During the reaction the solution was agitated by passing a weak N_2 stream through a filter plate at the bottom of the vessel. Starting products were $CpV(CO)_4$ (Strem), $[Et_4N][V(CO)_6]$ (obtained from $[Na(diglyme)_2][V(CO)_6]$ and $[Et_4N]Br$ in $MeOH/H_2O$ mixtures; cf. [5]), and $PhP(CH_2CH_2PPh_2)_2$, prepared by a procedure given by King and Kapoor [29]. Silicagel (Kieselgel 60, 70-230 mesh ASTM, Merck) was dried for 2 h (room temperature, 1 Torr), stored under N_2 and suspended in absolute THF and/or toluene. Before use in a preparative column designed for work under a protective inert gas atmosphere, the carrier material was thoroughly washed with anhydrous solvent.

The IR spectra of approximately 0.02 *M* THF or MeCN solutions were recorded on a Perkin—Elmer 325 spectrometer. The NMR spectra of ca. 0.2 *M* THF/CD_3CN (3 : 1) solutions were recorded on a Bruker WH 90 PFT spectrometer with rotating 10 mm diameter vials at 36.43 ($\{^1H\}^{31}P$) and 23.66 (^{51}V) MHz. Chemical shifts are relative to external H_3PO_4 (80% in D_2O) or $VOCl_3$ (in $CDCl_3$, 2 : 1). Positive signs indicate downfield shifts. The absolute error is less than 1 ppm (for sharp lines) and up to 5 ppm for broad resonances.

cis-Tetraethylammonium tetracarbonyl(1,1,4,7,7-pentaphenyl-1,4,7-triphosphaheptane)vanadate(—I), cis-$[Et_4N][V(CO)_4PhP(CH_2CH_2PPh_2)_2]$ (I)

A solution of 0.867 g $[Et_4N][V(CO)_6]$ (2.48 mmol) and 1.511 g triphos (2.83 mmol) in 100 ml THF was irradiated for 2.5 h. The mixture was evaporated to about 10 ml and allowed to stand over-night at 0°C. The precipitate (*mer*-$[Et_4N]$-$[V(CO)_3triphos]$) was filtered off. To the filtrate, 20 ml of methylcyclohexane (MeCy) were added to precipitate a dark red oil. The oil was dissolved in 10 ml

THF. Addition of 20 ml MeCy and stirring over-night yielded a sticky product. Further purification by passage over a styragel column (20 X 1 cm, ca. 0.1 g of the product dissolved in 1 ml THF; carrier: Styragel 100 Å, Waters; elutant: THF) followed by precipitation with MeCy resulted in the formation of powdery, orange to orange-yellow I. In substance, I is only moderately air-sensitive. (Found: C, 66.9; H, 6.6; N, 1.7; P, 11.0; V, 5.9. $C_{46}H_{53}NO_4P_3V$ calcd.: C, 66.75; H, 6.45; N, 1.69; P, 11.22; V, 6.15%.)

mer-Tetraethylammonium tricarbonyl(1,1,4,7,7-pentaphenyl-1,4,7-triphosphaheptane)vanadate(—I), mer-$[Et_4N][V(CO)_3PhP(CH_2CH_2PPh_2)_2]$ *(II)*

A solution of 0.814 g $[Et_4N][V(CO)_6]$ (2.33 mmol) and 1.356 g triphos (2.54 mmol) in 100 ml THF was irradiated for 5.5 h. The precipitate (II) was filtered off. On evaporation to about 10 ml, additional II separated out. The combined portions of II were washed three times with THF (2 ml) and dried under high vacuum to yield an air-sensitive, brick-red powder with a metallic luster. (Found: C, 67.6; H, 6.9; N, 1.7; P, 11.1; V, 6.2. $C_{45}H_{53}NO_3P_3V$ calcd.: C, 67.58; H, 6.68; N, 1.75; P, 11.62; V, 6.37%.) II is sparingly soluble in THF and moderately soluble in MeCN. The solutions are extremely air-sensitive. Solid II is sometimes pyrophoric.

cis-Dicarbonyl-η^5*-cyclopentadienyl(1,1,4,7,7-pentaphenyl-1,4,7-triphosphaheptane)vanadium(+I), cis-*$[\eta^5\text{-}CpV(CO)_2PhP(CH_2CH_2PPh_2)_2]$ *(III)*

A solution of 0.571 g $CpV(CO)_4$ (2.5 mmol) and 1.345 g triphos (2.5 mmol) in ca. 100 ml THF was irradiated for 11 min. The solution was evaporated to dryness, the residue treated with 10 ml toluene, and separated from undissolved *trans*-product by filtration. To the filtrate, 70 ml n-heptane were added with stirring. Dark red III (still containing small amounts of the *trans*-complex) separated out. For purification, the product was filtered off, dissolved in 3 ml toluene, and reprecipitated with 20 ml heptane. Repeating this procedure 2 to 3 times yielded spectroscopically pure III. The compound was dried under high vacuum for 2 h. III is well soluble in THF, MeCN and toluene. (Found: C, 69.2; H, 5.6; P, 12.6; V, 7.2. $C_{41}H_{38}O_2P_3V$ calcd.: C, 69.69; H, 5.42; P, 13.15; V, 7.21%.)

trans-Dicarbonyl-η^5*-cyclopentadienyl(1,1,4,7,7-pentaphenyl-1,4,7-triphosphaheptane)vanadium(+I), trans-*$[\eta^5\text{-}CpV(CO)_2PhP(CH_2CH_2PPh_2)_2]$ *(IV)*

A solution of 0.504 g $CpV(CO)_4$ (2.2 mmol) and 1.356 g triphos (2.5 mmol) in ca. 100 ml THF was irradiated for 45 min. The solution was concentrated to about 20 ml; 5 ml toluene were added, followed by 80 ml n-heptane to precipitate dark-brown crystals of IV. 250—300 mg of the product were reprecipitated from toluene/THF (5 ml + 1 ml) with 30 ml heptane, and the compound dried under high vacuum and at 55°C for 3 h to yield pure, moderately air-sensitive IV, which is poorly soluble in toluene but well soluble in THF. (Found: C, 70.3; H, 5.8; P, 13.2; V, 7.1. $C_{41}H_{38}O_2P_3V$ calcd.: C, 69.69; H, 5.42; P, 13.15; V, 7.21%.)

Bis-[fac-tricarbonyl-(1,1,4,7,7-pentaphenyl-1,4,7-triphosphaheptane)-vanadium(0)], $\{fac\text{-}[V(CO)_3triphos]\}_2$ *(V)*

A solution of 0.8 g of I in the minimum amount of THF (ca. 4 ml) was passed through a column packed with silica gel (20 × 2.5 cm; eluant toluene). The first orange-yellow fraction was drawn off, evaporated to dryness, redissolved in 2 ml THF, and V was precipitated by addition of ca. 10 ml n-heptane. After stirring over-night, the product was filtered off, recrystallized from THF/heptane and dried under high vacuum (Found: C, 66.5; H, 5.3; P, 13.5; V, 7.6. $C_{37}H_{33}O_3P_3V$ calcd.: C, 66.38; H, 4.97; P, 13.88; V, 7.61%.) V is moderately soluble in THF and MeCN. The solid complex is comparatively air-stable. Melting point (N_2, sealed tube) 220—224°C (dec.).

Results and discussion

IR data for the CO stretching region, and ^{31}P NMR and ^{51}V NMR data are listed in Tables 1 and 2 for complexes I—V, together with the corresponding parameters for the monosubstituted products $[Et_4N][V(CO)_5triphos]$ and $[\eta^5\text{-}CpV(CO)_3triphos]$, for which spectroscopic evidence substantially supports their intermediate formation. Figures 1—4 show selected representative spectra of the complexes, together with proposed structures.

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

On UV irradiation of a THF solution containing $[Et_4N][V(CO)_6]$ and $PhP(CH_2CH_2PPh_2)_2$(triphos) in about equimolar amounts, the hexacarbonyl anion undergoes substitution in three steps corresponding to the formation of mono-, *cis*-di-, and *mer*-trisubstituted anions (eq. 1—3), with simultaneous colour shift from the initial yellow to a final dark orange-red. Hence, the course of reaction is analogous to that we observed with biligate diphosphaalkanes and the tetradentate 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos), which substituted a maximum of three CO groups exclusively in meridional positions [6]. In the case of triphos, the irradiation time is, however, much shorter, probably because II is only sparingly soluble in THF, thus diminishing the back-reaction in eq. 3. Furthermore, in this case, the disubstituted species I could be isolated.

$$[V(CO)_6]^- + \text{triphos} \rightarrow [V(CO)_5\text{triphos}]^- + CO \quad (1)$$

$$[V(CO)_5\text{triphos}]^- \rightarrow cis\text{-}[V(CO)_4\text{triphos}]^- + CO \quad (2)$$

$$cis\text{-}[V(CO)_4\text{triphos}]^- \rightarrow mer\text{-}[V(CO)_3\text{triphos}]^- + CO \quad (3)$$

CO substitution by phosphine ligands in the isoelectronic complexes $CpV(CO)_4$ [14] and $M(CO)_6$ (M = Cr, Mo, W) [30] follows an S_N1 mechanism with intermediate formation of $\{CpV(CO)_3\}$ and $\{M(CO)_5\}$, respectively. This mechanism was also proposed for substitution in the anionic $[V(CO)_6]^-$ [24]. However, first results drawn from a quantitative investigation of the photo-induced substitution of CO in $[V(CO)_6]^-$ for PPh_3 favour an S_N2 mechanism [31].

For isolation of I and II, the solution is irradiated until the IR spectrum no longer shows the band at 1950 cm^{-1} indicative of monosubstitution. This requires about 2.5 h of UV irradiation. At this stage, dark-red II partly precipitated out. Further amounts of II separate out, when the concentrated solution is allowed to stand at 0°C. From the solution, orange I is precipitated with heptane or methylcyclohexane after passage through Styragel 100 Å.

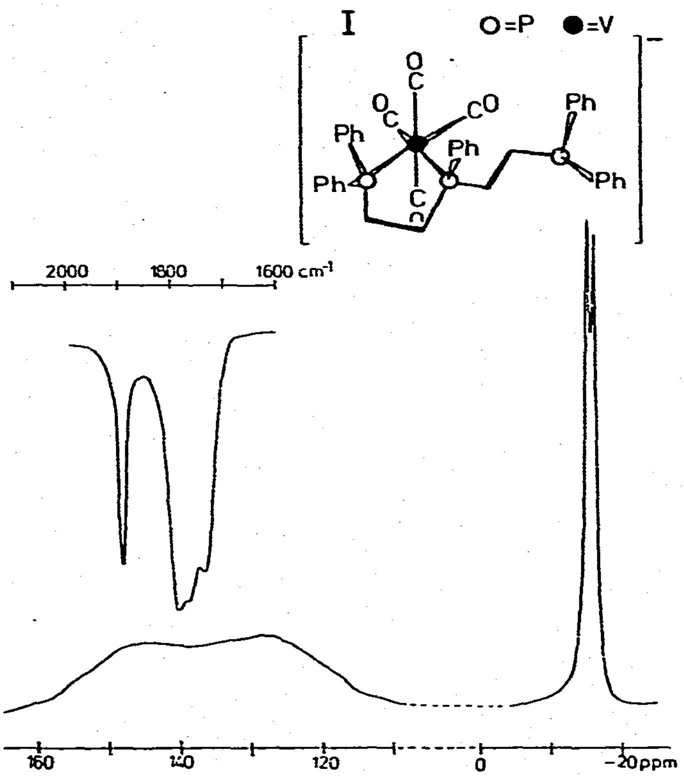


Fig. 1. IR (MeCN) and ^{31}P NMR (234 K) spectrum, and proposed structure of *cis*-[V(CO)$_4$triphos]$^-$ (I). For the ^{51}V NMR spectrum see Fig. 2.

Proposed structures for I and II, based on IR, ^{31}P NMR and ^{51}V NMR spectra are shown in Fig. 1 and 2.

The IR spectrum of I is consistent with the pattern for other disubstituted derivatives of the [V(CO)$_6$]$^-$ anion [4,6]; vanadium chemical shift and vanadium—phosphorus nuclear-spin coupling constant (cf. Table 1) are those expected for the five-membered cyclic structure without substantial strains or angle distortions in the ring system [6]. The phosphorus NMR data (Table 2) indicate that the only phosphorus species present in the unligated state is a terminal PPh$_2$ group of triphos: shift value and $^3J(^{31}P—^{31}P)$ coupling constant are close to those reported for the free ligand by DuBois et al. [32]. Resonances corresponding to the ligated phosphorus atoms are scarcely detectable at room temperature. However, two broad signals (+83 and +68 ppm) appear at 243 K. At 193 K, only one broad and weak signal is observed, probably because of line broadening caused by the increased viscosity of the solution. The general difficulty in obtaining distinct signals for P-atoms directly bond to vanadium originates from inferences through the quadrupolar ^{51}V nucleus (nuclear spin = 7/2). Qualitatively the down-field shift of the phosphorus resonances in vanadium

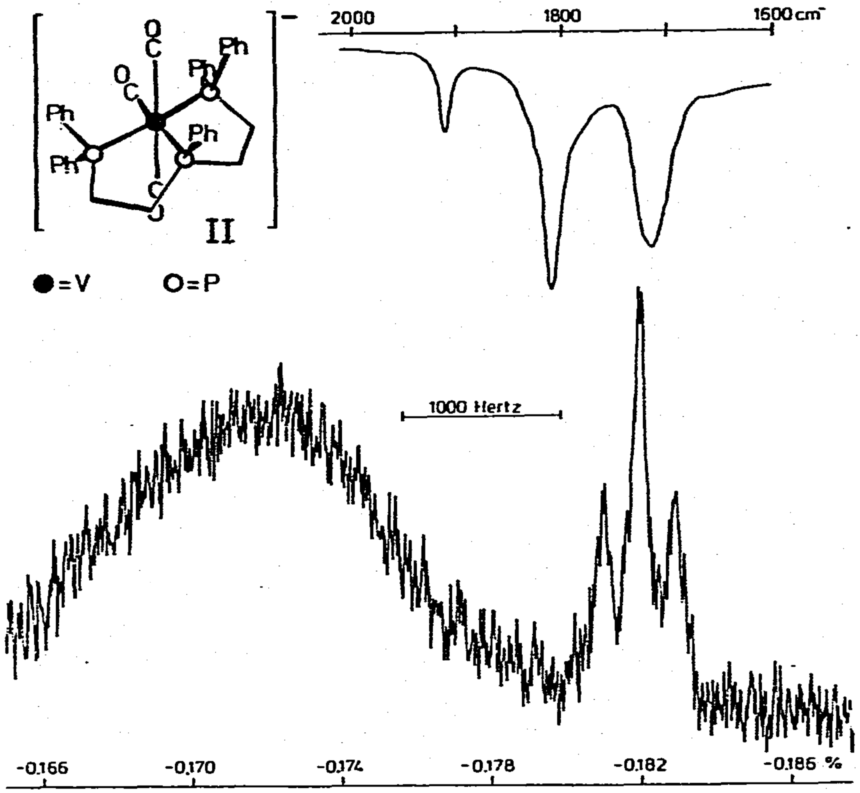


Fig. 2. IR (MeCN) and ^{51}V NMR (295 K) spectrum, and proposed structure of *mer*-$[V(CO)_3triphos]^-$ (II). The structure (corresponding to the broad signal) is idealized (for discussion see text); the triplet centred at —0.182% is due to structural units of I.

TABLE 1

IR SPECTRA IN THE CO-STRETCHING REGION AND ^{51}V NMR DATA FOR CARBONYLVANADIUM COMPOUNDS

	$\nu(C{\equiv}O)$ [a] (cm^{-1})	δ (^{51}V) [c] (%)	ΔB [f] (Hz)
$[Et_4N][V(CO)_5triphos]$	1965 1857 1818	—0.182	530 [g]
cis-$[Et_4N][V(CO)_4triphos]$ (I)	1903 1800 (1770) (1740)	—0.183 [d]	575
mer-$[Et_4N][V(CO)_3triphos]$ (II)	1910 1805 1714	—0.172 [e]	1910
$[\eta^5\text{-}CpV(CO)_3triphos]$	1950 1865 1850	—0.137	440
cis-$[\eta^5\text{-}CpV(CO)_2triphos]$ (III)	1868 1795 [b]	—0.123	530
trans-$[\eta^5\text{-}CpV(CO)_2triphos]$ (IV)	1798 1764	—0.097	650
$\{$*fac*-$[V(CO)_3triphos]\}_2$ (V)	(1927) 1920 (1835) 1820	—0.164	915

[a] In THF or THF/MeCN (II, V); wave numbers in brackets are shoulders. [b] A weak band at 1955 cm^{-1} is not assigned. [c] In THF/CD_3CN (3 : 1) relative to an external $VOCl_3$ standard; negative sign = upfield $VOCl_3$. [d] Triplet, $^1J(^{31}P{-}^{51}V)$ 223 Hz. [e] Plus a weak triplet at —0.183%, see text for discusion. [f] Overall peak-to-peak line width of the first derivative; in case of II and V half-widths are recorded. [g] Average peak-to-peak width of the lines constituting the triplet is 105 Hz.

TABLE 2

^{31}P NMR PARAMETERS [a] FOR TRIPHOS-SUBSTITUTED CARBONYLVANADIUM COMPOUNDS

	T (K)	Unligated P-functions		Ligated P [b]
		$\delta(^{31}PPh_2)$ (ppm)	$\delta(^{31}PPh)$ (ppm)	$\delta(^{31}PPh_2, ^{31}PPh)$ (ppm)
$PhP(CH_2CH_2PPh_2)_2$(triphos) [c]	[c]	−12.8 (d, 29)	−16.6 (t)	
cis-$[Et_4N][(V(CO)_4$triphos] (I)	293	−13.3 (d, 31)		non-significant
	243	−15.0 (d, 31)		non-significant
	200	−16.4 (d, 35)		+68, +83
mer-$[Et_4N][V(CO)_3$triphos] (II)	200	[d]	[d]	+62, +87
cis-[η^5-CpV$(CO)_2$triphos] (III)	293	−13.6 (d, 26)		non-significant
	200	−15.5 (d, 26)		+102, +114
trans-[η^5-CpV$(CO)_2$triphos) (IV)	200	−15.7 (d, 29)	−18.7 (t, 27)	+122
$\{$*fac*-$[V(CO)_3$triphos]$\}_2$ (V)	293			+90

[a] Shift values in THF/CD_3CN relative to an external H_3PO_4 (85% in H_2O) standard. In brackets: $^3J(^{31}P-^{31}P)$ nuclear-spin coupling constants in Hz; d = doublet, t = triplet. Negative signs indicate shifts upfield H_3PO_4.
[b] The lower field shift value (= more positive δ) is tentatively assigned to coordinated PPh-groups (see text).
[c] Room temperature in $CDCl_3$ (cf. [32]). [d] Additional weak signals are observed (see text).

complexes described here are of the same order of magnitude as, for example, in oligotertiary phosphine complexes of platinum [33]. There remains the unresolved difficulty of assigning the two signals to either ligated PPh_2 or PPh. The latter, however, should be subjected to more substantial structural changes upon coordination, which may well result in enhanced down-field shift.

II exhibits the same IR pattern (cf. Fig. 2 and Table 1) as that described for *mer*-$[Et_4N][V(CO)_3$tetraphos] [6], having local C_{2v} symmetry, the CO groups spanning the irreducible representation $\Gamma = 2A_1 + B_1$. The ^{51}V resonance is shifted down-field by about 110 ppm relative to I, which is consistent with increased π-delocalization of electrons from vanadium to the CO groups upon going from a di- to a tri-substituted complex, a fact which is also reflected in the IR spectra. No line splitting is observed because of considerable line broadening to be expected for *mer*-trisubstituted, pseudo-octahedral complexes with quadrupolar metal centres [34]. In addition to the signal centered at −0.172%, there is a weak triplet (−0.183%), indicating the presence of structural units of the complex type I. Since such a species necessarily gives rise to unligated phosphorus functions, the latter should be detected in the ^{31}P spectrum. In fact, a weak doublet and triplet, centered at −15.8 ppm (d, J 24 Hz) and −18.7 (t, J 27 Hz) ppm, respectively, indicate free PPh_2 and PPh. Additionally, two broad bands at +87 and +62 ppm again represent ligated PPh_2 and PPh groups. NMR data for II therefore suggest an oligomeric structure with some limited participation by *cis*-$[V(CO)_4$triphos$]^-$ units. Hence, the structure given for II in Fig. 2 must be considered as idealized.

Reactions of triphos with [η^5-CpV$(CO)_4$]: The preparation of cis- and trans-[η^5-CpV$(CO)_2$triphos] (III and IV)

cis-CpV$(CO)_2$triphos was formerly described by King and Kapoor [28], who obtained the complex in an analytically impure form by refluxing the starting reagents in toluene. Under UV irradiation, [η^5-CpV$(CO)_4$] and triphos, dissolved in equimolar amounts in THF, react immediately to form, via a short-lived intermediate [η^5-CpV(CO)$_3$triphos], III and IV (eq. 4—6). The mono-substituted species vanishes after about 10 min of irradiation. III is formed simultaneously, whilst the formation of IV commences as soom as the monosubstituted species is converted to III. After 10 to 15 min, a mixture of III and IV is obtained, containing increasing amounts of IV. UV-reduced reorientation of III to IV is

$$\mathrm{CpV(CO)_4 + triphos \rightarrow CpV(CO)_3triphos + CO} \quad (4)$$

$$\mathrm{CpV(CO)_3triphos \rightarrow \mathit{cis}\text{-}[CpV(CO)_2triphos)] + CO} \quad (5)$$

$$\mathit{cis}\text{-}\mathrm{[CpV(CO)_2triphos] \rightarrow \mathit{trans}\text{-}[CpV(CO)_2triphos]} \quad (6)$$

complete after about 45 min. Further irradiation is accompanied by rapid decomposition of an apparently unstable intermediate {CpV(CO)triphos}. The compounds can be isolated by precipitation with heptane. They form dark reddish-brown powders, which are readily soluble in THF and MeCN, and

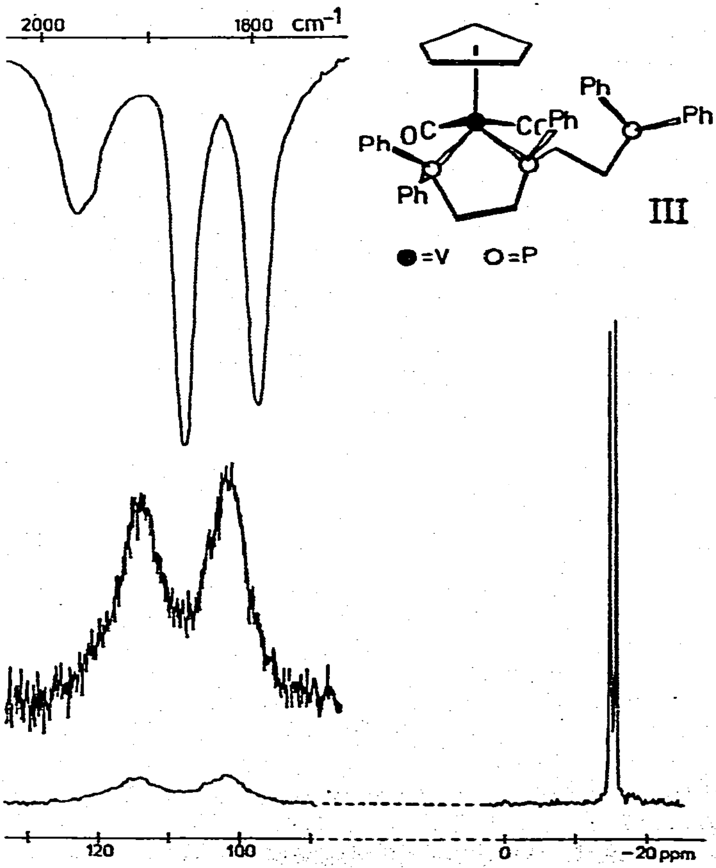


Fig. 3. IR (THF) and ^{31}P NMR (200 K) spectrum, and proposed structure of *cis*-[η^5-CpV(CO)$_2$triphos] (III). Broad lines are indicative of coordinated P-functions.

sparingly soluble in alkanes. The solutions are sensitive to oxygen. IV, which is less soluble in toluene and toluene/heptane mixtures than III can be obtained in spectroscopically pure form by several reprecipitations from THF/toluene/heptane.

III and IV are clearly distinguished by IR and NMR spectra (cf. Fig. 3 and 4, Tables 1 and 2). As for ligated PPh_2 and PPh, the ^{31}P NMR spectra recorded at room temperature are not very significant. At 200 K, however, relatively sharp and intense signals appear also for those P-atoms which are directly bond to vanadium. In the case of III, two such signals corresponding to ligated PPh_2 and PPh groups are shown in addition to a doublet which is to be assigned to a nonligated, terminal PPh_2. The structure proposed by King is thus confirmed [28]. In the case of IV, a doublet and a (less intense) triplet indicate unligated terminal PPh_2 and central PPh groups, which is in accord with an assumed isomeric mixture, where the *trans* positions are spanned either by the PPh_2 and the PPh function (IVA in Fig. 4) or by two terminal PPh_2 groups (IVB). The latter should additionally give rise to conformational isomers, as indicated in Fig. 4. The natural line width of the ^{51}V resonance signal prevents resolution sufficient for observation of separate signals for IVA and IVB. The *trans*-configuration of IV is, however, supported by the low field position of the resonance which is of the same order of magnitude as that reported for *trans*-[η^5-CpV(CO)$_2$(PMe$_3$)$_2$] [5]. As with other disubstituted CpV(CO)$_2$(PR$_3$)$_2$ complexes containing bulky phosphines, no vanadium—phosphorus coupling was observed.

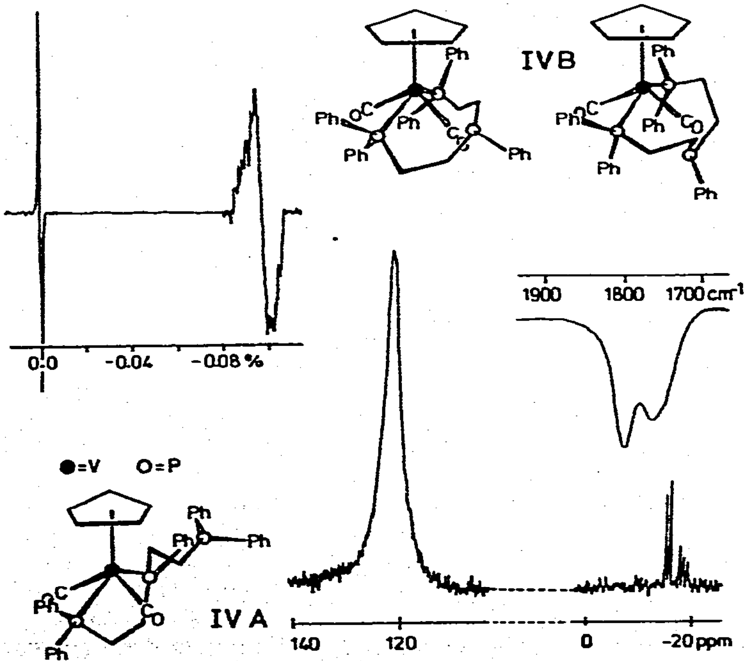


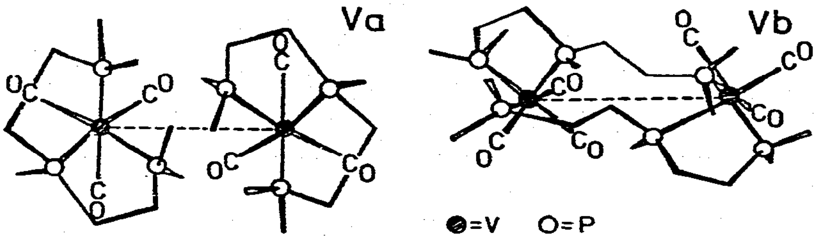
Fig. 4. IR (THF), ^{31}P NMR (200 K) and ^{51}V NMR (295 K) spectrum, and proposed structures of *trans*-[η^5-CpV(CO)$_2$triphos] (IV). For details see text.

The formation of $\{fac\text{-}[V(CO)_3triphos]\}_2$ *by reaction of* $cis[V(CO)_4triphos]^-$ *on silica gel*

When a THF or toluene solution of I is passed through a column packed with silicagel, it reacts with partial oxidation to yield a compound with zero-valent vanadium of possible composition $\{fac\text{-}[V(CO)_3\text{triphos}]\}_2$ (V). Additionally, a yet unidentified product is obtained which, according to its IR spectrum (ν(C≡O) 1983, 1871, and 1815 cm^{-1}) is a mono-substituted complex containing a phosphorus ligand other than triphos. Hence, the formation of V from I on silicagel is accompanied by a partial breakdown of triphos. For a phosphine-monosubstituted derivative of $[V(CO)_6]^-$, the CO stretching frequencies lie at unusually high wave numbers (for comparison see e.g. [19]), suggesting bridging PPh_2 or PPh between two $[V(CO)_5]^-$ units. Investigations of this species is continuing.

V, which can be obtained as a yellow, powdery, air-sensitive substance by heptane precipitation from the first fraction of the THF or toluene extract, is well characterized by analytical and spectroscopic data. The IR spectrum, which exhibits a simiarly to that of $fac\text{-}[V(CO)_3MeC(CH_2PPh_2)_3]$ described by Behrens and Lutz (ν(C≡O) 1914 and 1805 cm^{-1} in CH_2Cl_2) [26], is that expected for trisubstitution in the facial positions of an octahedron. The ^{51}V NMR spectrum shows a broad absorption at —0.164%, this confirming the diamangetism of the compound. Therefore, we suggest a dinuclear formulation with a symmetry centre as illustrated below, with bridging or non-bridging triphos ligands (structural variations are, of course, possible). The compound thus exhibits structural similarity with the isoelectronic species $V_2(CO)_{12}$ [1,2] and $[V(CO)_4(CN)_2]_2^{4-}$ [24] discussed by Ozin and co-workers [2]. The line width is distinctly less than that for the *meridional* complex II, again supporting *facial* configuration [34]. The ^{31}P NMR spectrum shows only one broad resonance, which is assigned to ligated P-atoms.

As to the mechanism leading to the formation of V, we suggest a reaction



involving disintegration of an intermediate $H[V(CO)_4\text{triphos}]$ to yield (in analogy to the decomposition of $HV(CO)_6$ [35]) V and active hydrogen, which in turn may act on the triphos ligand to induce reductive fission or be trapped by carbon monoxide at the reaction site. Oxidation/reduction mechanisms on SiO_2 carriers were attributed to {Si—OH} arrangements present in silica gel [36]. The existence of these potentially acid groups may well lead to the intermediate formation of a hydridocarbonyl complex similar to the known $H[V(CO)_4Ph_2P\text{-}(CH_2)_2PPh_2]$ [37].

Concluding remarks

The complexes *trans*-[η^5-CpV(CO)$_2$triphos] (IV) and {*fac*-[V(CO)$_3$triphos]}$_2$ (V) display new structural principles within the framework of low-oxidation state vanadium chemistry. The preparation of either complex incorporates unusual preparative pathways, in that IV is obtained by photo-induced conformational rearrangement of an initially formed complex of *cis*-configuration (III), and V is produced by oxidative fragmentation of *cis*-[Et$_4$N][V(CO)$_4$triphos] (I) on siliga gel. The mechanisms of these reactions are at present under investigation in our laboratory. The complexes containing unligated terminal or central phosphorus functions (I, III, IV) are of potential interest in that coupling to carbonyl compounds of transition metals of groups VI, VII, and VIII can be carried out [31], thus giving rise to species containing two metal centres. Neutral complexes of this type containing triphos-bridged carbonyl manganese and carbonylchromium units were described previously [38]. Complexes with two or more transition metal nuclei of relatively high receptivity in NMR experiments will probably provide easy access to information on electronic effects in the coordination sphere. Such nuclei are ^{59}Co [34,39], ^{55}Mn [40], and ^{51}V, among others.

Acknowledgement

We acknowledge support of this work by the Deutche Forschungsgemeinschaft. We wish to thank Prof. Dr. R. Nast, Prof. Dr. Hj. Sinn, and the Institutsrat of the Institut für Anorganische und Angewandte Chemie, University of Hamburg, for actively supporting this project.

References

1 T.C. DeVore and H.F. Franzen, Inorg. Chem., 15 (1976) 1318; L. Hanlau, H. Huber and G.A. Ozin, Inorg. Chem., 15 (1976) 2592.

2 T.A. Ford, H. Huber, W. Klotzbücher, M. Moskovits and G.A. Ozin, Inorg. Chem., 15 (1976) 1666.

3 P. Hacket and A.R. Manning, J. Chem. Soc. Dalton Trans., (1975) 1606.

4 J.E. Ellis and R.A. Faltynek, Inorg. Chem., 15 (1976) 3169; J.E. Ellis and R.A. Faltynek, J. Organometal. Chem., 93 (1975) 205.

5 D. Rehder, W.L. Dorn and J. Schmidt, Transition Met. Chem., 1 (1976) 233; D. Rehder, J. Magn. Reson., 25 (1977) 177.

6 D. Rehder, L. Dahlenburg and I. Müller, J. Organometal. Chem., 122 (1976) 53.

7 J.E. Ellis and M.C. Palazotto, J. Amer. Chem. Soc., 98 (1976) 8264; J.E. Ellis, R.A. Faltynek and S.G. Hentges, J. Amer. Chem. Soc., 99 (1977) 626.

8 T. Kruck and H. Breuer, Chem. Ber., 107 (1974) 263; T. Kruck and H. Molls, Z. Anorg. Allgem. Chem., 420 (1976) 159; D. Rehder, Z. Naturforsch. B, 31 (1976) 273.

9 D. Rehder, W.L. Dorn and J. Schmidt, Transition Met. Chem., 1 (1976) 73.

10 G. Fachinetti and C. Floriani, J. Chem. Soc. Chem. Commun., (1975) 578; G. Fachinetti, S. DelNero and C. Floriani, J. Chem. Soc. Dalton Trans., (1976) 1046; icl., ibidem, 203.

11 N.G. Connelly and M.D. Kitchen, J. Chem. Soc. Dalton Trans., (1976) 2165.

12 J.E. Ellis, R.A. Faltynek and S.G. Hentges, J. Organometal. Chem., 120 (1976) 389.

13 A. Davison and J.E. Ellis, J. Organometal. Chem., 23 (1970) C1; J.S. Allinson, B.J. Aylett and H.M. Colquhoun, J. Organometal. Chem., 112 (1976) C7.

14 G.C. Faber and R.J. Angelici, Inorg. Chem., 9 (1970) 1586.

15 B.V. Lokshin, A.A. Pasinsky, N.E. Kolobova, K.N. Anisimov and Yu.V. Makarov, J. Organometal. Chem., 55 (1973) 315.

16 A.R. Siedle and R.B. Johannesen, J. Org. Chem., 40 (1975) 2002; A.M. Bond and R. Colton, Inorg. Chem., 15 (1976) 2036.

17 R.D. Wilson and R. Bau, J. Amer. Chem. Soc., 96 (1974) 7601; D.G. Schmidling, J. Mol. Struc., 24 (1975) 1; M. Schneider and E. Weiss, J. Organometal. Chem., 121 (1976) 365.

18 M. Schneider and E. Weiss, J. Organometal. Chem., 121 (1976) 345; ibidem, 189; U. Franke and E. Weiss, ibidem., 355.

19 D. Rehder and J. Schmidt, Transition Met. Chem., 2 (1977) 41; D. Rehder and J. Schmidt, J. Inorg. Nucl. Chem., 36 (1974) 333.

20 G.M. Bodner and L.J. Todd, Inorg. Chem., 13 (1974) 1335.

21 K.A. Rubinson, J. Amer. Chem. Soc., 98 (1976) 5188.

22 R.B. King and G. Palyi, Inorg. Chem. Acta, 15 (1975) L 23.

23 M.S. Wrighton, D.I. Handeli and D.L. Morse, Inorg. Chem., 15 (1976) 434.

24 D. Rehder, J. Organometal. Chem., 37 (1972) 303.

25 A. Davison and J.E. Ellis, J. Organometal. Chem., 31 (1971) 39.

26 H. Behrens and K. Lutz, Z. Anorg. Allgem. Chem., 356 (1967) 225.

27 H. Behrens and H. Brandl, Z. Naturforsch. B, 22 (1967) 1353.

28 R.B. King and P.N. Kapoor, J. Amer. Chem. Soc., 93 (1971) 4158.

29 R.B. King, P.N. Kapoor and R.N. Kapoor, Inorg. Chem., 10 (1971) 1841.

20 W. Strohmeier, Angew. Chem., 76 (1964) 873; H. Schumann, O. Stelzer, J. Kuhlmey and U. Niederreuther, Chem. Ber., 104 (1971) 993.

31 J. Kittsteiner, D. Rehder and M. Waitz, unpublished results.

32 D.L. DuBois, W.H. Meyers and D.W. Meek, J. Chem. Soc. Dalton Trans., (1975) 1011.

33 R.B. King and J.B. Cloyd Jr., Inorg. Chem., 14 (1975) 1550.

34 A. Yamasaki, F. Yayima and S. Fujiwara, Inorg. Chem. Acta, 2 (1968) 39; F. Yayima, Y. Koike, A. Yamasaki, and S. Fujiwara, Bull. Chem. Soc. Japan, 47 (1974) 1442.

35 W. Hieber, E. Winter and E. Schubert, Chem. Ber., 95 (1962) 3070.

36 A.A. Malygin, A.N. Volkova, S.I. Kol'tsov and V.B. Aleskovskii, J. Gen. Chem. USSR, 46 (1976) 2085.

37 A. Davison and J.E. Ellis, J. Organometal. Chem., 36 (1972) 131.

38 I.S. Butler and N.J. Coville, J. Organometal. Chem., 80 (1974) 235.

39 A. Johnson and G.W. Everett, Inorg. Chem., 12 (1973) 2801; D. Rehder and J. Schmidt, Z. Naturforsch. B, 27 (1972) 625.

40 G.M. Bancroft, H.C. Clark, R.J. Kidd, A.T. Bake and H.G. Spinney, Inorg. Chem., 12 (1973) 728.