

## THE COORDINATIVE PROPERTIES OF BIFUNCTIONAL ARSENIC LIGANDS IN CARBONYLVANADIUM COMPOUNDS

WOLFGANG R.W. ROOSE, DIETER REHDER <sup>\*</sup>, HARALD LÜDERS and KLAUS H. THEOPOLD

*Institut für Anorganische und Angewandte Chemie der Universität, Martin-Luther-King-Platz, D-2000 Hamburg 13 (F.R.G.)*

(Received March 7th, 1978)

### Summary

The complexes *cis*- $[\eta^5\text{-CpV}(\text{CO})_2\widehat{\text{LL}}]$  ( $\widehat{\text{LL}} = \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$  (dpase),  $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$  (arphos), and *o*-phenylenebis(dimethylarsine) (diars)) were isolated from the photo-induced reaction between  $\eta^5\text{-CpV}(\text{CO})_4$  and the corresponding ligand. With  $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$ , the monosubstitution products  $[\text{Et}_4\text{N}]_2[\{\text{V}(\text{CO})_5\}_2(\mu\text{-}\widehat{\text{LL}})]$  ( $\widehat{\text{LL}} = \text{dpase}$ , arphos) are initially obtained. Further irradiation results in the formation of *cis*- $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4(\text{arphos})]$  or a mixture of *cis*- $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4(\text{dpase})]$  and *cis*- $[\text{Et}_4\text{N}]_2[\{\text{V}(\text{CO})_4\}_2(\mu\text{-dpase})_2]$ , respectively. The complexes have been investigated by IR and  $^{51}\text{V}$  NMR spectroscopy. Mass spectral data are presented for the neutral complexes.

### Introduction

Recently, we published findings on the photo-induced reaction between ditertiary phosphines  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $\widehat{\text{PP}}$ ,  $n = 0-4$ ) and  $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$  or  $\eta^5\text{-CpV}(\text{CO})_4$ , respectively, showing that disubstitution usually ( $n = 1-4$ ) yields the monometallic species *cis*- $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4\widehat{\text{PP}}]$  and *cis*- $[\eta^5\text{-CpV}(\text{CO})_2\widehat{\text{PP}}]$  in which the bis-phosphines act as chelating ligands [1]. If  $n = 0$ , however, bridging structures are favoured [2]. Bridging structures were also reported for the tritertiary phosphine  $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$  [3], whereas the potentially triligate  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$  exclusively forms chelate complexes [4], and the tetratertiary  $(\text{CH}_2\text{PPhCH}_2\text{CH}_2\text{PPh}_2)_2$  acts as a bridging and as a chelating ligand [1]. Whether chelated or bridged structures are preferred may depend on (i) the donor/acceptor ability of the coordinating functions, (ii) the bulkiness of the ligating groups, and (iii) the extent of ring strains and angle distortions in the cyclic system. In the light of these considerations, we discuss here the coordinative properties of 1,2-bis(diphenylarsino)ethane (dpase), 1-diphenylarsino-2-diphenylphosphinoethane (arphos) and *o*-phenylenebis(dimethylarsine) (diars) towards  $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$

and  $\eta^5\text{-CpV}(\text{CO})_4$ . Considerable use has been made of IR and  $^{51}\text{V}$  NMR spectroscopic data, including those for the known arsinecarbonylvandium complexes *cis*- $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4(\text{diars})]$  [5],  $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{AsPh}_3]$  [6,7] and  $\eta^5\text{-CpV}(\text{CO})_3\text{-AsPh}_3$  [7], and the bis-arsine and arsinophosphine derivatives of the isoelectronic Group VI hexacarbonyls [8–10].

## Experimental

### General method and materials

The general procedure for the preparation of carbonylvandium derivatives is described elsewhere [1]. Two slightly differing irradiation types of apparatus (Mangels, Bonn) were employed in this work. For monosubstitution, the reaction mixture was magnetically circulated using a teflon rotary pump. Where disubstitution products were envisaged, the solution was agitated by passing a nitrogen stream through a filter plate at the bottom of the reaction vessel. Because of the oxygen sensitivity of the reaction products, all operations were carried out under nitrogen and in anhydrous solvents. Starting materials were obtained from commercial sources (Alfa, Strem) and purified by sublimation ( $\text{CpV}(\text{CO})_4$ ), recrystallization (arphos, dpase; from ethanol) or redistillation (diars).  $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$  was converted into  $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$  [1], and *cis*- $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4\text{diars}]$  was prepared by a published method [5].

### Spectroscopic measurements

IR: ca. 0.02 M THF or  $\text{CH}_3\text{CN}$  solutions in 0.1 mm KBr cuvettes; Perkin-Elmer spectrometer 337; absolute error  $\pm 1$  to  $\pm 3\text{ cm}^{-1}$ .  $^{51}\text{V}$  NMR: ca. 0.2 M THF or  $\text{CH}_3\text{CN}$  solutions in rotating 7.5 mm diameter vials; 23.66 MHz, Bruker WH 90 PFT spectrometer, external lock  $\text{CDCl}_3$ , standard  $\text{VOCl}_3/\text{CDCl}_3$  2/1; absolute error less than 1 ppm.  $\{^1\text{H}\}^{31}\text{P}$  NMR: ca. 0.2 M THF/ $\text{CH}_3\text{CN}$  (1/1) in rotating 5 mm diameter vials; 36.44 MHz, Bruker WH 90 PFT spectrometer, external standard  $\text{H}_3\text{PO}_4/\text{D}_2\text{O}$  80%. Mass spectra: Varian MAT 112 mass spectrometer; ionization energy 72 eV.

Analytical data and properties of the complexes are collected in Table 1, mass spectra for *cis*- $[\eta^5\text{-CpV}(\text{CO})_2\text{LL}]$  ( $\text{LL} = \text{arphos, dpase and diars}$ ) are shown in Table 2.

*Bis(tetraethylammonium) decacarbonyl- $\mu$ -(1,1,4,4-tetraphenyl-1-arsa-4-phosphabutane)divanadate(-I)*,  $[\text{Et}_4\text{N}]_2[\{\text{V}(\text{CO})_5\}_2(\mu\text{-Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2)]$  (I) and *cis-tetraethylammonium tetracarbonyl(1,1,4,4-tetraphenyl-1-arsa-4-phosphabutane)vanadate(-I)*, *cis*- $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2)]$  (II)

A solution of 1.04 g (2.98 mmol)  $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$  and 1.32 g (2.98 mmol) arphos in 100 ml THF was irradiated for 90 min and allowed to stand overnight at room temperature. Dark-red crystals of II were then filtered off, washed twice with 10 ml portions of heptane, and dried under high vacuum. Yield 0.90 g (41%).

The filtrate, containing I and residual amounts of II, was concentrated to 20 ml and transferred to a Duran vessel of appropriate capacity. After addition of 2 ml of freshly distilled allyl chloride saturated with  $\text{N}_2$ , the solution was irradiated for 10 min, using a UV-high pressure mercury lamp (Hanau) placed

TABLE I  
ANALYTICAL DATA AND PROPERTIES

	Empirical formula	Molecular mass	Analysis (found (calcd.)) (%)						
			C	H	As	N	P	V	
I	Yellow powder	1084.87	56.3 (57.57)	5.8 (5.95)	6.4 (6.91)	2.5 (2.58)	2.9 (2.86)	9.6 (9.39)	
II	Dark-red crystals	735.61	61.0 (62.05)	6.1 (6.03)	10.3 (10.19)	2.0 (1.90)	4.2 (4.21)	7.0 (6.93)	
III <sup>a</sup>	Yellow crystals	1128.82	53.1 (53.63)	6.1 (5.73)	10.7 (10.14)	3.0 (2.84)	—	10.1 (10.34)	
IV <sup>b</sup>	Orange-red powder	779.56	58.5 (58.55)	5.8 (5.69)	—	1.9 (1.80)	—	6.5 (6.54)	
V	Red-brown powder	614.43	64.5 (64.51)	4.7 (4.76)	11.6 (12.19)	—	5.1 (5.04)	8.5 (8.29)	
VI	Dark-brown powder	658.33	59.4 (60.20)	4.5 (4.44)	—	—	—	7.5 (7.74)	
VII	Cocoa-brown powder	458.14	44.6 (44.57)	4.6 (4.62)	—	—	—	11.4 (11.12)	

<sup>a</sup> Analytical data given for the 1/1 adduct III · [Et<sub>4</sub>N][V(CO)<sub>6</sub>]. <sup>b</sup> The empirical formula and molecular mass are given for the monometallic species IVa.

TABLE 2

MASS SPECTRA OF *cis*-[ $\eta^5$ -CpV(CO)<sub>2</sub>LL] (LL = arphos, dpase, diars), IONIZATION ENERGY 72 eV

Ion <sup>1+</sup>	CpV(CO) <sub>2</sub> arphos		CpV(CO) <sub>2</sub> dpase		CpV(CO) <sub>2</sub> diars	
	I (%) <sup>a</sup>	m/e	I (%)	m/e	I (%)	m/e
M (parent ion)	1.3	614	0.4	658	4.1	458
M minus 2 CO	12.8	558	1.2	602	5.5	402
L	83.3	442	7.0	486	13.7	286
L minus C <sub>2</sub> H <sub>4</sub>	11.5	414	8.2	458		
L minus CH <sub>3</sub>					100.0	271
L minus 2 CH <sub>3</sub>					47.9	256
L minus 3 CH <sub>3</sub>					6.9	241
L minus 4 CH <sub>3</sub>					6.9	226
L minus 2 Ph	53.9	288				
L minus 4 Ph	3.9	134	2.2	178		
CpVAsPh <sub>2</sub>	6.4	345	0.7	345		
CpVPh <sub>2</sub>	7.7	301				
CpVAsPh	5.1	268				
AsPh <sub>3</sub>			2.8	306		
PPh <sub>3</sub>	93.6	262				
AsPh <sub>2</sub>	30.8	229	100.0	229		
PPh <sub>2</sub>	55.1	185				
As <sub>2</sub> Ph	50.0	227	26.8	227		
AsPPh	100.0	183				
AsPh	38.5	152	28.7	152		
PPh	18.0	108				
AsC <sub>6</sub> H <sub>4</sub>	0.6	151	14.7	151	20.6	151
Cp <sub>2</sub> V	11.5	181	6.3	181		
CpV	0.7	116	9.8	116	4.1	116
Cp	0.7	65	1.1	65	12.5	65
V	18.0	51	2.8	51	6.9	51

<sup>a</sup> Relative intensity (100% = C<sub>6</sub>H<sub>5</sub>AsP<sup>+</sup> (CpV(CO)<sub>2</sub>arphos), C<sub>12</sub>H<sub>10</sub>As<sup>+</sup> (CpV(CO)<sub>2</sub>dpase), C<sub>8</sub>H<sub>10</sub>As<sub>2</sub><sup>+</sup> (CpV(CO)<sub>2</sub>diars)).

about 5 cm outside the Duran tube. The reaction mixture (consisting of I, which does not react with allyl chloride, and  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>V(CO)<sub>3</sub>arphos [12]) was precipitated with n-heptane, filtered off, washed with 2 ml of THF followed by three 10 ml portions of diethyl ether, and the yellow complex I remaining on the filter plate was dried under high vacuum. Yield 0.27 g (17%).

*Bis(tetraethylammonium) deca carbonyl- $\mu$ -(1,1,4,4-tetraphenyl-1,4-diarsabutane)divanadate(-I), [Et<sub>4</sub>N]<sub>2</sub>[{V(CO)<sub>5</sub>]<sub>2</sub>( $\mu$ -Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>)] (III)*

A solution of 1.14 g (3.26 mmol) [Et<sub>4</sub>N][V(CO)<sub>6</sub>] and 1.62 g (3.33 mmol) dpase in 100 ml THF was irradiated for one hour and the solution evaporated to 10 ml. On addition of 30 ml heptane, a sticky red-brown product was obtained which, after decantation of the supernatant liquid, was stirred with 10 ml THF for one hour. Yellow, crystalline III which separated out was filtered off, washed with 1 ml THF and with two 5 ml portions of heptane. From the filtrate, an equal amount of III was precipitated with heptane. Total yield 1.03 g (56%). The analysis (Table 1) and spectra (Table 3) indicate that III is actually a 1/1 adduct with [Et<sub>4</sub>N][V(CO)<sub>6</sub>]; recrystallization and variation of preparative conditions do not effect the composition.

*cis*-Tetraethylammonium tetracarbonyl(1,1,4,4-tetraphenyl-1,4-diarsabutane)-vanadate(-I), *cis*-[Et<sub>4</sub>N][V(CO)<sub>4</sub>(Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>)] (IVa) and *cis*-bis(tetraethylammonium) octacarbonyl-μ-(1,1,4,4-tetraphenyl-1,4-diarsabutane)divanadate (-I), *cis*-[Et<sub>4</sub>N]<sub>2</sub>[{V(CO)<sub>4</sub>}<sub>2</sub>(μ-Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>)<sub>2</sub>] (IVb)

0.94 g (2.69 mmol) [Et<sub>4</sub>N][V(CO)<sub>6</sub>] and 1.25 g (2.57 mmol) dpase dissolved in 100 ml THF where irradiated for 6 h, while a weak N<sub>2</sub>-stream was bubbled through the solution. The dark-red solution was treated with n-heptane until precipitation of IV was complete (ca. 80 ml). The orange-red powder (consisting of a mixture of IVa and IVb) was filtered off, recrystallized from 5 ml acetonitrile, and dried under high vacuum. Yield 0.27 g (14%).

*cis*-Dicarbonyl-η<sup>5</sup>-cyclopentadienyl(1,1,4,4-tetraphenyl-1-arsa-4-phosphabutane)-vanadium(+I), *cis*-[η<sup>5</sup>-CpV(CO)<sub>2</sub>(Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)] (V)

A solution of 0.48 g (2.11 mmol) CpV(CO)<sub>4</sub> and 0.98 g (2.22 mmol) arphos dissolved in 100 ml THF was irradiated for 30 min, with a weak N<sub>2</sub>-stream passing through the solution. After evaporation to 20 ml, V was precipitated by addition of 50 ml heptane, filtered off, washed with three 10 ml portions of heptane, and dried under high vacuum. Yield 0.83 g (64%).

*cis*-Dicarbonyl-η<sup>5</sup>-cyclopentadienyl(1,1,4,4-tetraphenyl-1,4-diarsabutane)vanadium(+I), *cis*-[η<sup>5</sup>-CpV(CO)<sub>2</sub>(Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>)] (VI)

Preparation and isolation of VI was carried out as described for V. Reagents: 2.71 g (5.57 mmol) dpase and 1.26 g (5.52 mmol) CpV(CO)<sub>4</sub>; irradiation time 95 min. Yield 2.12 g (58%).

*cis*-Dicarbonyl-η<sup>5</sup>-cyclopentadienyl[*o*-phenylenebis(dimethylarsine)]vanadium(+I), *cis*-[η<sup>5</sup>-CpV(CO)<sub>2</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>}] (VII)

A solution of 1.72 g (7.54 mmol) CpV(CO)<sub>4</sub> and 2.0 ml (ca. 7 mmol) diars in 100 ml THF was irradiated for 3 h, the solution concentrated to 10 ml, and VII precipitated by treatment with 80 ml of heptane. Yield 3.29 g (95%).

## Results and discussion

IR and NMR spectroscopic data are listed in Table 3. Structural assignments were based on data for ditertiary phosphine complexes [1].

### CO-Substitution in [Et<sub>4</sub>N][V(CO)<sub>6</sub>]

**Monosubstitution.** Photo-induced substitution of carbon monoxide in [V(CO)<sub>6</sub>]<sup>-</sup> with ditertiary phosphines PP initially yields the monosubstituted, monometallic species [V(CO)<sub>5</sub>PP]<sup>-</sup> [1]. Simultaneously, the *cis*-disubstituted product is formed, which can, however, be removed by conversion to the hydrido complex on silica gel [11] or by reaction with allyl chloride [12]. A different reaction takes place when THF solutions containing [Et<sub>4</sub>N][V(CO)<sub>6</sub>] and arphos or dpase in about equimolar amounts are irradiated. The ligands adapt a bridging function to form monoligate bimetallic complexes [Et<sub>4</sub>N]<sub>2</sub>[{V(CO)<sub>5</sub>}<sub>2</sub>(μ-arphos)] (I) and [Et<sub>4</sub>N]<sub>2</sub>[{V(CO)<sub>5</sub>}<sub>2</sub>(μ-dpase)] (III). Although disubstitution does not occur readily with these compounds, the reaction mixture from [Et<sub>4</sub>N][V(CO)<sub>6</sub>] and arphos contains considerable amounts of disubstitution product after compara-

TABLE 3  
IR AND  $\delta^{51V}$  NMR DATA ON ARSINE COMPLEXES OF  $[\text{V}(\text{CO})_6]^-$  AND  $\eta^5\text{-CpV}(\text{CO})_4$

	$\nu(\text{C}\equiv\text{O})$ ( $\text{cm}^{-1}$ ) <sup>a</sup>		$\delta^{51V}$ (ppm) <sup>b</sup>	
	A <sub>1</sub> (2)	A <sub>1</sub> (1)	E	
$[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{PPh}_2\text{Et}]^c$	1964	1858	1821	-1842 (D, 225)
$[\text{Et}_4\text{N}]_2[\text{V}(\text{CO})_5]_2(\mu\text{-arphos})$ (I)	1960	1850(sh)	1815	-1823; -1847 (D, 250)
$[\text{Et}_4\text{N}]_2[\text{V}(\text{CO})_5]_2(\mu\text{-dpase})$ (III) <sup>d</sup>	1965	1858	1825	-1824
$[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{AsPh}_3]$ [7]	1967	1827	1859	-1800
	A <sub>1</sub> (2)	A <sub>1</sub> (1)	B <sub>1</sub>	B <sub>2</sub>
<i>cis</i> - $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4\text{dppe}]$ [1]	1903	1799	1780	1747
<i>cis</i> - $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4\text{arphos}]$ (II)	1900	1795	1783	1750
<i>cis</i> - $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4\text{diars}]^e$	1901	1791	1777	1743
<i>cis</i> - $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4\text{dpase}]$ (IVa)				-1754
<i>cis</i> - $[\text{Et}_4\text{N}]_2[\text{V}(\text{CO})_4]_2(\mu\text{-dpase})_2$ (IVb)	1895	1792(sh)	1780	-1781
	A'	A''		
<i>cis</i> - $[\eta^5\text{-CpV}(\text{CO})_2\text{dppe}]$ [1]	1870	1799		-1120 f
<i>cis</i> - $[\eta^5\text{-CpV}(\text{CO})_2\text{arphos}]$ (V)	1867	1796		-1030 f
<i>cis</i> - $[\eta^5\text{-CpV}(\text{CO})_2\text{diars}]$ (VII)	1865	1794		-992
<i>cis</i> - $[\eta^5\text{-CpV}(\text{CO})_2\text{dpase}]$ (VI)	1870	1800		-937

<sup>a</sup> Assignment of bands according to ref. 14. <sup>b</sup> Ca. 0.2 M THF or MeCN solutions. All resonance signals are upfield (negative sign) a  $\text{VOCl}_3$  standard. <sup>c</sup>  $[\eta^3\text{p-51V}]$  coupling constants (in brackets) are in Hz; D = doublet, T = triplet. <sup>d</sup> Unpublished. <sup>e</sup> The substance is a 1/1 adduct with  $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$ . Data for  $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$  in THF:  $\nu(\text{C}\equiv\text{O})$  1893w and 1857vs;  $\delta^{51V}$  -1952 ppm. <sup>f</sup> IR data from ref. 6. <sup>g</sup> No coupling observed due to line broadening.

tively short irradiation times. From this mixture, I is isolated after elimination of the disubstituted species by subsequent irradiation in the presence of  $C_6H_5Cl$ .

III and  $^{51}V$  NMR spectra of I and III are in accord with the local  $C_{3v}$  symmetry of the  $[V(CO)_5]$  moieties (cf. Table 3). The  $^{51}V$  NMR spectrum of I shows two signals for vanadium bonded via phosphorus and arsenic, respectively. The lower field shift value is assigned to the  $\{V(CO)_5\}$  moiety bonded to the  $AsPh_2$  site, which exhibits lower ligand strength than the  $PPh_2$  group [7,13] (see also Fig. 1). In the  $^{31}P$  NMR spectrum no signal corresponding to uncoordinated  $PPh_2$  is observed supporting the proposed structure.

**Disubstitution.** When irradiation times are prolonged up to 2 h (arphos) and 8 h (dphos) and CO is removed by continuous passage of  $N_2$  through the solution, disubstitution progresses to a point at which the product can be isolated in reasonable yields. The product from arphos is *cis*- $[Et_2N][V(CO)_4(arphos)]$  (II), with a chelated structure analogous to disubstitution with tertiary phosphines. Disubstitution with dphos, however, results in the formation of a mixture of two products represented by two distinct  $^{51}V$  NMR signals at  $-1734$  and  $-1721$  ppm (cf. Table 3). Recently, we noted that there is a correlation between  $^{51}V$  NMR shift values and the ring size (i.e. ring strain and distortion of the  $CO$  bond angle at the vanadium center) to the extent that lower shift values correspond with enhanced ring strain [14]. We assume the two disubstituted species likely to be formed are *cis*- $[Et_2N][V(CO)_4(dphos)]$  (IIa) and *trans*- $[Et_2N][V(CO)_4(dphos)]$  (IIb). The *trans*-disubstituted ring compound (IIb) is apparently less favored than the *cis*-isomer (IIa) in the system of  $Et_2N$ . Consequently, the *cis*-

field NMR signal must be assigned to IVb. However, this conclusion while likely, is not definite.

#### CO-Substitution in $\eta^5\text{-CpV}(\text{CO})_4$

With  $\text{CpV}(\text{CO})_4$ , the ligands arphos, dpase and diars rapidly react to the monometallic monoligand complexes *cis*- $[\eta^5\text{-CpV}(\text{CO})_2\text{arphos}]$  (V), *cis*- $[\eta^5\text{-CpV}(\text{CO})_2\text{dpase}]$  (VI), and *cis*- $[\eta^5\text{-CpV}(\text{CO})_2\text{diars}]$  (VII), thus paralleling the course of reaction between  $\text{CpV}(\text{CO})_4$  and  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1, 2, 4$ ) [1]. The compounds are isolated by precipitation with *n*-heptane after approximately 1 h of irradiation. IR and  $^{51}\text{V}$  NMR spectra (Table 3) are consistent with the proposed formulation. The  $^{31}\text{P}$  NMR spectrum of V shows a relatively broad signal (half-width 165 Hz) at +117 ppm, characteristic of phosphorus coordinated to vanadium.

#### Conclusion

$^{51}\text{V}$  NMR shifts  $\delta(\text{V})$  can be employed to arrange ligands according to their strength ( $\sigma$ -donor and  $\pi$ -acceptor ability) with respect to their position in the spectrochemical series [13]. Thus,  $|\delta(\text{V})|$  is proportional to ligand strength, where  $|\delta(\text{V})|$  values are understood to parallel shielding of the  $^{51}\text{V}$  nucleus. This relation holds under the restriction that variations of  $\delta(\text{V})$  are dominated by variations in the paramagnetic term of the overall shielding, and that increasing ligand strength is reflected by increasing ligand field splitting. On this view, the diamagnetic term, covalency of the vanadium—ligand bond and nephelauxetic effects impart constant contributions throughout our series of similar ligands. In terms of this simplified concept, the ligands arphos, dpase and diars may be arranged within a series of increasing ligand strength according to  $\text{AsPh}_3 \approx \text{dpase} \approx \text{arphos}(\text{As}) < \text{diars} < \text{arphos}(\text{As}, \text{P}) < \text{arphos}(\text{P}) \approx \text{dppe} \approx \text{PEtPh}_2$  (for  $\delta(\text{V})$  values see Table 3). Basically, the arsenic ligands are weaker than the ligands coordinated via phosphorus functions, while among the ditertiary phosphines, the dimethylarsenic group is distinctly stronger than the  $\text{AsPh}_2$  group. The relatively weak donor—acceptor ability of arphos and dpase along with steric factors may explain the lower reaction rate for disubstitution as compared to diars or dppe, and hence the tendency to form binuclear complexes on substituting CO in the  $[\text{V}(\text{CO})_6]^-$  anion. This tendency is more pronounced for dpase. No bridging structures are, however, formed from  $\text{CpV}(\text{CO})_4$  in prolonged reaction.

The disubstituted anionic complexes exhibit a structural similarity to the products obtained from the reaction between  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) and arphos or dpase, in that monometallic and bimetallic species of the general composition  $\text{M}(\text{CO})_4\text{dpase}$ ,  $\text{M}(\text{CO})_2(\text{dpase})_2$  and  $\text{M}_2(\text{CO})_6(\text{dpase})_3$  ( $\text{M} = \text{Mo}, \text{W}$ ) are formed [8]. The analogy is still more striking with the arphos complexes  $\text{M}_2(\text{CO})_8(\text{arphos})_2$  [10]. However, no bridging structures for monosubstitution were described. Monosubstitution with arphos yielded  $\text{Cr}(\text{CO})_5\text{arphos}$ ; the ligand appears to be bonded through phosphorus [9].

#### Acknowledgement

We acknowledge support of this work by the Deutsche Forschungsgemeinschaft.



## References

- 1 D. Rehder, L. Dahlenburg and I. Müller, *J. Organometal. Chem.*, **122** (1976) 53.
- 2 D. Rehder, *J. Organometal. Chem.*, **137** (1977) C25.
- 3 H. Behrens and H. Brandl, *Z. Naturforsch. B*, **22** (1967) 1353.
- 4 I. Müller and D. Rehder, *J. Organometal. Chem.*, **139** (1977) 293.
- 5 J.E. Ellis and R.A. Faltynek, *J. Organometal. Chem.*, **93** (1975) 205.
- 6 A. Davison and J.E. Ellis, *J. Organometal. Chem.*, **31** (1971) 239.
- 7 R. Talay and D. Rehder, *Chem. Ber.*, **111** (1978) 1978.
- 8 F. Zingales, F. Canziani and R. Ugo, *Gaz. Chim. Ital.*, **92** (1962) 761.
- 9 J.A. Connor, J.P. Day, E.M. Jones and G.E. McEwen, *J. Chem. Soc. Dalton Trans.*, (1973) 347.
- 10 S.C. Tripathi, S.C. Srivastava and A.K. Shrimal, *J. Organometal. Chem.*, **73** (1974) 343.
- 11 U. Puttfarcken and D. Rehder, *J. Organometal. Chem.*, **157** (1978) 321.
- 12 U. Francke and E. Weiss, *J. Organometal. Chem.*, **121** (1976) 355.
- 13 D. Rehder and J. Schmidt, *J. Inorg. Nucl. Chem.*, **36** (1974) 333; D. Rehder, W.L. Dorn and J. Schmidt, *Trans. Met. Chem.*, **1** (1976) 74.
- 14 F.A. Cotton, *Inorg. Chem.*, **3** (1964) 702.