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# SUBSTITUTION PRODUCTS OF $[V(CO)_6]^-$ AND $[\eta^5\text{-}CpV(CO)_4]$ WITH DI- AND TETRA-TERTIARY PHOSPHINES

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## Summary

Complexes of the type *cis*-$[R_4N][V(CO)_4Ph_2P(CH_2)_nPPh_2]$ (R = Et, $n$ = 2, 3, 4; R = n-Bu, $n$ = 1, 3) have been prepared by photosubstitution of $[R_4N][V(CO)_6]$. UV irradiation of $[\eta^5\text{-}CpV(CO)_4]$ in the presence of $Ph_2P(CH_2)_nPPh_2$ results in the formation of *cis*-$[\eta^5\text{-}CpV(CO)_2Ph_2P(CH_2)_nPPh_2]$ ($n$ = 1, 2, 4) or, in the case of $n$ = 3, of a polymeric compound *cis*-$[\eta^5\text{-}CpV(CO)_2Ph_2P(CH_2)_3PPh_2]_m$. Evidence is presented for a relationship between $^{51}V$ chemical shifts and the ring size of the chelated structures.

Photosubstitution of $[Et_4N][V(CO)_6]$ with the potentially tetradentate $Ph_2P(CH_2)_2PPh(CH_2)_2PPh(CH_2)_2PPh_2$ (tetraphos) yields an isomeric mixture of a mono-metallic triligate complex *mer*-$[Et_4N][V(CO)_3\text{tetraphos}]$ and the probably polymeric *cis*-$[Et_4N]_{2n}[\{V(CO)_4\}_2\text{tetraphos}]_n$. The structures are discussed on the basis of IR and $^{31}P$ NMR spectra.

## Introduction

Phosphine and arsine substituted hexacarbonyl vanadates(—I) are currently of interest because of their high reactivity compared to that of the $[V(CO)_6]^-$ anion itself, which is remarkably inert when attached to large cations such as $[Et_4N]^+$, $[Bu_4N]^+$ and $[PPh_4]^+$. Substituted phosphines and related Group V donors are easily introduced (usually via photoreaction) into $[V(CO)_6]^-$ and $[\eta^5\text{-}CpV(CO)_4]$, yielding complexes of the composition $[V(CO)_nL_{6-n}]^-$ ($n$ = 4, 5) [1—6,16] and $[\eta^5\text{-}CpV(CO)_mL_{4-m}]$ ($m$ = 2, 3) [7—16], respectively. Ellis and co-workers describe several $[V(CO)_4\widehat{LL}]^-$ complexes, where $\widehat{LL}$ = dppe,

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dmpe and diars * [2,6] while Behrens and Brandl [9] prepared chelate complexes of composition [$\eta^5$-CpV(CO)$_2$dppe] and [{$\eta^5$-CpV(CO)$_3$}$\mu$-triphos{$\eta^5$Cp-V(CO)$_2$}] *.

No systematic investigation of carbonyl vanadium compounds containing di- or oligotertiary phosphines has previously been described. Extending our earlier work on complexes of the type [V(CO)$_5$PR$_3$]$^-$ [5] and [$\eta^5$-CpV(CO)$_3$PR$_3$] [15], we now describe the preparation and properties of a number of compounds containing the ditertiary phosphines dppm, dppe, dppp, and dppb, as well as the potentially tetradentate tetraphos *.

In general, the chelate complexes turn out to be thermally much stabler and substantially less air-sensitive than the corresponding complexes containing two monotertiary phosphines [16], and this may well stimulate further investigations in this field.

## Experimental

### *General method and materials*

All operations were carried out under nitrogen and in anhydrous solvents. Photolytic substitution reactions with [V(CO)$_6$]$^-$ were conducted at room temperature in commercially available vessels (Mangels, Bonn) of about 120 ml capacity, fitted with a cooling system and a quartz immersion well. The radiation source was a high pressure mercury lamp (Hanau, radiation flux 47 W). During photolysis, the solution was circulated magnetically. A weak N$_2$ stream was conducted through the reaction vessel in order to remove photolytically-released CO.

Substitution reactions with [$\eta^5$-CpV(CO)$_4$] were carried out in cylindrical quartz vessels of 20 to 100 ml capacity, fitted with gas inlet tube, reflux condenser, and gas outlet. Irradiation was carried out by placing the mercury lamp close to the reaction vessel. During the reaction, the system was cooled with pressurized air so as to maintain the temperature below 60—70°C. A weak N$_2$ stream was bubbled through the solution to remove CO and to agitate the mixture.

[Na(diglyme)$_2$][V(CO)$_6$], [$\eta^5$-CpV(CO)$_4$] and phosphines were taken from commercial sources (Strem, Alfa, Maybridge) and used without further purification, except for [$\eta^5$-CpV(CO)$_4$] which was resublimed. [Et$_4$N][V(CO)$_6$] and [n-Bu$_4$N][V(CO)$_6$] were prepared as follows: 20.5 g of [Na(diglyme)$_2$][V(CO)$_6$] (0.04 mol) were dissolved in 60 ml of CH$_3$OH and the solution was filtered and treated with 9.0 g [Et$_4$N]Br or 13.0 g [n-Bu$_4$N]Br (0.043 mol) in 40 ml of CH$_3$OH. To this mixture, 100 ml of O$_2$-free H$_2$O was added. After stirring for half an hour, the yellow precipitate was filtered off, washed with four 50 ml portions of CH$_3$OH/H$_2$O 1 : 1, and dried under high vacuum.

IR spectra were recorded on a Perkin—Elmer 325 spectrophotometer, using approximately 0.02 *M* THF or CH$_3$CN solutions or Nujol mulls. $^{31}$P{$^1$H} NMR

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* dmpe = bis(dimethylphosphino)ethane, dppm = bis(diphenylphosphino)methane, dppe = bis(diphenylphosphino)ethane, dppp = bis(diphenylphosphino)propane, dppb = bis(diphenylphosphino)butane, triphos = 1,1,1-tris(diphenylphosphinomethylene)ethane, tetraphos = 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphospha-decane, diars = *o*-phenylene-bis(dimethylarsine).

spectra were obtained with a Bruker WH 90 NMR spectrometer. $^{51}$V NMR spectra were recorded at 11.200 MHz and about 1 T using a Varian wideline spectrometer DP 60. The sample solutions (0.2—0.3 *M*) were sealed under $N_2$ in 15 mm diameter vials. Chemical shifts $\tau_V$ were measured relative to an external $VOCl_3$ standard, "absolute" values were calculated according to $\tau_{abs} = (0.566 + \tau_V) - 1.950$ (%), taking $[V(CO)_6]^-$ as a reference ($\tau_V = -0.566$) [4,15]. Peak-to-peak line widths and $^1J(^{51}V—^{31}P)$ coupling constants were measured at a modulation amplitude of 4.1—8.2 $\mu$T. The relative standard deviation of the $\tau_V$-values is 0.5—2%, depending on the width of the resonance line.

### *General procedure for the preparation of $[R_4N][V(CO)_4Ph_2P(CH_2)_nPPh_2]$ [I, R = n-Bu, n = 1; II, R = Et, n = 2; III, R = Et, n = 3; IV, R = n-Bu, n = 3; V, R = Et, n = 4]*

A solution of 2.00 mmol of $[R_4N][V(CO)_6]$ and 2.20 mmol of $Ph_2P(CH_2)_nPPh_2$ in 100—120 ml of THF was irradiated for four hours, then evaporated to 15 ml and allowed to stand overnight. II, IV and V separated as orange-yellow crystals, which were filtered off and washed three times with 5 ml portions of benzene/heptane/THF 4 : 2 : 1 and once with 5 ml of heptane. In the case of I and III, the concentrated solutions were treated with 5 ml of benzene, followed by dropwise addition of 20 ml heptane. The suspension was stirred for at least three hours. (Sometimes, the precipitate was sticky and in this case 30 ml of heptane/cyclohexane 1 : 1 was added with stirring, the supernatant mixture discarded, and the residue redissolved in 5 ml THF and treated as described.) The precipitate was filtered off, washed with two 5 ml portions of heptane and recrystallized from a THF/benzene (1 : 2) solution with heptane.

This procedure also yielded additional quantities of II, IV and V. Yields, properties and analytical data are listed in Table 1.

### *Dicarbonyl-$\eta^5$-cyclopentadienyl-1,1-bis(diphenylphosphino)methane-vanadium-(+I) [$\eta^5$-CpV(CO)$_2$dppm] (VI)*

A solution of 510 mg of $[\eta^5\text{-CpV(CO)}_4]$ (2.20 mmol) and 880 mg dppm

TABLE 1

ANALYTICAL DATA AND PROPERTIES OF $[R_4N][V(CO)_4Ph_2P(CH_2)_nPPh_2]$

| Complex | Colour | Analysis found (calcd.) (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | C | H | N | P | V | Yield (%) |
| $[Bu_4N][V(CO)_4dppm]$ (I)<br>$C_{45}H_{58}NO_4P_2V$ | red to purplish-brown | 68.2<br>68.77 | 7.3<br>7.40 | 1.9<br>1.77 | 7.3<br>7.83 | 6.8<br>6.45 | 65 |
| $[Et_4N][V(CO)_4dppe]$ (II)<br>$C_{38}H_{44}NO_4P_2V$ | yellow-orange | 65.9<br>65.99 | 6.6<br>6.41 | 2.0<br>2.03 | 8.7<br>8.95 | 7.5<br>7.37 | 72 |
| $[Et_4N][V(CO)_4dppp]$ (III)<br>$C_{39}H_{46}NO_4P_2V$ | yellow-orange | 66.7<br>66.38 | 6.8<br>6.57 | 2.2<br>1.99 | 8.4<br>8.77 | 7.1<br>7.22 | 68 |
| $[Bu_4N][V(CO)_4dppp]$ (IV)<br>$C_{47}H_{62}NO_4P_2V$ | orange | 68.8<br>68.77 | 7.7<br>7.98 | 1.7<br>1.71 | 7.7<br>7.54 | 6.0<br>6.21 | 80 |
| $[Et_4N][V(CO)_4dppb]$ (V)<br>$C_{40}H_{48}NO_4P_2V$ | orange | 66.8<br>66.76 | 6.7<br>6.72 | 1.9<br>1.95 | 8.2<br>8.60 | 6.9<br>7.08 | 83 |

(2.30 mmol) in 60 ml THF was irradiated for 2 hours. The dark red-brown solution was evaporated to dryness, the residue redissolved in 15 ml benzene, and VI precipitated by addition of 20 ml of heptane. After stirring for 15 min, the precipitate was filtered off, washed three times with 10 ml portions of heptane and dried, yielding wine-red VI, which is moderately air-sensitive. Yield: 940 mg (77%). (Found: C, 69.2; H, 4.8; P, 10.8; V, 9.2. $C_{32}H_{27}O_2P_2V$ calcd.: C, 69.02; H, 4.89; P, 11.12; V, 9.16%).

*Dicarbonyl-$\eta^5$-cyclopentadienyl-1,2-bis(diphenylphosphino)ethane-vanadium(+I) [$\eta^5$-CpV(CO)$_2$dppe] (VII)*

The complex was prepared as described above for VI. Yield: 1210 mg (81%). (Found: C, 69.6; H, 5.2; P, 11.1; V, 8.9. $C_{33}H_{29}O_2P_2V$ calcd.: C, 69.49; H, 5.12; P, 10.85; V, 8.93%.)

*Dicarbonyl-$\eta^5$-cyclopentadienyl-1,4-bis(diphenylphosphino)butane-vanadium(+I) [$\eta^5$-CpV(CO)$_2$dppb] (VIII)*

A solution of 600 mg [$\eta^5$-CpV(CO)$_4$] (2.60 mmol) and 1120 mg dppb (2.60 mmol) in 60 ml THF was irradiated for one and a half hours. The dark brown solution was evaporated to 5 ml and allowed to stand for 1 week. Dark-red crystals with a purplish iridescent luster separated. The supernatant solution was decanted, the crystals rinsed three times with 3 ml portions of THF and dried under vacuum. The mother liquor was treated with 20 ml of heptane to give a sticky dark product, which redissolved on addition of 5 ml benzene. The solution was evaporated to dryness and the residue redissolved in 10 ml of benzene. Pure VIII was precipitated by addition of 75 ml of heptane. After stirring for 1 hour the purplish-red powder was filtered off, washed once with 5 ml of heptane and dried under vacuum. Total yield: 710 mg (45%). VIII is moderately air-sensitive. (Found: C, 70.3; H, 5.6; P, 10.5; V, 8.3. $C_{35}H_{33}O_2P_2V$ calcd.: C, 70.24; H, 5.56; P, 10.34; V, 8.51%.)

*Dicarbonyl-$\eta^5$-cyclopentadienyl-1,3-bis(diphenylphosphino)propane-vanadium-(+I) [$\eta^5$-CpV(CO)$_2$dppp]$_n$ (IX)*

A solution of 460 mg [$\eta^5$-CpV(CO)$_4$] (2.00 mmol) and 865 mg dppp (2.10 mmol) in 60 ml THF was irradiated for 1 hour to give an orange-red precipitate of IX. The product was filtered off, washed twice with two 6 ml portions of THF and with two 8 ml portions of benzene and dried under high vacuum. (Found: C, 70.3; H, 5.5; P, 10.5; V, 8.5. $C_{34}H_{31}O_2P_2V$ calcd.: C, 69.87; H, 5.35; P, 10.60; V, 8.72%.) Yield: 980 mg (83%). It is insoluble in heptane, benzene, ether, methylene chloride, acetonitrile, acetone, pyridine and methanol and sparingly soluble in THF. The complex is air-stable for several hours.

*mer-Tetraethylammonium tricarbonyl-(1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane)-vanadate(—I) [Et$_4$N][V(CO)$_3$tetraphos] (X) and cis-Bis-(tetraethylammonium)$\mu$-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane-bis[tetracarbonyl-vanadate(—I)] [Et$_4$N]$_{2n}$[{V(CO)$_4$}$_2$tetraphos]$_n$ (XI)*

A solution of 700 mg [Et$_4$N][V(CO)$_6$] (2.00 mmol) and 1.55 g tetraphos (2.30 mmol) in 120 ml THF was irradiated for 24 hours, during which time, the solution became deep red indicating the formation of X. Simultaneously a yellow solid (XI) precipitated, which was filtered off, washed with three 5 ml portions of THF and dried under high vacuum. Although the product was practically pure, small amounts (approximately 50 mg) were reprecipitated from $CH_3CN$. (Found: C, 63.5; H, 6.6; N, 2.2; P, 9.4; V, 8.0. $C_{66}H_{82}N_2O_8P_4V_2$ calcd.: C, 63.06; H, 6.58; N, 2.24; P, 9.84; V, 8.10%.) Yield: 260 mg (21%). The compound is moderately air-sensitive.

In the case of X, the reaction mixture was filtered, evaporated to about 10 ml and treated with 20 ml of toluene. Then 100 ml of cyclohexane/heptane 1 : 1 was added with vigorous stirring. After one hour's stirring, the precipitate was filtered off, washed twice with 5 ml portions of cyclohexane and redissolved in 5 ml of THF. After addition of 15 ml of toluene the solution was filtered, and X was reprecipitated by addition of 75 ml of cyclohexane/heptane, 2 : 1. The dried product was a dark red, extremely air-sensitive, granular powder. (Found: C, 68.4; H, 6.7; N, 1.4; P, 12.9; V, 5.6. $C_{53}H_{62}NO_3P_4V$ calcd.: C, 68.02; H, 6.68; N, 1.50; P, 13.24; V, 5.44%.) Yield: 680 mg (36%).

## Results and discussion

### *Preparation and spectral properties of cis-[$R_4N$][$V(CO)_4Ph_2P(CH_2)_nPPh_2$] (I)—(V)*

These compounds are readily formed in THF solution by photo-induced introduction of the bis-phosphine into the $[V(CO)_6]^-$ anion. Monitoring the reaction by IR reveals a two-step CO substitution *:

$$[V(CO)_6]^- + \widehat{LL} \rightarrow [V(CO)_5\widehat{LL}^*]^- + CO \text{ (fast)}$$

$$[V(CO)_5\widehat{LL}^*]^- \rightarrow [V(CO)_4\widehat{LL}]^- + CO \text{ (slow)}$$

Although there is substantial IR spectroscopic evidence for the existence of $[V(CO)_5\widehat{LL}^*]^-$ anions (Table 2), we could not isolate the pure mono-ligate species. Conversion into the biligate species is complete after about four hours of irradiation.

From the concentrated solutions, the complexes II, IV and V separate as crystalline, orange powders. Alternatively the orange-yellow compounds II—V and the purple I can be precipitated with benzene/heptane. IR and $^{51}V$ NMR data are listed in Table 2. The IR spectra of the disubstituted products are consistent with $C_{2v}$ symmetry $[\Gamma(CO) = 2\,A_1 + B_1 + B_2]$, i.e. substitution occurs exclusively in *cis*-positions.

### *Photolytic substitution of [$\eta^5$-$CpV(CO)_4$]*

The photochemical reaction between $[\eta^5\text{-}CpV(CO)_4]$ and $Ph_2P(CH_2)_nPPh_2$ in THF solution at elevated temperatures leads exclusively to the *cis*-disubstituted complexes $[\eta^5\text{-}CpV(CO)_2Ph_2P(CH_2)_nPPh_2]$ [VI, $n = 1$; VII, $n = 2$; VIII, $n = 4$.]. For $n = 3$, an insoluble, and thus probably polymeric product $[\eta^5\text{-}CpV(CO)_2\text{-}dppp]_m$ (IX) with bridging dppp is formed.

VI, VII and VIII can be precipitated by addition of benzene/heptane mixtures to the concentrated THF solution. The IR spectra indicate that the photo-

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* An asterisk denotes non-ligated P of the bis-phosphine $\widehat{LL}$.

TABLE 2

IR AND NMR DATA FOR BIS(DIPHENYLPHOSPHINO)ALKANE SUBSTITUTED CARBONYLVANADATES(—I) AND CARBONYLCYCLOPENTADIENYLVANADIUM(+I) COMPOUNDS

| | $\nu$(C≡O) (cm$^{-1}$) | | | | Phase | $\tau_V$ [a] (%) | $-\tau_{abs}$ [b] (%) | $\Delta H$ ($\mu$T) | $J(^{51}V-^{31}P)$ (Hz) |
|---|---|---|---|---|---|---|---|---|---|
| $[V(CO)_5\widehat{LL}^*]^-$ [c] | | | | | | | | | |
| $\widehat{LL}^*$ = dppm | 1962 | 1857 | 1821 | | THF | | | | |
| $\widehat{LL}^*$ = dppe | 1964 | 1858 | 1820 | | THF/$CH_3CN$ | 0.183 | 1.201 | 30 | 190 [d] |
| $\widehat{LL}^*$ = dppp | 1961 | 1858 | 1821 | | THF | | | | |
| $[V(CO)_4\widehat{LL}]^-$ | | | | | | | | | |
| $\widehat{LL}$ = dppm I | 1901 | 1800 | 1780 | 1743 | THF | 0.159 | 1.225 | 39 | — |
| $\widehat{LL}$ = dppe II [f] | 1903 | 1799 | 1780 | 1747 | THF/$CH_3CN$ | 0.179 | 1.205 | 54 | 230 [e] |
| $\widehat{LL}$ = dppe II [f] | 1898 | 1783 | 1766 | 1723 | Nujol | | | | |
| $\widehat{LL}$ = dppp III, IV | 1888 | 1782 | 1758 | 1740 | $CH_3CN$ | 0.171 | 1.213 | 49 | 190 [e] |
| $\widehat{LL}$ = dppb V | 1897 | 1795 | 1770 | 1746 | THF | 0.171 | 1.213 | 62 | — |
| $[\eta^5\text{—}CpV(CO)_3\widehat{LL}^*]$ [c] | | | | | | | | | |
| $\widehat{LL}^*$ = dppm | 1950 | 1872 | 1845 | | THF | | | | |
| $\widehat{LL}^*$ = dppb | 1949 | 1861 | 1831 | | THF | | | | |
| $[\eta^5\text{-}CpV(CO)_2\widehat{LL}]$ | | | | | | | | | |
| $\widehat{LL}$ = dppm VI | 1871 | 1808 | | | THF | 0.087 | 1.297 | 35 | — |
| $\widehat{LL}$ = dppe VII [g] | 1870 | 1799 | | | THF | 0.111 | 1.273 | 51 | — |
| $\widehat{LL}$ = dppb VIII | 1860 | 1774 | | | THF | 0.136 | 1.248 | 38 | — |
| $[\eta^5\text{-}CpV(CO)_2dppp]_n$ [h] | 1830 | (1818) | 1758 | (1728) | Nujol | | | | |

[a] Up-field an external $VOCl_3$ standard. [b] "Absolute" chemical shift; $\tau_{abs} = (\tau_V + 0.566) - 1.950$ refs. 4, 15. [c] * denotes an unligated P atom of the bisphosphine $\widehat{LL}$. [d] Doublet. [e] Triplet. [f] The IR data are in good accordance with those reported in ref. 2. [g] 1865 and 1787 cm$^{-1}$ in $CH_2Cl_2$ [9]. [h] Bands in brackets probably originate from trebly substituted structural units.

induced substitution proceeds in two steps via the monoligate species, which again were not isolated. The CO stretching frequencies for the monoligate and biligate complexes are shown in Table 2. For IX, two weak "extra" bands (1818 and 1728 $cm^{-1}$) are observed, suggesting participation of trebly-substituted species in the polymeric structure.

### $^{51}V$ *NMR spectra of* $[V(CO)_4\widehat{LL}]^-$ *and* $[\eta^5\text{-}CpV(CO)_2\widehat{LL}]$

The $^{51}V$ NMR data are summarized in Table 2. Except for I, $^{51}V$ chemical shifts for the $[V(CO)_4\widehat{LL}]^-$ series are of the same order of magnitude as those for $[V(CO)_4(PR_3)_2]^-$ ions [16]. The remarkable down-field shift in the case $[V(CO)_4dppm]^-$ may be due to enhanced ring strains within the $\underline{V—P—C—P}$ system, providing less shielding for the vanadium nucleus. In turn, the phosphorus atoms would be more shielded than in the corresponding dppe and dppp complexes, an effect which has been observed by Appleton et al. [17] in Pt—dppm complexes.

Appleton [17] and Braterman et al. [18] showed that Pt—$^{31}P$ coupling is weaker in Pt—dppm complexes than in other bis-phosphine platinum compounds, and this again they attributed to strains within the ring system and distortion of angles. We suggest that a similar effect is responsible for the fact that no coupling was observed in $[V(CO)_4dppm]^-$, whereas II, III and IV show the expected triplets with coupling constants of about 200 Hz (Table 2).

It is noteworthy that the chemical shift values for $[\eta^5\text{-}CpV(CO)_2\widehat{LL}]$ complexes move down-field with decreasing ringsize. Simultaneously, the $\nu(CO)$ stretching modes increase, indicating less electron density to be delocalized towards the CO-ligands. We interpret these effects in terms of hindered P—V $\sigma$-overlap (i.e. hindered P → V $\sigma$-donation) due to distortions of the P—V—P angles and strains within the small ring systems.

### *The reaction between* $[V(CO)_6]^-$ *and tetraphos*

A considerable number of transition metal-tetraphos complexes have recently been described, and their structures and spectral properties discussed [19—24].

From the photochemically induced reaction between $[Et_4N][V(CO)_6]$ and tetraphos in THF solution, two well defined compounds were isolated: a monometallic triligate complex *mer*-$[V(CO)_3\text{tetraphos}]^-$ (X), and a phosphine-bridged product of empirical composition *cis*-$[Et_4N]_2[\{V(CO)_4\}_2\text{tetraphos}]$ (XI), which is probably polymeric.

The initial reaction is the elimination of one CO and its replacement by a tetraphos-P, as shown by IR spectroscopy. Absorption bands characteristic of biligate *cis*-$[V(CO)_4\text{tetraphos}]^-$ (Table 3) appear after about ten minutes. At this stage XI begins to precipitate. CO-frequencies associated with the monoligate and biligate forms disappear after about three and eight hours, respectively. However, in order to obtain analytically and spectroscopically pure samples of X, irradiation has to be maintained for at least 24 hours.

From the concentrated, red solution, X is precipitated with a toluene/cyclohexane/heptane mixture. After reprecipitation it forms an exceedingly air-sensitive (sometimes pyrophoric) dark-red powder which is very soluble in THF, acetone and toluene. IR spectra (cf. Table 3) are in accord with a meridional position of the three ligated P-atoms [$\Gamma(CO) = 2\,A_1 + B_1$, assuming, in a first

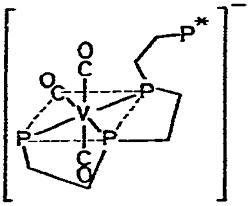
TABLE 3

IR DATA FOR THE REACTION PRODUCTS BETWEEN $[Et_4N][V(CO)_6]$ AND tetraphos

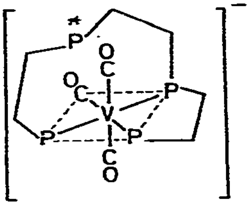
| | Phase | $\nu(C{=}O)$ $(cm^{-1})$ | | | |
|---|---|---|---|---|---|
| $[V(CO)_5tetraphos]^-$ | THF | 1961 | 1856 | 1818 | |
| *cis*-$[V(CO)_4tetraphos]^-$ | THF | 1896 | 1792 | 1770 | 1733 |
| *mer*-$[V(CO)_3tetraphos]^-$ (X) | THF | 1898 | 1810 | 1715 | |
| *mer*-$[Et_4N][V(CO)_3tetraphos]$ (X) | Nujol | 1895 | 1803 | 1705 | |
| *cis*-$[Et_4N]_{2n}[\{V(CO)_4\}_2tetraphos]_n$ (XI) | Nujol | 1888 | 1809 | 1785 | 1745 |

approximation, $C_{2v}$ symmetry]. The "normal" $^{51}V$ chemical shift ($\tau_V = 0.181\%$ upfield a $VOCl_3$ standard; $\Delta H = 58$ $\mu T$) indicates that there are no substantial strains in the bicyclic structure. The high sensitivity towards air is to be expected for vanadium(—I) carrying only three CO groups as $\pi$-acceptors.

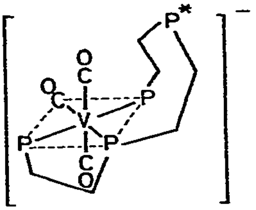
The triligate function of the tetraphos is supported by $^{31}P$ NMR measurements ($^1H$-decoupled). Our observations on phosphine-substituted carbonyl vanadates show that only broad and weak $^{31}P$ signals, if any, are to be expected for P-atoms directly bond to vanadium. There are, however, two multiply split, sharp $^{31}P$ NMR signals for X with an approximate intensity ratio of 1 : 4. In the light of NMR data for the uncoordinate tetraphos [25], the spectrum may be



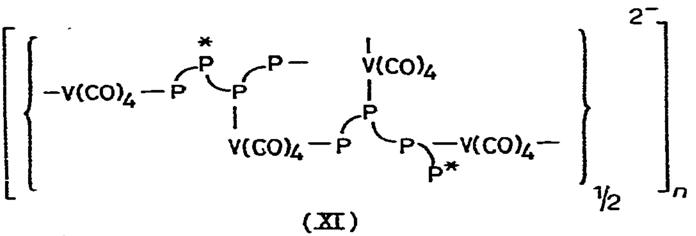
(Xa)



(Xb)



(Xb)



(XI)

Fig. 1. Proposed structures for *mer*-$[V(CO)_3tetraphos]^-$ [Xa and Xb] and $[Et_4N]_{2n}[\{V(CO)_4\}_2tetraphos]_n$ [XI]; P* = unligated P.

interpreted as follows: The first, weak signal, a triplet with the centre line at 15.9 ppm and a coupling constant of 25 Hz, must be associated with an unligated —PPh— group coupling with the two adjacent P atoms. The second signal of higher intensity comprises a doublet at 12.0 ppm (coupling constant 29 Hz), which is allocated to a terminal, unligated —$PPh_2$ group. Three other signals remain unassigned. We propose the structures Xa and Xb (Fig. 1), with the isomer Xb constituting less than 25% of the isomeric mixture.

XI is obtained as a yellow to yellow-orange powder, which is insoluble in all common solvents, but sparingly soluble in acetonitrile, from which it may be reprecipitated. Elementary analysis indicates a V : P ratio of 1 : 2. IR data (Table 3) show clearly that the molecule contains *cis*-$[V(CO)_4\overset{\frown}{LL}]^-$ units. The $^{31}P$ NMR spectrum in $CD_3CN$ shows two rather weak but definite signals centred at 13.5 ppm and 17.3 ppm, respectively, which we assign to unligated —$PPh_2$ and —PPh— groups. A polymeric structure is therefore proposed, with tetraphos acting as a triligate bridging ligand (Fig. 1).

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