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Preliminary communication

VANADAPHOSPHA-ALKANES AND -CYCLOALKANES PREPARED BY PHOTOREACTION OF CARBONYL-VANADIUM COMPOUNDS WITH TETRAPHENYLDIPHOSPHINES

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Summary

Reaction between Ph_2PPPh_2 and $[Et_4N][V(CO)_6]$ yields *cis*-$[Et_4N]_2[(\mu\text{-}Ph_2PPPh_2)_2\{V(CO)_4\}_2]$, which may have a cyclic structure, and $[Et_4N]_2[(\mu\text{-}Ph_2PPPh_2)\{V(CO)_5\}_2]$. An "open-chain", monometallic species $[\eta^5\text{-}CpV(CO)_3Ph_2PPPh_2]$ is formed with $[\eta^5\text{-}CpV(CO)_4]$. Proposed structures are based on IR, ^{31}P, and ^{51}V NMR spectra.

We recently described our findings on the UV-induced reaction of $[Et_4N][V(CO)_6]$ and $[\eta^5\text{-}CpV(CO)_4]$ with mono- and oligo-tertiary phosphines, emphasizing the preparative potential [1] and features of the semi-empirical interpretation of ^{51}V NMR spectra in terms of the electronic correlations in the metal—ligand sphere [2, 3]. We now report initial results on the photolytic introduction of tetraphenyldiphosphine (Ph_2PPPh_2) into carbonylvanadium compounds. New structural principles are shown to arise with this ligand.

On UV irradiation of THF solutions containing $[Et_4N][V(CO)_6]$ and Ph_2PPPh_2 (for experimental details see Ref. 1), a dark-red substance is precipitated from which an air-sensitive, red powder (I) can be isolated. According to analytical and spectroscopic data, I is a *cis*-disubstituted complex *cis*-$[Et_4N]_2[(\mu\text{-}Ph_2PPPh_2)_2\{V(CO)_4\}_2]$ (Found: C, 64.6; H, 7.9; N, 2.3; P, 8.8; V, 7.9. $C_{36}H_{40}NO_4P_2V$ calcd.: C, 65.16; H, 6.08; N, 2.11; P, 9.34; V, 7.68%), possibly having the cyclic structure of a 1,4-divanada-2,3,5,6-tetraphosphacyclohexane. The filtrate from the above mixture, on treatment with O_2-free water and subsequent reprecipitation from THF/methylcyclohexane, yields a yellow, air-sensitive powder (II). Data of II are consistent with its formulation as a 1,4-divanada-2,3-diphosphabutane, hence $[Et_4N]_2[(\mu\text{-}Ph_2PPPh_2)\{V(CO)_5\}_2]$ (Found: C, 59.3; H, 6.2; N, 2.6; P, 6.2; V, 9.8. $C_{25}H_{30}NOPV$ calcd.: C, 59.18; H, 5.96; N, 2.76; P, 6.10; V, 10.24%).

Spectroscopic parameters are summarized in Table 1. Proposed structures are

TABLE 1

SPECTROSCOPIC DATA FOR TETRAPHENYLDIPHOSPHINE-SUBSTITUTED CARBONYL-VANADIUM COMPOUNDS

	$\nu(C{\equiv}O)$ [a] (cm^{-1})	$\delta(^{51}V)$ (%) [b]	$^{1}J(^{31}P-^{51}V)$ (Hz)	$\delta(^{31}P)$ [c] (ppm)
cis-$[(\mu\text{-}Ph_2PPPh_2)_2\{V(CO)_4\}_2]$ (I)	1896, 1833, 1800, 1774	−0.178 t	235	+124
$[(\mu\text{-}Ph_2PPPh_2)\{V(CO)_5\}_2]$ (II)	1967, 1860, 1828	−0.186 d	205	+55, +28
$[\eta^5\text{-}CpV(CO)_3Ph_2PPh_2]$ (III)	1958, 1865(sh), 1858	−0.141 d	155	−16.8 [d], +71

[a] Ca. 0.02 *M* in MeCN/THF (2/1). [b] Ca. 0.2 *M* in MeCN/THF (2/1) relative to an external $VOCl_3$ standard (negative values indicate upfield shifts). [c] Ca. 0.15 *M* in MeCN/CD_3CN/THF (2/1/1) relative to an external H_3PO_4 (85% in D_2O) standard at room temperature; positive shift values (broad lines, indicating coordinated P-functions) are downfield H_3PO_4. [d] Unligated Ph_2P.

shown in Fig. 1. IR and NMR features support the proposed structures (cf. refs. 1, 3, and 4). The "normal" ^{51}V chemical shift value and vanadium—phosphorus coupling constant for I suggest a cyclic structure as represented by the six-membered ring without substantial ring strains or angle distortions. For II, two broad ^{31}P resonances corresponding with phosphorus functions directly bonded to the quadrupolar ^{51}V nucleus, reflect non-equivalent PPh_2 groups, possibly originating from different orientations of the two phosphorus sites with respect to the equatorial CO groups, as indicated in Fig. 1, structure II.

The UV-induced reaction between Ph_2PPPh_2 and $[\eta^5\text{-}CpV(CO)_4]$ at room temperature gives almost exclusively a monosubstituted product $[\eta^5\text{-}CpV(CO)_3\text{-}Ph_2PPh_2]$ (III; for spectra see Table 1). If irradiation is carried out at elevated

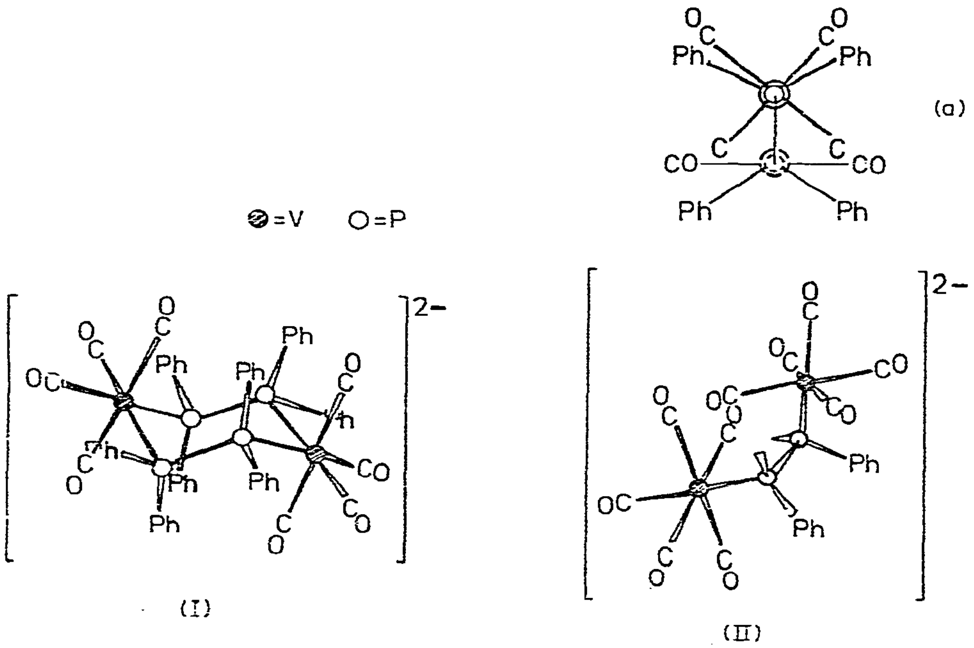

Fig. 1. Proposed structures for *cis*-$[(\mu\text{-}Ph_2PPh_2)_2\{V(CO)_4\}_2]^{2-}$ (I) and $[(\mu\text{-}Ph_2PPh_2)\{V(CO)_5\}_2]^{2-}$ (II). (a) Compound II viewed "from the top" (along the V—P-axis); upper outer circle, V(1); upper inner circle, P(1); lower outer circle P(2); lower inner circle V(2).

temperatures, a second product is formed in small amounts which is indicated by IR and ^{51}V NMR results (lowest ν(C≡O) 1788 cm^{-1}, δ(V) −0.124 ppm) to be *cis*-[η^5-CpV(CO)$_2$(Ph$_2$PPPh$_2$)$_2$] (IV). IV is, however, thermally unstable and so could not be isolated. III, which may be considered as a 1-vanada-2,3-diphosphapropane, is obtained as a dark red oil by passage of the reaction mixture through a silicagel column. A sharp ^{31}P NMR signal at −16.8 ppm, corresponding with unligated PPh$_2$-, and a broad signal at +71 ppm, assigned to ligated PPh$_2$, indicate an open-chain structure for III with non-bridging phosphine. III therefore exhibits structural similarity with the isoelectronic tetracarbonyltetraphenyldiphosphinerhenium iodide described by Hieber and Opavsky [5]. The ^{51}V chemical shift and C≡O stretching frequencies are similar to those observed for strong π-accepting phosphines such as P(OR)$_3$ [3, 6]. The strong π-interaction between tetraphenyldiphosphine and vanadium is probably due to enhanced π-delocalization of vanadium *d* electrons into vacant *d* functions of the P atoms (or accepting MO orbitals localized on the phosphine) by $d - d$ interaction between ligated and unligated phosphorus. This "three-centre d_π-interaction" would also be responsible for the non-observed P—P coupling.

While tetraphenyldiphosphine essentially behaves like a strong monotertiary phosphine in its reactions with [η^5-CpV(CO)$_4$], its ligand behaviour towards the anionic [V(CO)$_6$]$^-$ ressembles that observed in substitution reactions with iron and nickel carbonyl [7]. Unlike ditertiary phosphines of the type Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1—4), which give rise to monometallic biligate chelated species [1], Ph$_2$PPPh$_2$ clearly prefers to form binuclear bridged structures.

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