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σ-Alkenyl and halogeno complexes of vanadium (I and II). The crystal structures of $(ClV(CO)_2(Ph_2PCH_2CH_2PEt_2)_2 \cdot$ benzene, $Br_2V(Me_2PCH_2CH_2PMe_2)_2$ and $I_2V(Me_2PCH_2CH_2PMe_2)_2 \cdot$ toluene *

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Abstract

Various σ-alkenyl complexes of the general composition (alkenyl)V$(CO_{6-n}p_m$ (where $n = 2$, 3 and p_m is a potentially m-dentate phosphine coordinated through n of its donor centres, $n \leq m$) have been prepared by photo-induced hydrovanadation of the alkynes 2-butyne, 1-hexyne, 3-hexyne and 3,3-dimethyl-1-butyne. In each case the Z isomer is formed exclusively or as the predominant product. Reaction of hexacarbonylvanadate with pyridinium bromide and p_m leads to the bromo complexes $BrV(CO)_{6-n}p_m$ ($n = 2$–4). In the case of $p_m = Me_2PCH_2CH_2PMe_2$ (dmpe), the complex Br_2V(dmpe) is also formed. The complex $I_2V(dmpe)_2 \cdot$ toluene was obtained as a by-product from the reaction between $[Et_4N][V(CO)_4dmpe]$ and perfluoro-isopropyl iodide. The face-capped, trigonal-prismatic complex $ClV(CO)_2(pepe)_2 \cdot$ benzene (pepe = $Ph_2PCH_2CH_2PEt_2$) was obtained from the photo-reaction between $HV(CO)_4$pepe and $[Et_4N]Cl$. Single-crystal X-ray diffraction studies were carried out on all three complexes. The ^{51}V NMR chemical shifts for the seven-coordinate complexes $XV(CO)_np_m$ have been used to arrange the ligands X in a magnetochemical series of ligand strengths (alkenyl ≅ alkyl < $SiMe_3$ < H ≅ Br ≅ I < O_2CR < Cl ≅ N_3 < CN).

Key words: Vanadium; Alkenyl; Phosphine; Crystal structure; Halide

1. Introduction

We have recently shown that hydrido complexes of the general composition $HV(CO)_{6-n}p_m$ ($m \leq n$) react photochemically with alkenes to form σ-alkyl complexes by hydride transfer and simultaneous C coordination to vanadium (hydrovanadation of the olefinic double bond) [1]; p_m denotes an m-dentate phosphine (Scheme 1), coordinating through n of its phosphorus centres. In the present paper we demonstrate that hydrovanadation can also be carried out with alkynes, leading to the hitherto unknown σ-alkenyl complexes of composition (alkenyl)$V(CO)_{6-n}p_m$.

This type of reaction is of interest, inter alia, in the context of modelling the alkyne reductase activity of vanadium nitrogenase from *Azotobacter*, yielding ethylene and ethane by reductive protonation of acetylene [2]. The initiating step in this enzymatic reaction is possibly the side-on coordination of the substrate acetylene to vanadium in the active centre of the enzyme, followed by transfer of hydride either by NADH, or mediated through an intermediate hydridic vanadium species. The halide complexes (Hal)$V(CO)_3(PR_3)_3$ in fact react with alkynes to form (Hal)$V(CO)_2(PR_3)_2(\pi$-alkyne) [3], with the alkyne coordinated to V^I in the side-on fashion and acting as a four-electron donor. Replacing halide by hydride leads to reactive intermediates that immediately undergo hydride transfer to form alkenyl complexes, a reaction that models the formation of the first reduction product in enzymatic action, and which is reminiscent of the *in vitro* reduction of alkynes to Z-alkenes by zinc in the presence of niobium halides [4]. Several new phosphine-stabilized halide complexes of V^I and V^{II} are also described.

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* Dedicated to Professor H. Werner on the occasion of his 60th birthday.

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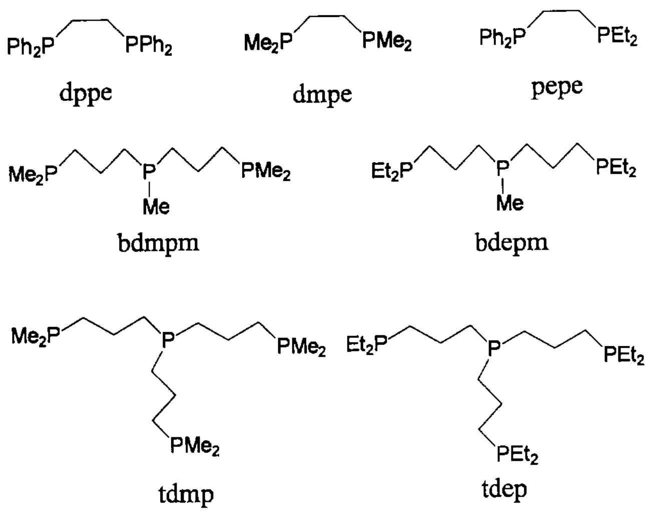


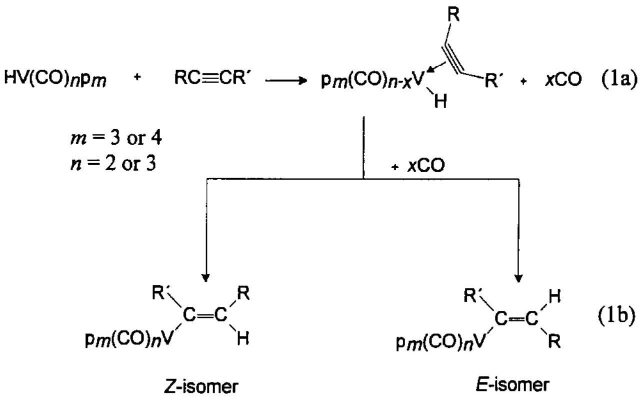
Scheme 1.

2. Results and discussion

2.1. *Alkenyl complexes*

2.1.1. *Preparation and reaction mechanism*

The complexes (alkenyl)V(CO)$_4$p$_m$ and (alkenyl)V(CO)$_3$p$_m$ have been prepared by UV irradiation of the hydrido complexes HV(CO)$_4$p$_m$ and HV(CO)$_3$p$_m$, respectively, in the presence of a *ca.* ten-fold excess of the alkyne. The compounds form black-red powders, which are stable under inert gas. Neutral, paramagnetic species V(CO)$_2$(p$_m$)$_2$ also obtained in small amounts as a result of photo-fragmentation of the hydrido complexes and rearrangement of the fragments [1b] are removed by fractional crystallization. The initiating step of the hydrovanadation of the alkyne possibly is a substitution of CO and side-on coordination of the alkyne to the vanadium centre (eq. (1a)), followed by hydride transfer and recombination with CO (eq. (1b)). Evidence for this assumption comes (i) from the existence of complexes of composition IV(CO)$_2$p$_2$(η^2-alkyne) [3] and BrVp$_4$(η^2-alkyne) [5], and (ii) from the observation, by ^{51}V NMR (*vide infra*), that the complexes (alkenyl)V(CO)$_{6-n}$p$_m$ are present either as a single (the *Z*) isomer ($n = 2$) or, where there are two isomers ($n = 3$), with the *Z* isomer clearly dominating over the *E* isomer. This stereoselectivity is suggestive of a mechanism in which hydride transfer occurs within an intermediate mixed hydride-alkyne-complex. Stereoselectivity has also been observed in the *in vitro* reductive protonation of alkynes by Zn/NbCl$_x$, and low-valent niobium-η^2-alkyne comlexes have been postulated in this case [4] and recently shown to exist [6].



2.1.2. *Characterization*

Characteristic spectroscopic data are collated in Table 1. The ν(CO) region in the IR spectra shows four bands for the tetracarbonyl complexes, and three bands for the tricarbonyl species. This is essentially the same pattern as that observed for seven-coordinated

TABLE 1. Selected spectroscopic data for the complexes (σ-alkenyl)V(CO)$_{6-n}$p$_m$

Complex	ν(CO) [a] (cm^{-1})	δ(^{51}V) [b] (ppm)	δ(^{1}H) [c] (ppm)
(3-hexenyl)V(CO)$_4$dppe	1929 (1850) 1833 1799	−1060	5.59 [d] [5.37]
(2-butenyl)V(CO)$_4$dppe	1932 (1850) 1829 1801	−1061	5.59 [5.12]
(1-hexenyl)V(CO)$_4$dppe	1930 (1850) 1832 1801	−1064	5.58 [5.67]
(3,3-dimethyl-1-butenyl)V(CO)$_4$dppe	1931 (1950) 1833 1798	−1072	5.60 [5.80]
(3-hexenyl)V(CO)$_4$bdmpm	1917 (1840) 1825 1805	−1064	
(3-hexenyl)V(CO)$_4$bdepm	1914 (1850) 1838 1821	−1049	
(3-hexenyl)V(CO)$_3$bdmpm	1891 1778 1757	−843 {−847}	
(3-hexenyl)V(CO)$_3$bdepm	1889 1775 1755	−798 {−826}	

[a] Relative intensities are as follows: Tetracarbonyls s (sh) s vs; tricarbonyls s vs vs.

[b] In THF solution relative to VOCl$_3$. Values in curly brackets correspond to the (minor) *E* isomer.

[c] Without entry: not observed due to paramagnetic impurities (V(CO)$_{6-n}$p$_m$). Values in square brackets are those for the same H in the alkene.

[d] Triplet, $^4J_{H-P} = 5.4$ Hz.

alkyl [1] and hydrido complexes [1a,7], and may imply a similar structure in solution for alkenyl, alkyl and hydrido complexes, *i.e.* with the seventh ligand capping a face of a basic $\{V(CO)_{6-n}p_m\}$ octahedron and a *cis* arrangement for $n = 2$ and a *mer* arrangement for $n = 3$ (in the case of the hydrido complexes, the *fac* configurations have also been documented [1a]). The ν(CO) are shifted to lower wave numbers by *ca.* 80 cm^{-1} in alkenyl with respect to those for hydrido complexes, and are comparable to those of the alkyl complexes, indicating that the coordinating carbons of the alkenyl (and alkyl) groups are more basic than the hydride ligand.

A corresponding difference between alkenyl and alkyl complexes on the one hand, and hydrido complexes on the other hand is found in the ^{51}V NMR pattern: $\delta(^{51}V)$ values for $(alkenyl)V(CO)_{6-n}p_m$ are around -1050 ppm for $n = 2$, and between -800 and -850 ppm for $n = 3$, and hence deshielded by *ca.* 650 ppm with respect to those for the related hydrides [1]. For $n = 3$, for which Z and (minor product) E isomers are observed; the latter isomer shows a slightly higher shielding of the ^{51}V nucleus (Table 1) as a consequence of the steric influence of the substituent R (eq. (1b)) [8].

The ^1H NMR spectra of the alkenyl complexes (Table 1) clearly indicate the presence of olefinic hydrogen on C_β at *ca.* 5.6 ppm, thus proving the presence of olefinic sp^2 carbons. A resolved $^1H-^{31}P$ coupling has been observed only in a single case *viz.* (3-hexenyl)$V(CO)_4$dppe, for which the ^4J coupling constant is 5.4 Hz.

2.2. *Halogeno complexes*

2.2.1. *Preparation and characteristics*

While seven-coordinated halide complexes of Nb^I and Ta^I of the general composition $(Hal)M(CO)_{6-n}p_m$ are well documented in the literature [9], the corresponding complexes of vanadium are scarce. To our knowledge, the only examples of this class of compound containing vanadium are $IV(CO)_4$dppe [10], $ClV(CO)_2(dmpe)_2$ and $(NC)V(CO)_2(dmpe)_2$ [11]. Some Nb and Ta complexes of this kind have been employed successfully by Lippard and his group in reductive C-C coupling [12]. We report here a general route to the bromo complexes $BrV(CO)_{6-n}p_m$ (eq. (2); see Scheme 1 for p_m). For comparison, $IV(CO)_4$dppe, prepared according to eq. (3) has been reinvestigated; for the intermediate dinuclear, iodo-bridged complex anion see refs. [3] and [13]. Finally, the chloro complex $ClV(CO)_2(pepe)_2$ (eq. (4)) has been synthesized.

TABLE 2. Spectroscopic data for the complexes $(Hal)V(CO)_{6-n}p_m$

Complex	ν(CO) (cm^{-1})	$\delta(^{51}V)$ (ppm) [a]
$IV(CO)_4$dppe	1993s 1921sh 1880vs 1859sh	-1706
$BrV(CO)_4$dppe	1988m 1870sh 1852vs	-1698
$BrV(CO)_4$pepe	1983m 1865vs, br	-1756
$BrV(CO)_4$bdmpm	1980m 1860vs, br	-1738
$BrV(CO)_4$bdepm	1885m 1868vs, br	-1733
$BrV(CO)_4$tdmp	[b]	-1735
$BrV(CO)_4$tdep	[b]	-1741
$BrV(CO)_4$dmpe	[b]	-1804 (t, 152)
$BrV(CO)_3$bdmpm	1945m 1845vs 1810vs	-1020 (q, 142)
$BrV(CO)_3$bdepm	1941m 1842vs 1811vs	-1000 (q, 129)
$BrV(CO)_3$tdmp	1945m 1842s 1812s	-1023 (q, 142) [c]
$BrV(CO)_3$tdep	1935m 1839vs 1808s	-1009 (q, 136) [d]
$BrV(CO)_2(pepe)_2$	1825s 1760m	-624
$BrV(CO)_2(dmpe)_2$	1822s 1759m	-859 (quint., 159)

[a] Where appropriate, multiplicity and $^1J(^{31}P-^{51}V)$ (Hz) are shown in parentheses; unresolved unless otherwise indicated.

[b] Minor product, not observed in the IR.

[c] An additional minor product at -1010 (unresolved) was unassigned.

[d] An additional minor product at -989 (unresolved) was unassigned.

The bromo complexes are prepared by treatment of hexacarbonylvanadate with pyridinium bromide in the presence of p_m (eq. (2)), a procedure analogous to that used for the bromo-niobium complexes [9h]. The tendency to split off CO from the carbonylmetalate is, however, less pronounced in the case of vanadium, and it is therefore necessary to promote the reaction by irradiation with UV light. In the case of p_m = dmpe, $Br_2V(dmpe)_2$ is formed as a by-product. The bromo complexes form red, microcrystalline powders which are stable when kept under inert gas. Crystalline $I_2V(dmpe)_2$ was isolated as a minor product in an attempt to prepare a σ-akyl complex from $[Et_4N][V(CO)_4dmpe]$ and iso-C_3F_7I.

$$[V(CO)_6]^- + 2[HPy]Br + p_m \xrightarrow{h\nu} BrV(CO)_{6-n}p_m + nCO + H_2 + Br^- + 2py \quad (2)$$

$$[V(CO)_6]^- + I_2 \longrightarrow [\{V(CO)_4\}_2(\mu - I)_3]^- \xrightarrow{+dppe} IV(CO)_4dppe \quad (3)$$

$$HV(CO)_4pepe + [Et_4N]Cl \xrightarrow{h\nu} ClV(CO)_2(pepe)_2 \quad (4)$$

The IR pattern in the ν(CO) region (Table 2) is again very much the same as that for the seven-coordinate hydrido, alkyl and alkenyl complexes (*vide supra*). The positions of the bands are comparable to those of the hydrido complexes. The same is true for the ^{51}V chemical shifts (Table 2). As for other carbonyl complexes, the ^{51}V shielding decreases with decreasing number of strongly π-accepting carbonyls. Further, and again as for other complexes, ^{51}V shielding is less effective in phenylphosphine complexes than in those containing the more basic alkylphosphines, and larger in chelate 5-ring structures than in chelate 6-rings ("chelate effect", *cf.* [14]). The $\delta(^{51}V)$ values of the complexes $XV(CO)_{6-n}p_m$ can be used to arrange the groups X according to a "magnetochemical series of ligand strengths" [8,14,15], where the "strength" of the ligand is a weighted composite of its σ and π bonding power on the one hand, and the ligand polarizability on the other hand. The ^{51}V shielding, and hence the magnetochemical ligand strengths, increase in the series σ-alkyl ≅ σ-alkenyl < $SiMe_3$ < H ≅ Br ≅ I < O_2CR < Cl ≅ N_3 < CN, based on $XV(CO)_4$dppe for X = alkyl, alkenyl, silyl [7], Br and I, and on $XV(CO)_2(dmpe)_2$ for X = carboxyl, azide, cyanide, Cl (all from ref. [11]) and Br. A steric effect involving a decrease in the shielding with increasing steric demand of the ligands may also operate.

2.2.2. *X-ray structure analysis of $ClV(CO)_2(pepe)_2 \cdot$ benzene*

Crystals of this compound were obtained unintentionally by irradiation of a THF solution of 3,3-dimethyl-1-butyne which was contaminated with $[Et_4N]Cl$. Table 3 gives structure data, Table 4 lists selected bonding parameters and Table 5 lists atomic coordinates and isotropic thermal factors. Figure 1 shows an ORTEP plot and the numbering scheme for the compound. Like the complexes $ClNb(CO)_2(dppe)_2$ [9h] and $ClTa(CO)_2(dppe)_2$ [16], $ClV(CO)_2$-

TABLE 3. Structure data for $ClV(CO)_2(pepe)_2 \cdot$ benzene, $Br_2V(dmpe)_2$ and $I_2V(dmpe)_2 \cdot$ toluene

	$ClV(CO)_2(pepe)_2 \cdot$ benzene	$Br_2V(dmpe)_2$	$I_2V(dmpe)_2 \cdot$ toluene
Crystal data			
Empirical formula	$C_{44}H_{54}ClO_2P_4V$	$C_{12}H_{32}Br_2P_4V$	$C_{19}H_{40}I_2P_4V$
Molecular mass, g mol^{-1}	825.20	511.0	697.17
Crystal size, mm	0.08 × 0.30 × 0.38	0.15 × 0.18 × 0.25	0.2 × 0.2 × 0.3
Crystal system	triclinic	tetragonal	triclinic
Space group	$P\bar{1}$	$P4_2/ncm$	$P\bar{1}$
Unit cell dimensions:			
a, Å	11.882(5)	13.743(4)	8.705(2)
b, Å	14.008(6)		8.719(2)
c, Å	14.588(7)	12.240(4)	9.655(3)
α, °	72.70(4)		92.42(2)
β, °	72.36(3)		93.71(2)
γ, °	71.81(3)		91.76(2)
Volume, $Å^3$	2142.4(16)	2311.9(12)	730.2(3)
Z	2	4	1
Density (calcd.), g cm^{-3}	1.279	1.468	1.585
Absorpt. coefficient, cm^{-1}	5	42	5
$F(000)$	868	1028	343
Data collection			
2θ range, °	4.5 to 45.0	4.5 to 50.0	4.5 to 55.0
Index ranges	$-2 < h < 12$, $-14 < k < 15$, $-14 < l < 15$	$0 < h < 17$, $0 < k < 17$, $0 < l < 15$	$-11 < h < 11$, $-11 < k < 11$, $0 < l < 12$
Reflections collected	6050	4789	8208
Independent reflections	5620 (R_{int} = 8.78%)	1096 (R_{int} = 3.13%)	3383 (R_{int} = 8.10%)
Observed reflections	1387 ($F < 3\sigma(F)$)	450 ($F < 4\sigma(F)$)	2578 ($F < 4\sigma(F)$)
Solutions and refinement			
Quantity minimized	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0025F^2$	$w^{-1} = \sigma^2(F) + 0.0005F^2$	$w^{-1} = \sigma^2(F) + 0.0004F^2$
Number of param. refined	249	48	134
Final R (observed data)	0.107	0.0493	0.0589
Final wR (observed data) [a]	0.105	0.0496	0.0704
$wR2$ (all data) [b]	0.181		
Goodness of fit	1.26		1.48
Largest differ. peak, e $Å^{-3}$	0.70		0.98
Largest differ. hole, e $Å^{-3}$	−0.63		−2.38

[a] Conventional weighted R value.

[b] $wR2 = \sqrt{\left[\Sigma w\left(F_o^2 - F_c^2\right)^2 / \Sigma w F_o^4\right]}$ (*cf.* ref. [20]).

(pepe)$_2$ crystallizes in the triclinic space group $P\bar{1}$. The CO groups occupy *cis* positions in all three complexes, which can be described in terms of a trigonal prism $\{M(CO)_2(p_2)_2\}$ with the chloro ligand capping the face spanned by the four phosphorus atoms, and the two carbonyls in the ridge opposite to the p_4-plane. An alternative view is that of a distorted octahedron with Cl and the centre of the two CO groups in axial positions. The capped trigonal prism arrangement has also been reported for $ITa(CO)_4$dppe [9a] and $ClTa(CO)_3(PMe_3)_3$ [9c]. In contrast to the Nb complex [9h], there is no disorder between Cl and the two CO groups in the vanadium analogue. The bond distances d(V–Cl) (2.54 Å) and d(V–CO) (1.87 Å) are normal. The angle OC–V–CO (65°) is larger than the angles OC–Nb–CO (57°) and OC–Ta–CO (56°) in the chloro complexes of niobium and tantalum.

2.3. *X-ray structure analyses of $Br_2V(dmpe)_2$ and $I_2V(dmpe)_2 \cdot$ toluene*

$Br_2V(dmpe)_2$ is a by-product in the preparation of $BrV(CO)_2(dmpe)_2$ from $[Et_4N][V(CO)_4$dmpe] and [Hpy]Br (eq. (2)). It becomes the main product if an excess of [Hpy]Br is employed. $I_2V(dmpe)_2$ was formed as a by-product when $[Et_4N][V(CO)_4$dmpe] was treated with perfluoro-isopropyl iodide. Complexes of the composition $(Hal)_2V(p_2)_2$ were prepared previously from $V(Hal)_2(H_2O)_x$ and p_2 [17], "$VCl_2(THF)_2$" and p_2 [18], or by reduction of "$VX_3(THF)_3$" in the presence of the phosphine [19], and have been characterized by X-ray structure analysis in the case of Hal = Cl, p_2 = dppe and pepe [17], and Hal = Cl, p_2 = dmpe [18].

Structure data for the new $Hal_2V(dmpe)_2$ complexes are given in Table 3, bonding parameters in Table 6, and atomic coordinates in Tables 7 and 8. Figure 2 shows the ORTEP diagrams and numbering schemes for Br_2V(dmpe) and $I_2V(dmpe)_2$. $Br_2V(dmpe)_2$ crystallizes in the tetragonal space group $P4_2/ncm$. $I_2V(dmpe)_2$ crystallizes with one molecule of toluene in the triclinic space group $P\bar{1}$. The overall arrangement in both molecules is that of an octahedron with the two halide ligands in *trans* positions. The V–Hal and V–P bond

TABLE 4. Selected bonding parameters for $ClV(CO)_2(pepe)_2$

Bond lengths (Å)			
V–Cl	2.544(11)	V–C1	1.874(45)
V–P1	2.595(11)	V–C2	1.863(33)
V–P2	2.443(13)	C1–O1	1.192(54)
V–P3	2.487(13)	C2–O2	1.198(38)
V–P4	2.551(12)		
Bond angles (°)			
P1–V–P2	73.9(4)	P1–V–C1	80.5(3)
P1–V–P3	103.3(4)	C1–V–C2	65.3(18)
P3–V–P4	75.1(4)	C1–V–Cl	147.7(11)
P1–V–P4	159.9(4)	V–C1–O1	177.6(29)
P2–V–P3	165.1(4)	V–C2–O2	177.8(35)

TABLE 5. Fractional coordinates (×10^4) and isotropic thermal factors (pm^2 × 10^{-1}) for the non-hydrogen atoms of $ClV(CO)_2(pepe)_2 \cdot$ benzene [a]

	x	y	z	U_{eq}
V	1707(6)	9243(5)	7331(4)	45(4)
Cl	1448(9)	9070(8)	9164(7)	64(6)
P(1)	−596(9)	10124(8)	7795(7)	49(6)
P(2)	1578(9)	11048(8)	7215(7)	44(6)
P(3)	1763(9)	7373(8)	7913(7)	42(6)
P(4)	3885(9)	8363(8)	7506(7)	47(6)
O(1)	768(21)	8945(18)	5720(17)	65(15)
O(2)	3226(22)	9858(19)	5241(16)	79(15)
C(1)	1127(30)	9084(25)	6338(25)	34(10)
C(2)	2611(33)	9629(26)	6052(26)	46(11)
C(3)	−1589(32)	10398(27)	6931(25)	53(11)
C(4)	−1980(34)	9414(30)	6915(26)	72(13)
C(5)	−1464(29)	9405(24)	8986(22)	37(10)
C(6)	−2843(29)	10013(24)	9294(21)	37(10)
C(7)	−853(29)	11470(26)	8007(23)	42(11)
C(8)	325(28)	11588(22)	8199(21)	28(9)
C(9)	4340(30)	8934(26)	8273(24)	47(11)
C(10)	5016(36)	8177(30)	9048(29)	79(14)
C(11)	5105(34)	8325(27)	6381(24)	54(11)
C(12)	6347(34)	7708(28)	6496(25)	61(12)
C(13)	4106(32)	6994(27)	8061(25)	54(12)
C(14)	2881(28)	6699(23)	8682(22)	34(10)
C(21)	370(30)	6894(24)	8760(25)	42(10)
C(22)	157(36)	6800(29)	9804(30)	74(14)
C(23)	−995(35)	6495(27)	10293(26)	60(12)
C(24)	−1782(36)	6362(29)	9821(30)	71(13)
C(25)	−1536(39)	6501(32)	8814(33)	89(15)
C(26)	−330(39)	6878(31)	8193(29)	82(15)
C(31)	2287(29)	6540(26)	7056(22)	38(10)
C(32)	2267(34)	5485(31)	7370(27)	63(13)
C(33)	2720(34)	4802(28)	6696(28)	64(13)
C(34)	3362(37)	5190(33)	5706(29)	77(14)
C(35)	3397(36)	6233(34)	5398(29)	78(14)
C(36)	2938(33)	6923(29)	6003(27)	61(12)
C(41)	1231(27)	12016(25)	6117(21)	32(10)
C(42)	1408(27)	12984(25)	5990(22)	32(9)
C(43)	1057(33)	13826(28)	5166(26)	64(12)
C(44)	501(31)	13590(28)	4573(25)	54(12)
C(45)	310(31)	12597(29)	4686(25)	53(12)
C(46)	724(28)	11785(24)	5454(23)	35(10)
C(51)	2905(32)	11386(26)	7341(26)	50(11)
C(52)	3948(33)	11393(26)	6520(24)	48(11)
C(53)	5028(38)	11515(31)	6652(30)	78(14)
C(54)	4954(40)	11819(33)	7481(35)	99(17)
C(55)	3934(37)	11861(29)	8331(28)	70(13)
C(56)	2873(32)	11684(27)	8153(26)	54(12)
C(101)	2563(57)	5594(39)	1433(42)	135(21)
C(102)	3849(54)	5697(39)	1213(36)	120(19)
C(103)	4463(52)	5882(43)	1743(50)	143(22)
C(104)	3905(75)	5817(50)	2744(54)	200(30)
C(105)	2639(66)	5775(42)	3013(40)	147(23)
C(106)	1980(54)	5694(46)	2419(53)	163(24)

[a] C101 to C106 refer to benzene.

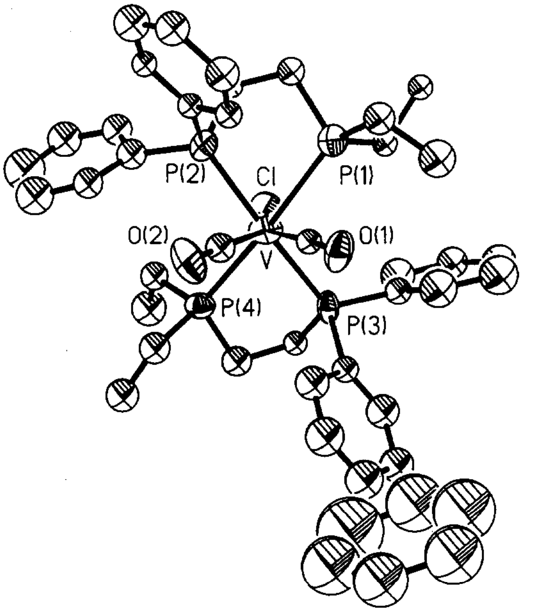


Fig. 1. ORTEP plot and numbering scheme for $ClV(CO)_2(pepe)_2$. Hydrogen atoms have been omitted for clarity.

lengths, and P–V–P bond angles are comparable to those in other $(Hal)_2V(p_2)_2$ complexes [17,18].

Thermal parameters and complete lists of bond lengths and angles for all three structures have been deposited with the Cambridge Crystallographic Data Centre.

3. Experimental details

3.1. General

All operations were carried out under an inert gas and in oxygen-free anhydrous solvents. The IR spectra were recorded on a Perking Elmer 1720 IFT spectrometer as THF solutions in 0.1 mm CaF_2 cuvettes. The NMR spectra were recorded at room temperature on a Bruker Am 360 spectrometer under the following conditions: ^1H, in THF-d_8, toluene-d_8 or benzene-d_6, standard TMS; ^{31}P, 145.78 MHz, in THF-d_8 or toluene-d_8, standard 80% H_3PO_4; ^{51}V, 94.73 MHz, in THF-d_8, toluene-d_8 or acetonitrile-d_3, standard $VOCl_3$.

X-ray structure data were collected on a Syntex $P2_1$ spectrometer for graphite-monochromated Mo Kα radiation at ambient temperature in the θ/2θ scan mode.

TABLE 6. Bonding parameters for $Br_2V(dmpe)_2$ and $I_2V(dmpe)_2$

$Br_2V(dmpe)_2$		$I_2V(dmpe)_2$	
Bond lengths (Å)			
V–Br	2.707(2)	V–I	2.827(1)
V–P	2.515(3)	V–P1/P2	2.530(2)
P–C1	1.813(14)	P1–C11	1.832(10)
P–C2	1.780(14)	P1–C12	1.843(12)
P–C3	1.826(15)	P1–C1	1.844(9)
C3–C3‴	1.306(30)	C1–C2	1.520(12)
Bond angles (°)			
Br–V–P	88.9(1)	I–V–P1/P2	88.9(1)/91.1(1)
P–V–P″	99.7(1)	P1–V–P2	80.6(1)
P–V–P‴	80.3(1)	P1–V–P2a	99.4(1)
V–P–C1	121.1(4)	V–P1–C11	121.7(4)
V–P–C2	122.7(5)	V–P1–C12	120.4(3)
P–V–C3	107.0(5)	V–P1–C1	106.7(3)

TABLE 7. Fractional coordinates (×10^5) and isotropic thermal factors (pm^2) for the non-hydrogen atoms of $Br_2V(dmpe)_2$

	x	y	z	U_{eq}
V	0	0	0	361(8)
Br	6042(9)	6042(9)	19011(14)	641(5)
P	−365(24)	−17064(20)	7423(26)	549(11)
C1	8460(102)	−21098(93)	17461(113)	1083(72)
C2	−676(146)	−27526(84)	−1146(131)	1432(87)
C3	−11518(96)	−18238(119)	15427(138)	1448(79)

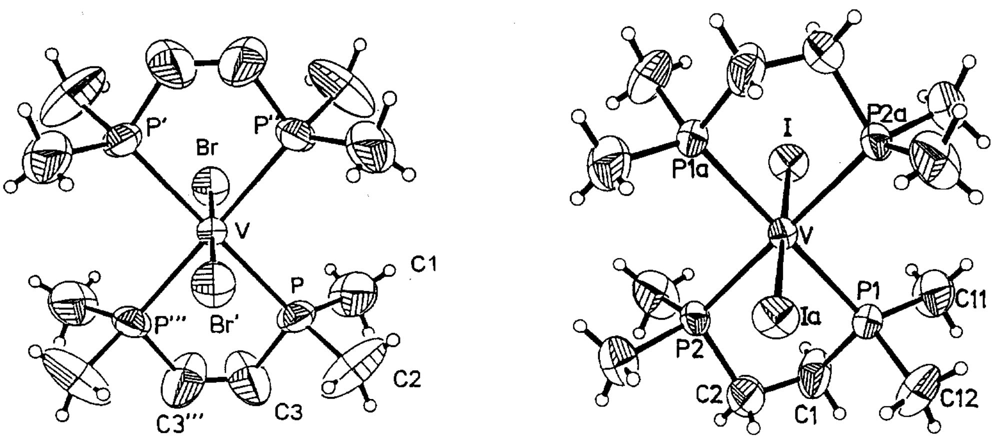


Fig. 2. ORTEP plots and numbering schemes for $Br_2V(dmpe)_2$ and $I_2V(dmpe)_2$.

TABLE 8. Fractional coordinates ($\times 10^4$) and isotropic thermal factors ($pm^2 \times 10^{-1}$) for the non-hydrogen atoms of $I_2V(dmpe)_2 \cdot$ toluene [a]

	x	y	z	U_{eq}
V	0	5000	0	31(1)
I	2270(1)	2765(1)	296(1)	53(1)
P(1)	−1603(2)	3543(2)	1636(2)	41(1)
P(2)	−1584(2)	3269(2)	−1754(2)	43(1)
C(1)	−2543(15)	1901(10)	613(8)	77(4)
C(2)	−3156(14)	2384(12)	−808(9)	82(4)
C(11)	−715(15)	2572(12)	3116(9)	83(4)
C(12)	−3239(14)	4454(10)	2425(10)	79(4)
C(21)	−2686(15)	4034(10)	−3234(8)	74(4)
C(22)	−724(15)	1623(10)	−2582(11)	86(4)
C(3)	5629(21)	−638(17)	5064(20)	60(5)
C(4)	5079(16)	257(11)	3799(9)	76(4)
C(5)	3999(35)	1247(24)	3943(29)	96(10)
C(6)	3278(23)	1672(16)	5149(21)	122(6)
C(7)	3805(30)	889(22)	6373(21)	78(8)

[a] C3 to C7 refer to toluene.

The structures were solved by direct methods and refined (full matrix least squares) with the programme system SHELXTL PLUS [20]. Absorption corrections were applied in the case of $I_2V(dmpe)_2$ by use of the program DIFABS [21]. Hydrogen atoms were placed in calculated positions and refined with isotropic thermal parameters. In the case of $Br_2V(dmpe)_2$ and $I_2V(dmpe)_2 \cdot$ toluene, all non-hydrogen atoms were refined anisotropically. In the case of $ClV(CO)_2(pepe)_2$, O, V, P and Cl were refined anisotropically, and carbons were refined isotropically. Details of the structure determination are contained in Table 3.

Alkynes and phosphines (p_m) were obtained from commercial sources or prepared by published procedures (p_m = bdmpm, bdepm, tdmp and tdep [22]). The following precursor complexes were prepared as previously described $[Et_4N][V(CO)_6]$ [23], $[Et_4N][V(CO)_4p_m]$ [7], $HV(CO)_{6-n}p_m$ [1].

3.2. *Preparation of complexes*

3.2.1. *$(C_6H_{11})V(CO)_4\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}$, C_6H_{11} = 3-hexenyl*

To a solution of 562 mg (1 mmol) of $HV(CO)_4$dppe in 10 ml of THF was added 2 g (12.2 mmol) of 3-hexyne. The mixture was irradiated for 2 h at room temperature by use a of high pressure mercury lamp (Philips HPK 125) placed close to the Duran Schlenk tube containing the reaction mixture. The reaction was monitored by IR spectroscopy. The solution changed colour from orange-brown to black-red as (3-hexenyl)$V(CO)_4$dppe was formed. After the irradiation the solution was evaporated to dryness and the residue, after complete removal of THF under high vacuum, redissolved in 15 ml of a 1 : 1 mixture of n-hexane and toluene. The solution was filtered through a 2 cm column of pretreated Celite, previously degassed and loaded under N_2. The filtrate was kept at 4°C for two weeks to allow the by-product $V(CO)_2(dppe)_2$ to crystallize out. This procedure was repeated twice to remove the remainder of this paramagnetic complex. The combined mother liquors were then evaporated, and the black-red powder dried under high vacuum for 2 h. Yield 479 mg (0.74 mmol) = 74%. Anal. Found: C, 67.2; H, 5.6; P, 9.5; V, 7.7. $C_{36}H_{35}O_4P_2V$ (644.56) calcd.: C, 67.08; H, 5.47; P, 9.61; V, 7.90%.

All other alkenyl complexes (*cf.* Table 1) were prepared similarly, in yields of 67–72%.

3.2.2. *$ClV(CO)_2\{(C_6H_5)_2PCH_2CH_2P(C_2H_5)_2\}_2 \cdot C_6H_6$*

The complex $ClV(CO)_2(pepe)_2 \cdot$ benzene crystallized spontaneously from the solution obtained by irradiation of a THF solution of 3,3-dimethyl-1-butyne and $HV(CO)_4$pepe containing $[Et_4N]Cl$ as an impurity. (The $HV(CO)_4$pepe had been prepared from $[Et_4N][V(CO)_6]$ by ion exchange chromatography on silica gel, $[Et_4N][V(CO)_4pepe]$ by photo-reaction between $[Et_4N][V(CO)_6]$ and pepe, and $[Et_4N][V(CO)_6]$ was obtained by precipitation from a solution of $Mg/Zn[V(CO)_6]_2$ or $Na[V(CO)_6]$ in methanol/water by treatment with an excess of $[Et_4N]Cl$. Incomplete washing of the $[Et_4N][V(CO)_6]$ meant that it was contaminated with chloride.) The compound crystallizes with an undefined amount of benzene of crystallization, which we were not able to locate unambiguously in the X-ray structure determination, a fact which may be responsible for the poor conventional *R* value of 10.5%.

3.2.3. *$BrV(CO)_4\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}$*

A stirred suspension of 0.35 g (1 mmol) of $[Et_4N][V(CO)_6]$, 0.40 g (1 mmol) of dppe and 0.32 g (2 mmol) of [Hpy]Br (pyridinium bromide) in 50 ml of THF was irradiated for 3 hours. As more of the bromo-complex was formed, as indicated by IR spectroscopic monitoring, the colour changed from yellow to red. The solution was evaporated to dryness, the residue dissolved in toluene and the solution filtered. The filtrate was concentrated to 15 ml and treated, with 15 ml of n-hexane with vigorous stirring. The solution was kept at 4°C for 2 days, during which red microcrystals of $BrV(CO)_4$dppe separated. The product was washed with three 10 ml portions of hexane and dried under high vacuum. Yield 0.48 g (0.75 mmol) = 75%. Anal. Found: C, 56.0; H, 3.8; P, 9.5; V, 7.7. $C_{30}H_{24}BrO_4P_2V$ (641.32) calcd.: C, 56.19; H, 3.77; P, 9.66;V, 7.94%.

The other seven-coordinated monobromo complexes listed in Table 2 were prepared analogously in yields of 64–74%.

3.2.4. $Br_2V\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}_2$

The reaction between $[Et_4N][V(CO)_6]$, [Hpy]Br and dmpe and a molar ratio of 1:2:2 yields $BrV(CO)_2(dmpe)_2$ (along with some $BrV(CO)_4dmpe$). $Br_2V(dmpe)_2$ is formed as an additional by-product or, if a ten-fold excess of [Hyp]Br is employed, as the main product. It can be crystallized from the THF solution by addition of hexane. Anal. Found: C, 28.4; H, 6.4; P, 24.0; V, 9.9. $C_{12}H_{32}Br_2P_4V$ (511.04) calcd.: C, 28.20; H, 6.31; P, 24.24; V, 9.97%. Suitable crystals for the X-ray structure analysis were formed in THF/hexane (1:1) after three weeks at 4°C.

3.2.5. $IV(CO)_4\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}$

A solution of 0.35 g (1 mmol) of $[Et_4N][V(CO)_6]$ in 30 ml of THF was cooled to -78°C and treated with 0.25 g (1 mmol) of iodine. Evolution of carbon monoxide started immediately, and the solution turned from yellow to red. The solution was allowed to warm to -50°C during 15 min and then treated with 0.40 g (1 mmol) of dppe, which enhanced the evolution of CO and caused turbidity of the solution. The mixture was warmed to room temperature during 30 min and stirred at ambient temperature for an additional 4 h. Filtration and evaporation left a viscous oil which was washed with 10 ml of n-hexane and the residue was dried under high vacuum for 3 h to yield 0.52 g (0.75 mmol) (75%) of a red powder of $IV(CO)_4dppe$, identified from its previously repeated IR data [10].

3.2.6. $I_2V\{Me_2PCH_2CH_2PMe_2\}_2 \cdot C_7H_8$ (C_7H_8 = toluene)

A solution of 440 mg (1 mmol) of $[Et_4N][V(CO)_4dmpe]$ in 30 ml of THF was cooled to -78°C and treated dropwise during 5 min with 3 mmol of perfluoro-isopropyl iodide. The solution turned dark red, and CO was evolved. The mixture was allowed to warm to room temperature overnight to give a green solution, which was evaporated to dryness. The sticky green residue was dissolved in 30 ml of toluene and the solution filtered. The green filtrate was concentrated to half of its volume and kept at 4°C for two weeks to yield red crystals of $I_2V(dmpe)_2 \cdot$ toluene.

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