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Reactions of hydridovanadium complexes: The formation of seven-coordinated σ-alkylvanadium(I) complexes by hydrovanadation of alkenes, and the molecular structure of *trans*-$[V(CO)_2(dppe)_2] \cdot 3C_6D_6$

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Abstract

σ-Alkyl complexes of $V^{(I)}$ of the general composition $(alkyl)V(CO)_{6-n}p_m$ have been prepared by UV-induced insertion of alkenes into the V–H bond of $HV(CO)_{6-n}p_m$. p_m is an oligophosphine coordinating through n phosphorus functions. Spectroscopic characteristics (IR and multinuclear NMR) suggest that the structure in solution is a face-capped octahedron, as for the hydrido complexes. Many new hydrido complexes and their anionic ($[V(CO)_{6-n}p_m]^-$) precursor compounds are also described. The crystal and molecular structures of *trans*-$[V(CO)_2(dppe)_2]$, which forms as a byproduct in a side reaction of the photo-induced hydride transfer, have been determined. The compound crystallizes in the orthorhombic space group $P22_12_1$ with the following cell parameters: a = 1220.4(2), b = 1421.5(3) and c = 1758.1(3) pm.

Key words: Vanadium; Alkyl complexes; Phosphane ligands; Hydrovanadation; ^{51}V NMR

1. Introduction

Neutral seven-coordinated hydrido complexes of vanadium derived from "$HV(CO)_6$" (= $[HOEt_2]$ $[V(CO)_6]$ in ether solution [1]) have been well characterized with respect to their synthesis, spectroscopic characteristics [2] and structure [3]. The reactivity pattern is less well established. The vanadium–hydrogen bond compares in stability with the vanadium–carbon bond. The bond dissociation energies are 220 kJ mol^{-1} for the V–H bond, and 210 kJ mol^{-1} for the V–C single bond (in $V–CH_3$) [4]. As a consequence, the V–H bond is relatively stable towards photo dissociation in the absence of a substrate. If hydrido complexes are irradiated in the presence of suitable subtrates, H^- is transferred. Thus η^5-cyclopentadienyl complexes are formed from pentafulvenes [5], and η^3-allyl complexes are obtained in the presence of 1,3-dienes [6].

The present work is a comprehensive treatment of the "insertion" of alkenes into the vanadium–hydrogen bond, a reaction which is more appropriately viewed as a hydride transfer to the alkene with simultaneous V–C bond formation, and hence a hydrovanadation of the olefinic double bond. It extends preliminary results on the hydrometallation in the alkene–vanadium [7] and alkene–tantalum systems [8]. Alternatively, alkylvanadium compounds have also been synthesized by salt metathesis from carbonylavanadates [9,10], a preparative route which is, however, limited to a restricted number of cases, as is the preparation of the $V^{(II)}$ complexes $(alkyl)_2V(p_2)_2$ from $Cl_2V(p_2)_2$ by the Grignard method [11].

A brief overview of new hydridovanadium complexes and their anionic precursor compounds, in most cases containing alkylated oligophosphines as supporting ligands, precedes the section directed towards the reactivity of the V–H bond.

The following numbering scheme will be used throughout for complexes: **1**, $[V(CO)_{6-n}p_m]^-$; **2**, $HV(CO)_{6-n}p_m$; **3**, $(alkyl)V(CO)_{6-n}p_m$; **4**, $V(CO)_{6-n}p_m$.

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Alkenes (Scheme 1) are numbered **a** to **i**. **3a–3i** refer to alkyl complexes generated from the alkenes **a** to **i**; **3m** stands for methyl complexes; a prime (**3′**) indicates complexes deuterated on C_β. Alkenes have been chosen so as to cover a sufficiently broad range of electronic and steric conditions and hence to provide a survey on their reactivity pattern. Phosphines (Scheme 2) are abbreviated by a three- to five-letter code, containing information on the substituents on phosphorus and the carbon backbone. With a few exceptions, we have chosen alkylated bis(phosphines) and tris(phosphines) capable of forming five- and six-membered chelate rings. This class of phosphines has turned out to provide an optimum of stability for the hydrido and alkyl complexes.

2. Results and discussion

2.1. Anionic precursor complexes (1)

The preparation of the complexes $[Et_4N][V(CO)_{6-n}p_m]$ ($[Et_4N]-\mathbf{1}$, $n = 1$–3) by the following photoreaction between hexacarbonylvanadate(−I) and selected phosphines p_m has been described earlier (see for example ref. 9):

$$[Et_4N][V(CO)_6] + p_m \xrightarrow{h\nu} [Et_4N][V(CO)_4p_m] \qquad (1)$$

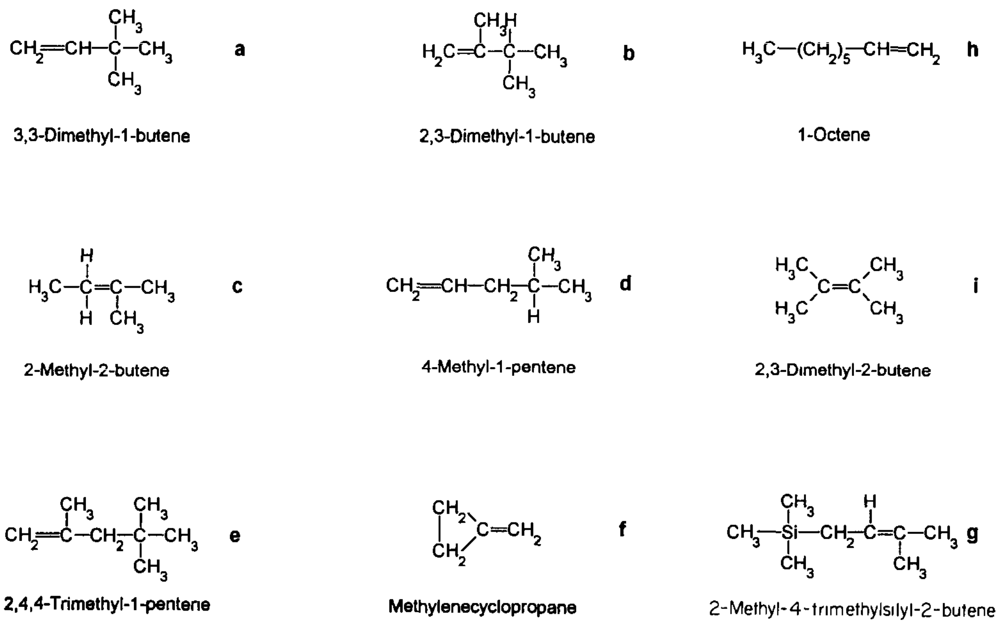
The main component, about 75%, usually is the tetracarbonylvanadate. For the synthesis of pure tricarbonylvanadate, $V(CO)_6$ is reacted with p_m to form, via the product of valence disproportionation, a neutral complex $V(CO)_3p_m$ [12], which is reduced with sodium to $Na-\mathbf{1}$:

$$V(CO)_6 + p_m \longrightarrow [V(p_m)_2][V(CO)_6]_2 \longrightarrow V(CO)_3p_m \xrightarrow{Na} Na[V(CO)_3p_m] \qquad (2a)$$

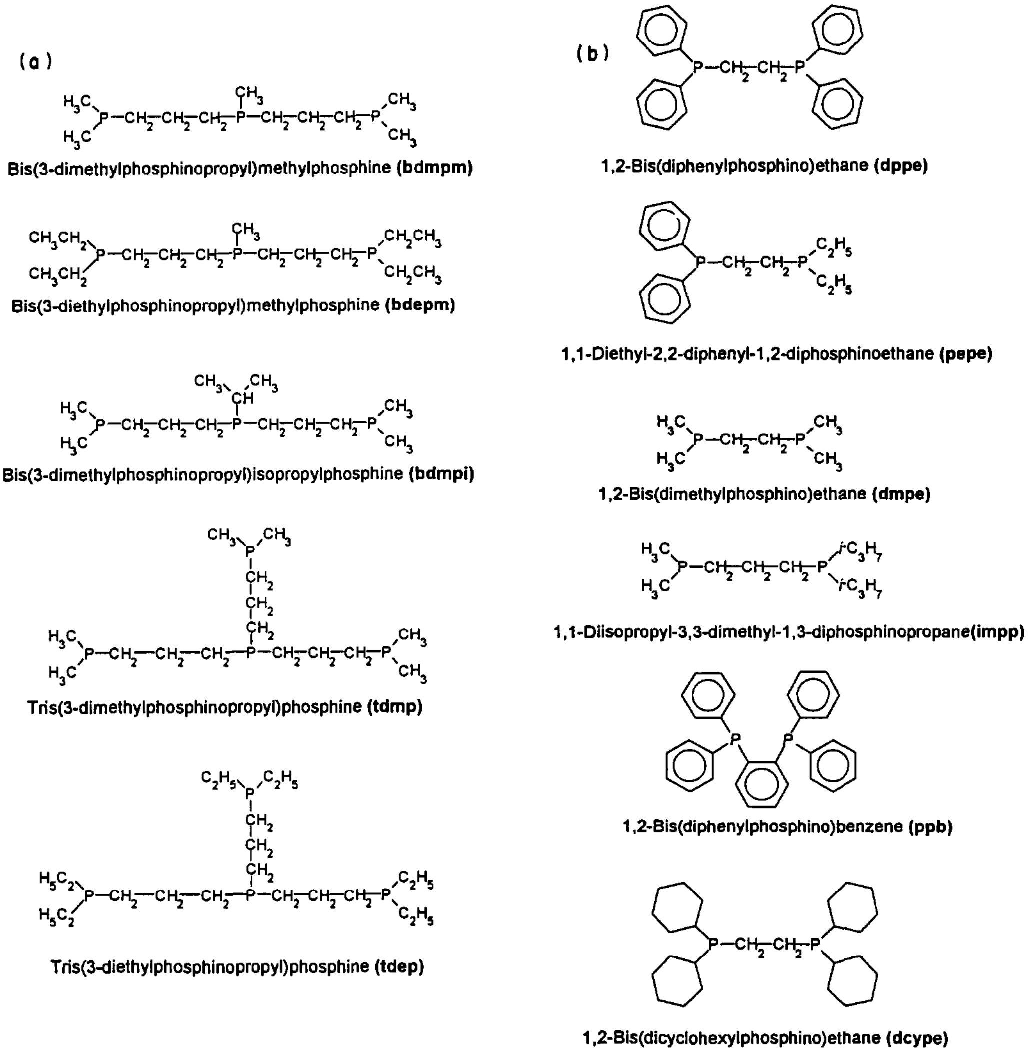
If the neutral tricarbonyl species is irradiated prior to reduction, the dicarbonyl complexes are generated:

$$V(CO)_3p_m \xrightarrow{h\nu} V(CO)_2p_m \xrightarrow{Na} Na[V(CO)_2p_m] \qquad (2b)$$

IR and ^{51}V NMR spectra are collated in Table 1. According to the IR patterns in the ν(CO) region, the anions $[V(CO)_{6-n}p_m]^-$ attain the *cis* ($n = 2,4$) and *mer* configurations ($n = 3$). The ^{51}V NMR spectra are usually well resolved, showing multiplets by $^1J(^{51}V-^{31}P)$ coupling. Coupling constants of the same size can be estimated from the overall linewidths of the ^{31}P NMR resonances, which exhibit broad plateau-like signals due to coupling with the spin $\frac{7}{2}$ nucleus ^{51}V. The chemical shifts $\delta(^{51}V)$ are typical for carbonylvanadates [13]. Shielding of the ^{51}V nucleus decreases with increasing substitution of CO for phosphines (compare also $[V(CO)_6]^-$; $\delta = -1952$ ppm). The spectra of the complexes containing potentially tridentate and tetradentate phosphines usually show more than one resonance, indicating that isomers are present, formed by alternating coordination modes of the phosphine, *i.e.* coordination through end-standing phosphorus only or mixed coordination by terminal and bridge-head P [9].



Scheme 1.



Scheme 2.

TABLE 1. IR and ^{51}V NMR data of selected carbonylphosphinevanadates (1)

Complex [a]	ν(CO) (cm^{-1})	δ(^{51}V) (ppm)
[Et_4N][$V(CO)_5$impp]	1955s, 1851m, 1805vs	-1882 (d, $^1J_{VP} = 208$ Hz), -1885 (d, $^1J_{VP} = 208$ Hz)
[Et_4N][$V(CO)_5$bdmpi]	1956w, 1853m, 1808s	-1881 (d, $^1J_{VP} = 208$ Hz), -1883 (d, $^1J_{VP} = 208$ Hz)
[Et_4N][$V(CO)_5$tdmp]	1953w, 1851m, 1806s	-1882 (d, $^1J_{VP} = 208$ Hz)
[Et_4N][$V(CO)_4$impp]	1885m, 1785vs, 1755sh, 1740sh	-1804 (t, $^1J_{VP} = 189$ Hz)
[Et_4N][$V(CO)_4$bdmpi]	1885m, 1775vs, 1760sh, 1740sh	-1807 (t, $^1J_{VP} = 199$ Hz), -1810 (t, $^1J_{VP} = 199$ Hz)
[Et_4N][$V(CO)_4$tdmp]	1882m, 1775vs, 1755sh, 1740sh	-1803 (t, $^1J_{VP} = 208$ Hz), -1805 (t, $^1J_{VP} = 208$ Hz)
[Et_4N][$V(CO)_3$bdmpi]	1910w, 1814s, 1680s	-1694
[Et_4N][$V(CO)_3$tdmp]	1905w, 1811s, 1680s	-1690
Na[$V(CO)_3$bdmpi]	1892w, 1790s, 1675s, br	-1681 (q, $^1J_{VP} = 203$ Hz)
Na[$V(CO)_3$bdmpm]	1887w, 1790s, 1670s, br	-1677 (q, $^1J_{VP} = 203$ Hz)
Na[$V(CO)_3$bdepm]	1895w, 1795s, 1670s, br	-1662 (q, $^1J_{VP} = 199$ Hz)
Na[$V(CO)_3$tdmp]	1888w, 1790s, 1670s, br	-1673 (q, $^1J_{VP} = 192$ Hz)

[a] See Scheme 2 for abbreviations of phosphines.

2.2. Hydrido complexes (2)

Type **2** complexes can be prepared by protonation of **1** according to [2b,9]

$$\mathrm{Na[V(CO)_4p_2]} + {}^{t}\mathrm{BuC_6\text{-}H_2O} \longrightarrow \mathrm{HV(CO)_4p_2} \tag{3}$$

or [2d,2c,7]

$$\mathrm{[Et_4N][V(CO)_4p_m]} + \{\mathrm{H\text{-}OSi}\} \longrightarrow \{\mathrm{Et_4N\text{-}OSi}\} + \mathrm{HV(CO)_4p_m} \tag{4}$$

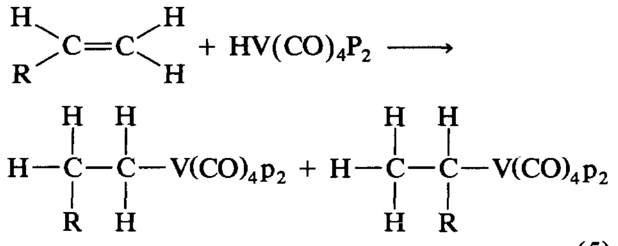
i.e by "direct" protonation (see ref. 9 for the possible mechanism) (eqn. (3)) or, with sufficiently better yields, by ion exchange chromatography on silica gel (eqn. (4)). On silica gel, tetracarbonylvanadates, tricarbonylvanadates and dicarbonylvanadates exchange $[Et_4N]^+$ by H^+; pentacarbonylvanadates do not react. The tetracarbonyls $HV(CO)_4p_m$ loose CO on standing in solution within hours to days (depending on the nature of the phosphine) to form $HV(CO)_3p_m$ (provided that $m > 2$). Irradiation of $HV(CO)_4p_m$ or $HV(CO)_3p_m$ yields $HV(CO)_2p_m$, together with small amounts of neutral $V(CO)_2p_m$ (**4**), demonstrating the relative stability of the V–H bond towards photocleavage.

As in the case of the tantalum analogues [8], the complexes $HV(CO)_3p_m$ often exist as two isomers, namely *mer* and *fac*, while the tetracarbonyl and dicarbonyl species are in the *cis* configuration. The *mer* and *fac* isomers are clearly distinct by their IR and ^{51}V NMR patterns (Table 2); there are three and two $\nu(CO)$ bands respectively. The $\delta(^{51}V)$ values for the meridional isomers are around −1580 ppm, and for the facial isomers around −1000 ppm. This deshielding in facial (C_{3v} symmetry) as compared with meridional complexes (C_{2v}) has been explained in terms of a smaller gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital in the case of the former, and hence a larger contribution of the paramagnetic deshielding term [13]. The structure of the hydrido complexes in solution, a face-capped octahedron with a restricted fluctionality, has been discussed in detail elsewhere [2c,2d,7,9].

2.3. σ-Alkyl complexes (3)

2.3.1. Preparation and properties

The general route to the type **3** complexes, the photo-induced hydrovanadation of the alkene, is as follows:



$$\mathrm{(H)(R)C{=}C(H)_2} + \mathrm{HV(CO)_4P_2} \longrightarrow \mathrm{H\text{-}C(H)(R)\text{-}C(H)(H)\text{-}V(CO)_4p_2} + \mathrm{H\text{-}C(H)(H)\text{-}C(H)(R)\text{-}V(CO)_4p_2} \tag{5}$$

Alkenes carrying phenyl substituents at the olefinic carbons do not react, and yields are very low, where these carbons are permethylated. With other alkenes, optimum yields are achieved with the tetracarbonyl complexes $HV(CO)_4p_2$. For p_2 = dmpe, $(alkyl)V(CO)_2(dmpe)_2$ is obtained. Yields are less with the tricarbonyls $HV(CO)_3p_3$, mainly as a consequence of longer reaction times and concommittant decomposition. In the case of $HV(CO)_3p_4$, only decomposition products have been observed. The dangling phosphorus function apparently prevents access of the alkene to the vanadium centre.

In most cases, the main product (and sometimes the only one) is the anti-Markownikow adduct. The relation [aM/M] between the anti-Markownikow product aM and the Markownikow product M in the case of 2-methyl-2-butene (**c**) is 4/1. For 3,3-dimethyl-1-butene (**a**), where the formation of the Markownikow product

TABLE 2. ^{51}V and ^{1}H NMR data of hydrido complexes (**2**)

Complex [a]	$\nu(CO)$ (cm^{-1})	$\delta^{51}V$ NMR(ppm)	$\delta^{1}H$ NMR(ppm)
$HV(CO)_4$impp	1981s, 1890sh, 1865vs, 1811vs	−1704 (t, $^1J_{VP}$ = 154 Hz)	−5.22 (dd, $^2J_{PH}$ = 18.5, 29.1 Hz)
$HV(CO)_3(impp)_2$	[b]	−1582 (q, $^1J_{VP}$ = 180 Hz)	[b]
mer[$HV(CO)_3$bdmpi]	1911s, 1820sh, 1810vs	−1581 (q, $^1J_{VP}$ = 180 Hz)	[c]
fac[$HV(CO)_3$bdmpi]	1900s, 1778vs	−993 (q, $^1J_{VP}$ = 142 Hz)	[c]
mer[$HV(CO)_3$bdmpm]	1931w, 1835s, 1810vs	−1582	−5.61 (td, $^1J_{PH}$ = 44.5, 17.8 Hz)
fac[$HV(CO)_3$bdmpm] [d]	1917s, 1780vs	−1017 (q, $^1J_{VP}$ = 142 Hz)	[b]
mer[$HV(CO)_3$tdmp]	1915m, 1820sh, 1805sh	−1579	−5.37 (q, $^1J_{PH}$ = 35 Hz)
fac[$HV(CO)_3$tdmp]	1903m, 1780vs	−1011	[b]
$DV(CO)_4$ppb	1989m, 1890sh, 1883vs, 1854vs	−1647	–

[a] See Scheme 2 for abbreviations of the phosphines.
[b] Not observed.
[c] Broad unstructured signal.
[d] This (minor) isomer has not been observed previously [9].

is disfavoured by the sterically demanding tertiary butyl group on C2, [aM/M] amounts to 10/1. No M product was observed with **e** and **g**. In two cases, 1-octene (**h**) and 4-methyl-1-pentene (**d**), the main component is the Markownikow product. ^{13}C NMR spectroscopy (see below) has been used for the differentiation between the M and aM product; they are also distinct by their $\delta(^{51}V)$ values (see below).

A general side reaction of the UV-induced hydrovanadation is the formation of paramagnetic $V(CO)_2(p_m)_2$ (**4**) in amounts of several per cent of the overall yield. Complexes **4** are separated from the alkyl complexes **3** by crystallization from a toluene–hexane solution. Compounds **3** are isolated from the mother liquor as dark red powders. They are soluble in polar solvents (tetrahydrofuran (THF) and MeCN) and unpolar solvents (benzene, toluene and hexane). The solutions are stable when kept under inert gas atmosphere up to about 65°C. The type **3** products formed from the reaction of **2** and 4-methyl-1-pentene (**d**) or 2,3-dimethyl-1-butene (**b**) undergo an α and β migration respectively of a methyl group (Scheme 3) to yield $MeV(CO)_4p_2$ (p_2 = dppe), and hence a rare case of C–C bond activation [14a]. β-methyl shifts, for example, are of relevance in the propylene polymerization as catalysed by zirconocene and related catalysts [14b,c].

Scheme 3.

2.3.2. *Spectroscopic characteristics and structure discussion*

The IR patterns of the alkyl complexes in the ν(CO) region (Table 3) are very similar to those observed for the hydrido complexes; tetracarbonyl species exhibit

TABLE 3. IR and ^{51}V NMR data of σ-alkyl complexes (**3**)

Complex [a]	Code [b]	δ [c] (ppm)	ν(CO) (cm^{-1})
(3,3-Dimethyl-1-butyl)$V(CO)_4$dppe	**3a**-dppe	−1044, {−1077}	1930s, 1840sh, 1825vs
(3-Methyl-2-butyl)$V(CO)_4$dppe	**3c**-dppe	−1062 (t), {−1077 (t)}	1930s, 1845sh, 1828vs
(1-Trimethylsilyl-3-methyl-2-butyl)$V(CO)_4$dppe	**3g**-dppe	−1045	1930s, 1850sh, 1830vs
(1-Octyl)$V(CO)_4$dppe	**3h**-dppe	−1074, {−1062}	1925s, 1845sh, 1830vs
(2,3-Dimethyl-1-butyl)$V(CO)_4$dppe	**3b**-dppe	−1054, {−1058}, −1028 [d]	1925s, 1835sh, 1820vs
(2,4,4-Trimethyl-1-pentyl)$V(CO)_4$dppe	**3e**-dppe	−1050	1923s, 1835sh, 1822vs
(4-Methyl-1-pentyl)$V(CO)_4$dppe	**3d**-dppe	−1065, {−1058}, −1031 [d]	1925s, 1840sh, 1826vs
(1,1-Dimethyl-2-methyl-1-propyl)$V(CO)_4$dppe	**3i**-dppe	−1086 [e]	[f]
(3,3-Dimethyl-1-butyl)$V(CO)_4(dcype)_2$	**3a**-dcype	−1076, {−1102}	1921s, 1835sh, 1818vs
(1-Cyclopropyl-1-methylen)$V(CO)_4$dcype	**3f**-dcype	−1052, {−1082}, −1068 [g]	1920s, 1835sh, 1818vs
(3-Methyl-2-butyl)$V(CO)_4$dcype	**3c**-dcype	−1087, {−1101}	1920s, 1835sh, 1819vs
(3,3-Dimethyl-1-butyl)$V(CO)_4$pepe	**3a**-pepe	−1076, {−1102}	1924s, 1840sh, 1825vs
(3-Methyl-2-butyl)$V(CO)_4$pepe	**3c**-pepe	−1079, {−1092}	1925s, 1840sh, 1827vs
(4-Methyl-1-pentyl)$V(CO)_4$pepe	**3d**-pepe	−1090, {−1086}, −1029 [d]	1923s, 1840sh, 1828vs
(3,3-Dimethyl-1-butyl)$V(CO)_4$ppb	**3a**-ppb	−1054, {−1078}	1930s, 1845sh, 1830vs
(3-Methyl-2-butyl)$V(CO)_4$ppb	**3c**-ppb	−1036, (−1053)	1933s, 1850sh, 1832vs
(3,3-Dimethyl-1-butyl)$V(CO)_4$dmpe	**3a**-dmpe	−1063 (t, $^{1}J_{VP}$ = 161 Hz)	[f]
(Methyl)$V(CO)_4$impp	**3m** [h]-impp	−1017 (t, $^{1}J_{VP}$ = 204 Hz)	1923s, 1840sh, 1817vs
(3,3-Dimethyl-1-butyl)$V(CO)_4$impp	**3a**-impp	−1172 (t, $^{1}J_{VP}$ = 137 Hz)	1928s, 1840sh, 1815vs
(1-Trimethylsilyl-3-methyl-2-butyl)$V(CO)_3$bdmpm	**3g**-bdmpm	−848	1820m, 1760s, 1740s
(Methyl)$V(CO)_3$bdmpm	**3m** [h]-bdmpm	−815	1825m, 1755s, 1735vs
(3,3-Dimethyl-1-butyl)$V(CO)_3$bdmpi	**3a**-bdmpi	−988 (q, $^{1}J_{VP}$ = 142 Hz), {−1024}	1839m, 1753m
(2,4,4-Trimethyl-1-pentyl)$V(CO)_2(dmpe)_2$	**3e**-$(dmpe)_2$	−769 (quint., $^{1}J_{VP}$ = 159 Hz)	1783w, 1725w
(3-Methyl-2-butyl)$V(CO)_2(dmpe)_2$	**3c**-$(dmpe)_2$	−769 (quint., $^{1}J_{VP}$ = 156 Hz)	1781w, 1723w
(3,3-Dimethyl-1-butyl)$V(CO)_2(dmpe)_2$	**3a**-$(dmpe)_2$	−769 (quint., $^{1}J_{VP}$ = 158 Hz)	1780m, 1722m

[a] See Scheme 2 for abbreviations of the phosphines. The denomination of the coordinated alkyl refers to the main (anti-Markownikow) product.

[b] *Cf*. Scheme 1 for the original alkene.

[c] Data given in curly brackets are for the byproduct (Markownikow).

[d] Signal for $MeV(CO)_4p_2$, formed by methyl elimination (see text, Scheme 3).

[e] Not observed.

[f] Very weak.

[g] Alkyl complex formed as a byproduct by ring opening.

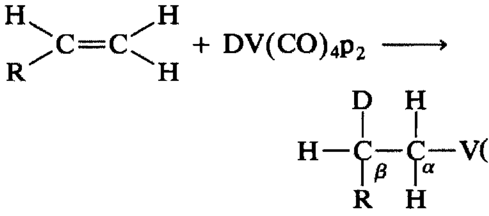
[h] m ≡ methyl.

two bands, one of which, at smaller wave numbers, is very broad and has a shoulder. Tricarbonyl complexes give rise to three bands, and dicarbonyl complexes to two (equally intense) bands. These results are compatible with basic octahedral structures {*cis*-$V(CO)_4p_2$}, {*mer*-$V(CO)_3p_3$} and {*cis*-$V(CO)_2p_4$}, and hence a structure comparable with the solution structure of hydridovanadium complexes [3,7], with the alkyl instead of the hydride capping a face of the octahedron. The facial arrangement of the {$V(CO)_3p_3$} moiety, which is present together with the meridional one in hydrido complexes, has not been observed for the alkyl analogues. All ν(CO) bands of the alkyl complexes are shifted to lower wavenumbers with respect to the hydrido complexes by 30–60 cm^{-1}, possibly reflecting the $+I$ effect of the alkyl ligands.

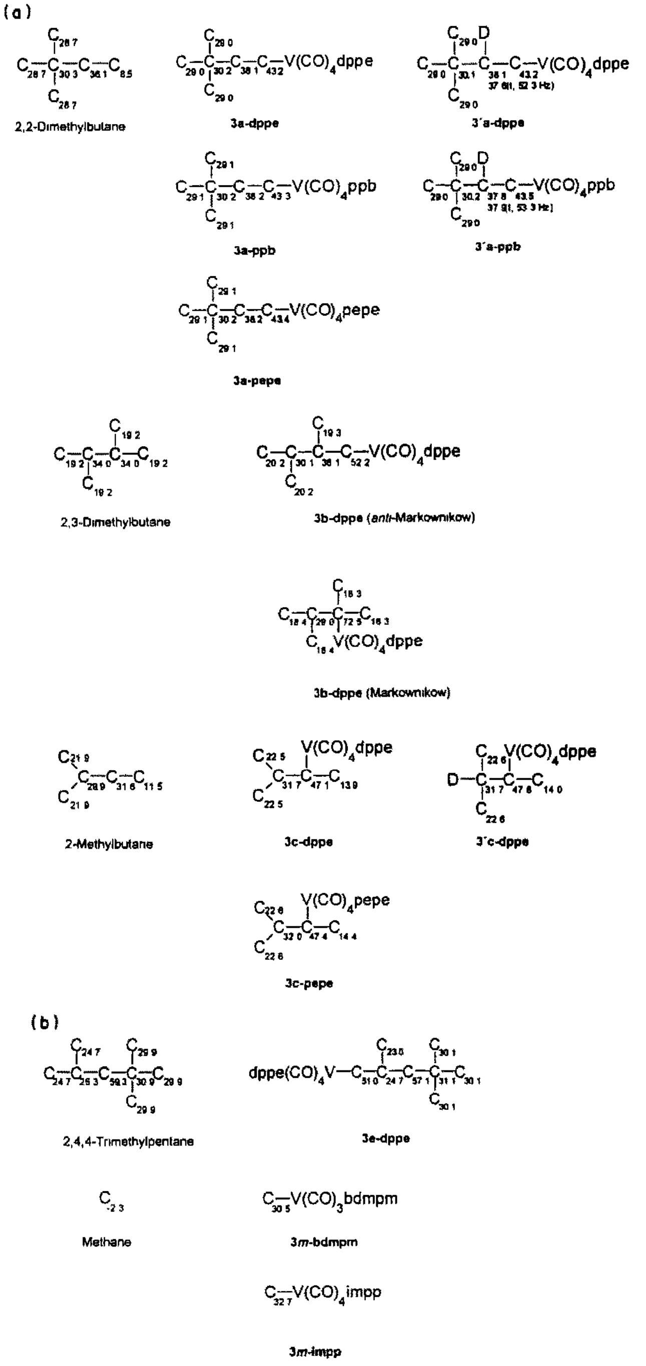
^{51}V NMR spectroscopy again is a diagnostic tool in analysing vanadium speciation in solution (Table 3). Depending on the degree of substitution of CO by p_m, $\delta(^{51}V)$ values are in the ranges of approximately −1000 to −1100 ppm (4CO), −800 to −1000 ppm (3CO) and −770 ppm (2CO). Comparison with the corresponding classes of hydrido complexes (Table 2) reveals a deshielding of the ^{51}V nucleus for the alkyl complexes of several hundred parts per million, classifying the σ-alkyl ligands as "weaker" (in the sense of their position in a magnetochemical series [13e]) and/or less polarizable than the hydride ligand. There is an increase in shielding with increasing steric demand of the carbon attached to vanadium ($C_{prim} < C_{sec} < C_{tert}$). This steric effect, which has been noted earlier [9] and discussed in detail elsewhere [13c], can be used to assign Markownikow and anti-Markownikow products.

^{13}C NMR results are summarized in Scheme 4. The signals for the alkyl carbon atoms directly coordinated to vanadium are slightly broadened. No ^{13}C–^{51}V coupling, reported previously for hexacarbonylvanadate [15], has been observed in these low symmetry complexes as a result of complete or almost complete relaxation decoupling. The resonances for the alkyl carbon atoms C_α, compared with the same carbon in the corresponding alkane, are shifted to low magnetic field by 30–40 ppm — hence a deshielding. C_β is not significantly affected.

^{13}C NMR spectroscopy also provides evidence that the hydrogenation of the alkene is in fact a hydride transfer from the metal:



$$RHC{=}CH_2 + DV(CO)_4p_2 \longrightarrow H\text{–}C_\beta(D)(R)\text{–}C_\alpha(H)(H)\text{–}V(CO)_4p_2 \quad (6)$$



Scheme 4.

If the alkene is reacted with $DV(CO)_4p_2$, the signal for C_β is a 1:1:1 triplet. $^1J(^2H-^{13}C)$ amounts to 53 Hz (**3'a** in Scheme 4).

^1H NMR spectra are considerably less diagnostic than ^{51}V and ^{13}C NMR and are not discussed here in detail for this reason. There are no significant differences between the chemical shifts and coupling constants of coordinated alkyl and corresponding alkane.

As an example, the resonance for the protons on C_α in **3a**-dppe, at 0.87 ppm, exhibits a triplet structure with a coupling constant of 6.7 Hz.

Some insight into the solution structure of the alkyl complexes can, however, be derived from the ^1H NMR spectrum of $^{13}CH_3V(CO)_3$bdmpm (**3m**-bdmpm). The ^1H NMR signal ($\delta = 0.98$ ppm) is a doublet of doublets (Fig. 1(a), centre) with $^1J(^1H-^{13}C) = 89.4$ Hz. This compares with $^1J(H-C) = 117.3$ Hz in CH_3I (Fig. 1(a), left), possibly indicating withdrawal of σ electron density from the C–H bonds by the (positively polarized) metal centre. $^3J(^1H-^{31}P)$ coupling accounts for the doublet splitting of 6.2 Hz. Only one of the three phosphorus atoms of the bdmpm ligand is close enough to the methyl group to allow for a sizable interaction between the ^1H and ^{31}P nuclei. Hence the structure is possibly unlike that of $MeV(CO)_2(dmpe)_2$, for which a quintet ($^3J(^1H-^{31}P) = 12$ Hz) at $\delta(^1H) = -1.80$ ppm, and a capped trigonal prismatic structure in the solid state (Fig. 1b, **I**) have been reported [10]. On the assumption that the capped trigonal bipyramid is retained in solution, the only structures compatible with the proton NMR spectrum of **3m**-bdmpm are **II** and **III** in Fig. 1b. Alternatively, a pentagonal bipyramid (**IV**), as found in the solid state for $HV(CO)_4$(dppe) [3b] and $HTa(CO)_2(dppe)_2$ [8], or a capped octahedron (Fig. 1(b), **V**) may be realized. The capped octahedron has been favoured for $HTa(CO)_2(dmpe)_2$ in the solid state [16] and made plausible for the solution structures of $HM(CO)_{6-n}P_m$ complexes (M ≡ V, Nb or Ta) [7–9,17]. The ^1H NMR spectrum of $HV(CO)_3$bdmpm, the hydrido complex analogous to **3m**-bdmpm, shows a triplet of doublets at room temperature (Fig. 1(a), right), corresponding to structure **V** and a fluctional behaviour (which equilibrates the two terminal PMe_2 groups), and three doublets at 210 K, indicative of a frozen-in state as represented by structure **V**. Owing to the heavier and bulkier methyl group, this structure may be frozen in the case of **3m**-bdmpm at ambient temperatures already, the second terminal PMe_2 and the bridge-head PMe being too far away to allow observation of resolved $^3J(^1H-^{31}P)$ coupling.

2.4. The structure of trans-[V(CO)$_2$(dppe)$_2$]·3C$_6$D$_6$ (4A)

Suitable crystals of **4A** were isolated by slow crystallization from the deuterobenzene solution of the reaction between $HV(CO)_4$dppe and the alkene **a**, leading to **3a**-dppe and small amounts of **4A**. The compound crystallizes in the orthorhombic space group $P22_12_1$.

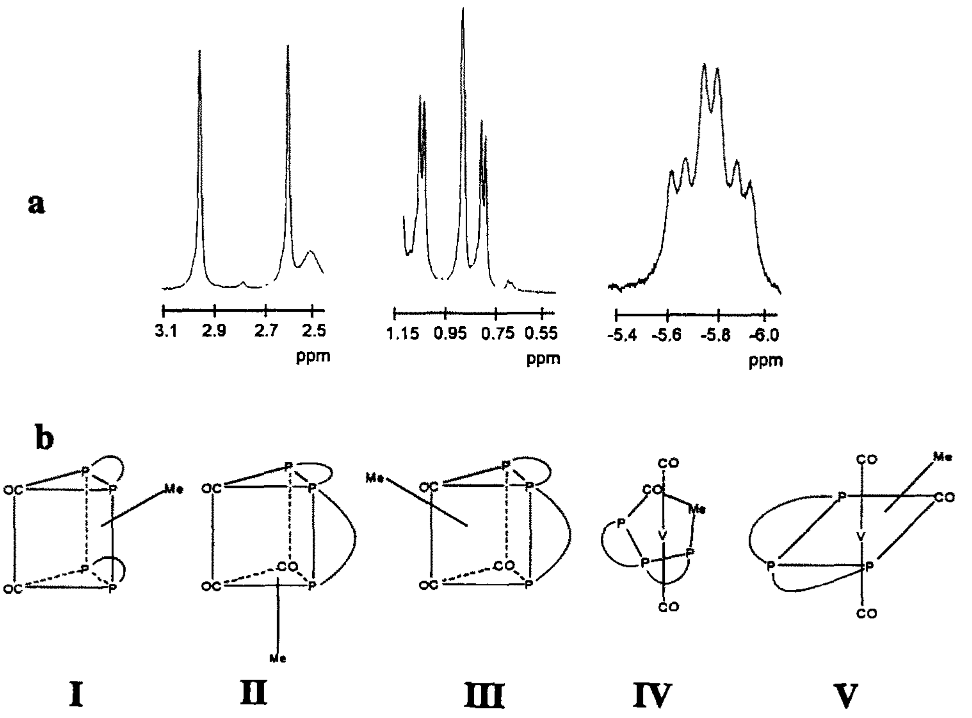


Fig. 1. (a) ^1H NMR spectra of $^{13}CH_3I$ (left), $^{13}CH_3V(CO)_3$bdmpm (**3m**-bdmpm, centre) and $HV(CO)_3$bdmpm (right). The central signal in the centre spectrum corresponds to $^{12}CH_3V(CO)_3$bdmpm. (b) **I**, solid state structure found for $CH_3V(CO)_2(dmpe)_2$; **II**–**V**, possible solution structures for **3m**-bdmpm, see text for discussion.

TABLE 4. Structure date of $V(CO)_2(dppe)_2 \cdot 3C_6D_6$ (**4A**)

Crystal data	
Empirical formula	$C_{72}H_{48}D_{18}O_2P_4V$
Molecular mass (g mol^{-1})	1156.16
Crystal dimensions (mm)	0.2×0.3×0.4
Crystal system	Orthorhombic
Space group	$P22_12_1$
Unit-cell dimensions	
a (Å)	12.204(2)
b (Å)	14.215(3)
c (Å)	17.581(3)
Volume (Å^3)	3049.9(10)
Z	2
Density (calculated) (g cm^{-3})	1.239
Absorption coefficient (cm^{-1})	31
$F(000)$	1194
Data collection	
Index ranges	$0 < h < 14$, $0 < k < 16$, $0 < l < 20$
Reflections collected	3146
Independent reflections (R_{int} = 5.58%)	3044
Observed ($F_o > 4\sigma F_o$) reflections	968
Solution and refinement	
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0003F^2$
Number of parameters refined	361
Final R indices (observed data)	R = 5.29%, wR = 5.21%
R indices (all data)	R = 18.71%, wR = 7.12%
Goodness of fit	0.665
Largest difference peak (electrons Å^{-3})	0.31
Largest difference hole (electrons Å^{-3})	−0.27

TABLE 5. Selected bond lengths (Å) and bond angles (°) of $V(CO)_2(dppe)_2 \cdot 3C_6D_6$ (**4A**)

Bond lengths		*Bond angles*	
V–C(1)	193.5(16)	C(1)–V–C(1′)	179.5(14)
V–P(1)	246.5(6)	P(1)–V–P(2)	82.3(2)
V–P(2)	245.8(6)	P(1)–V–P(1′)	99.0(3)
C(1)–O(1)	116.0(18)	P(1)–V–P(2′)	175.6(2)
P(1)–C(2)	182.9(15)	V–C(1)–O(1)	178.2(16)
P(1)–C(11)	180.3(22)	V–P(1)–C(2)	105.0(5)
P(1)–C(21)	186.3(19)	V–P(2)–C(3)	104.2(6)
C(2)–C(3)	148.5(23)	P(1)–C(2)–C(3)	109.5(11)
P(2)–C(3)	183.7(18)	P(2)–C(3)–C(2)	109.8(11)
P(2)–C(31)	180.1(20)	C(11)–P(1)–C(21)	102.4(9)
P(2)–C(41)	180.9(20)	C(31)–P(2)–C(41)	100.2(9)

TABLE 6. Fractional coordinates and isotropic thermal factors of the non-hydrogen atoms of $V(CO)_2(dppe)_2 \cdot 3C_6D_6$

	$x \times 10^5$	$y \times 10^5$	$z \times 10^5$	u_{eq} (pm)
V	1455(2)	0	0	45(1)
P(1)	146(2)	152(2)	1059(2)	51(1)
P(2)	2790(2)	275(2)	1021(2)	49(1)
C(1)	1438(10)	−1328(5)	179(5)	59(3)
O(1)	1426(7)	−2144(7)	286(7)	83(2)
C(2)	979(7)	107(6)	1925(7)	55(3)
C(3)	1966(7)	703(6)	1815(5)	63(3)
C(11)	−884(9)	−758(7)	1222(6)	49(3)
C(12)	−569(10)	−1659(8)	1487(6)	66(7)
C(13)	−1382(12)	−2371(7)	1547(7)	83(7)
C(14)	−2456(11)	−2184(9)	1387(7)	86(5)
C(15)	−2775(10)	−1327(7)	1134(7)	88(7)
C(16)	−1995(9)	−632(7)	1075(6)	72(7)
C(21)	−676(9)	1231(6)	1220(6)	46(3)
C(22)	−1100(8)	1434(7)	1938(6)	69(7)
C(23)	−1706(9)	2256(7)	2053(6)	75(7)
C(24)	−1891(10)	2876(7)	1469(7)	83(7)
C(25)	−1469(10)	2656(7)	774(7)	78(7)
C(26)	−840(8)	1858(7)	644(5)	56(3)
C(31)	3847(9)	1143(7)	896(5)	46(3)
C(32)	3606(10)	2128(6)	835(5)	60(3)
C(33)	4341(10)	2783(7)	682(6)	62(3)
C(34)	5415(10)	2539(8)	570(6)	80(7)
C(35)	5709(9)	1609(7)	644(6)	77(7)
C(36)	4939(9)	955(7)	801(5)	60(3)
C(41)	3567(9)	−658(7)	1491(5)	51(3)
C(42)	3706(9)	−1530(7)	1164(6)	63(3)
C(43)	4311(8)	−2222(8)	1538(7)	76(7)
C(44)	4730(9)	−2091(9)	2236(6)	76(7)
C(45)	4587(11)	−1227(8)	2594(6)	106(5)
C(46)	4031(8)	−567(7)	2216(6)	77(7)
C(101)	4569(29)	0	5000	164(18)
C(102)	4116(18)	240(19)	4359(12)	181(15)
C(103)	2989(16)	256(14)	4401(11)	152(8)
C(104)	2489(22)	0	5000	120(10)
C(201)	1296(23)	4113(10)	1569(11)	151(11)
C(202)	663(16)	4710(19)	1114(10)	169(9)
C(203)	1138(19)	5524(14)	938(11)	120(7)
C(204)	2140(22)	5769(11)	1071(12)	141(8)
C(205)	2748(15)	5218(17)	1571(11)	142(8)
C(206)	2308(19)	4389(18)	1709(12)	153(11)

Details of the structure solution and refinement are summarized in Table 4. Table 5 contains selected bond lengths and angles, and Table 6 the fractional coordinates and isotropic temperature factors of the non-hydrogen atoms. An ORTEP plot of *trans*-$[V(CO)_2(dppe)_2]$, with the solvens molecules neglected, is presented in Fig. 2.

Just as in the solvens-free modification **4B** (triclinic space group, $P1$) isolated earlier from THF [7], **4A** forms a distorted octahedron. In contrast, *trans*-$[V(CO)_2(dmpe)_2]$ has a close to ideal octahedral geometry [18]. There are differences between **4A** and **4B** with respect to the mode of distortion (Fig. 3). In **4B**, the OC–V–CO axis forms an angle of about 6° with the ideal plane spanned by the four P atoms. No such kink of the octahedral axis is observed in **4A**. However, here the P atoms do no longer form a plane. Rather,

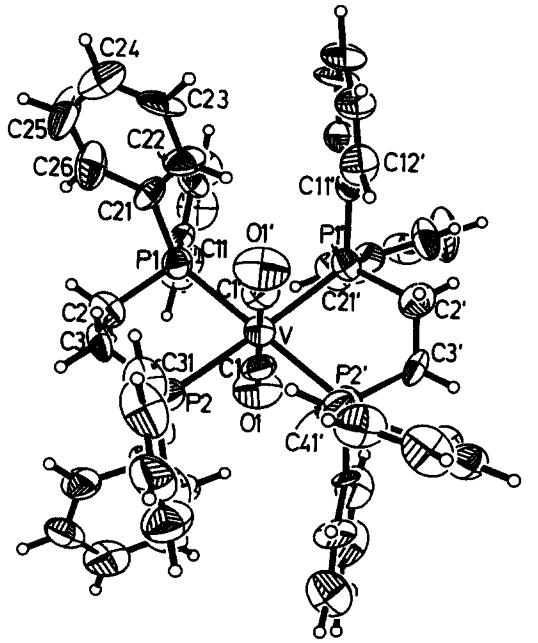


Fig. 2. ORTEP plot (50% probability ellipsoids) and numbering scheme of $V(CO)_2(dppe)_2$.

each set of P atoms mutually *trans* deviates from the normal of the idealized plane by about 2° (87.7° and 88.1° for P(1') and P(2), and 92.3° and 91.9° for P(1) and P(2')). The bond lengths d(V–P) and d(V–CO) are almost identical in **4A** and **4B**. The d(V–P) are longer by 0.08 Å in **4** than in *trans*-$[V(CO)_2(dmpe)_2]$, demonstrating the less pronounced π acceptor capacity of phenylphosphines *vs.* alkylphosphines, also reflected by the CO stretches (**4**, 1740 cm^{-1}, $V(CO)_2$dmpe, 1763 cm^{-1}).

3. Experimental details

3.1. General comments

All operations were conducted in an inert gas atmosphere and in dry oxygen-free solvents.

Irradiations were carried out with a high pressure mercury lamp HPK 125 (Philips) in a water-cooled quartz immersion well, placed close to a Duran Schlenk tube carrying the solution of the reactants and equipped with a gas inlet with a filter plate at the bottom to pass N_2 or Ar through the solution. This arrangement allows to filter off UV light with $\lambda < 360$ nm, and to remove CO evolved in the course of the reaction.

Silica gel (70–230 mesh ASTM, Merck) and Celite were freed from oxygen under high vacuum and loaded with nitrogen.

IR spectra were obtained on a Perkin–Elmer 1720 FT spectrometer as THF solutions in 0.1 mm CaF_2 cuvettes. NMR spectra were recorded on a Bruker AM 360 spectrometer in vials of 5 mm (^1H) or 10 mm diameter (^{13}C, ^{31}P and ^{51}V) in deuterated solvents (THF-d_8 or toluene-d_8) at 90.56 MHz (^{13}C), 145.78 MHz (^{31}P) and 94.73 MHz (^{51}V) and referenced externally against tetramethylsilane (^1H and ^{13}C), H_3PO_4 (^{31}P) and $VOCl_3$ (^{51}V).

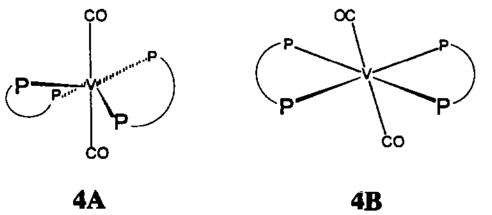
The X-ray structure analysis was undertaken on a Hilger & Watts Y 290 diffractometer with Mo Kα radiation at room temperature in the θ–2θ scan mode (θ range, 4.5–50°). The structure was solved and refined with the programme system SHELXTL Plus (VMS) [19]. H atoms were refined as rotors riding on the pivot C atoms with fixed isotropic thermal factors. No absorption correction was carried out.

Alkenes, and the phosphines dppe, dmpe and pepe were obtained from commercial sources. The following phosphines were prepared according to procedures given in the literature bdmpm, bdepm, tdmp and tdep [20]; impp and bdmpi [7].

3.2. Preparation of complexes

3.2.1. Carbonylphosphinevanadates (1)

Most of the complexes $[Et_4N][V(CO)_{6-n}p_m]$, constituting mixtures of pentacarbonylvanadates, tetracarbonylvanadates and tricarbonylvanadates (with a predominance for the tetracarbonyl species), were prepared from $[Et_4N][V(CO)_6]$ [21] and the phosphine by UV irradiation as described previously [9] in yields between 70 and 80%. The complexes $Na[V(CO)_3p_m]$ ($p_m \equiv$ bdmpi, bdmpm, bdepm and tdmp) were prepared in yields of 82–88% along the following route: a solution of 0.20 g (1 mmol) of $V(CO)_6$ (sublimed from a mixture of $[Na(diglyme)_2][V(CO)_6]$ and phosphoric acid) in 40 ml of n-hexane was treated with an equivalent amount (about 0.38 g) of the phosphine to yield a voluminous yellow precipitate of $[V(p_m)_2][V(CO)_6]_2$. The suspension was refluxed for 12 h, yielding a green solution of $V(CO)_3p_m$ which was filtered and evaporated to dryness. The residue was dissolved in 20 ml of THF and stirred at room temperature for 2 h with a tenfold molar excess of sodium sand to generate a red solution of the anionic compound. Excessive sodium



4A **4B**

Fig. 3. Views of the complexes $V(CO)_2 \cdot 3C_6D_6$ (**4A**) and $V(CO)_2$(dppe) (**4B**) with the distortions highlighted.

sand was filtered off, and Na[V$(CO)_3$p$_m$] precipitated as an orange-red powder with 20 ml of *n*-hexane.

3.2.2. *Hydrido complexes (2)*

The complexes HV$(CO)_{6-n}$p$_m$ were prepared with yields of 73–90% from [Et_4N][V$(CO)_{6-n}$p$_m$] by ion exchange chromatography on silica gel according to a procedure described in detail earlier [2c,7,9]: column dimensions; 6 cm diameter and 8 cm packing height; capacity, about 0.5 g (1 mmol); eluent, 150 ml of THF; elution time, about 20 min. Pentacarbonylvanadate and small amounts of hexacarbonylvanadate remain in the starting zone (and may be washed out with acetonitrile). Tetracarbonylvanadates, when containing tridentate or tetradentate phosphines, generate mixtures of HV$(CO)_4$p$_m$ and HV$(CO)_3$p$_m$ (increasing amounts of the latter with increasing time for the work-up). The hydrido complexes were precipitated from the concentrated (to 15 ml) THF solution with 30 ml of *n*-hexane to yield red oils which solidify under high vacuum and can be pulverized to give orange-red powdery products.

For the preparation of the deuterido complex DV$(CO)_4$ppb, an alternative procedure based on a method described by Davison and Ellis [22] was employed: 10 ml of freshly distilled tertiary butylchloride were mixed with 5 ml of a hexane solution containing 0.74 g (1 mmol) of [Et_4N][V$(CO)_4$ppb] and treated with 15 ml of D_2O. After vigorous stirring for 2 h at room temperature, the mixture was cooled to 0°C, and the yellow powder of DV$(CO)_4$ppb filtered off, washed with three 5 ml portions of D_2O and dried under high vacuum (yield, 70%).

3.2.3. *Alkyl complexes (3)*

In a typical procedure representative also of the preparation of other alkyl complexes, 562 mg (1 mmol) of HV$(CO)_4$dppe, dissolved in 10 ml of THF, were treated with 2.0 g (23.8 mmol) of 3,3-dimethyl-1-butene (**a**) and irradiated for 3 h. The reaction, monitored by IR, was accompanied by a colour change from cognac to dark red. The solution was evaporated to dryness and residual THF removed *in vacuo*. The residue was treated with 15 ml of a 1:1 mixture of toluene and *n*-hexane, filtered through a 2 cm column of Celite and allowed to stand at 4°C for a couple of days. During this time, the by product V$(CO)_2$(dppe)$_2$ crystallized from the solution. The procedure was repeated, until all byproduct had been crystallized (IR control). The solution was than evaporated to dryness, and the black-red powder of (3,3-dimethyl-1-butyl)V$(CO)_4$dppe (**3a**-dppe) was dried in high vacuum for 3 h (yield, 543 mg, 0.84 mmol (84%)).

The following complexes of composition (alkyl)V$(CO)_n$p$_m$ have been prepared accordingly from alkenes and HV$(CO)_4$p$_m$ (n = 4 and 2) or HV$(CO)_3$p$_m$ (n = 3); *cf.* Scheme 1 for the numbering of the alkene used in the reaction.

(i) $n = 4$; p$_m$ ≡ dppe; alkyl = 3-methyl-2-butyl (**c**), 1-trimethylsilyl-3-methyl-2-butyl (**g**), 1-octyl (**h**), 2,3-dimethyl-1-butyl (**b**), 2,4,4,-trimethyl-1-pentyl (**e**), 4-methyl-1-pentyl (**d**): $n = 4$; p$_m$ = dcype; alkyl = 3,3-dimethyl-1-butyl (**a**), 1-cyclopropyl-1-methyl (**f**), 3-methyl-2-butyl (**c**). $n = 4$; p$_m$ = pepe; alkyl = 3,3-dimethyl-1-butyl (**a**), 3-methyl-2-butyl (**c**), 4-methyl-1-pentyl (**d**). $n = 4$; p$_m$ = ppb; alkyl = 3,3-dimethyl-1-butyl (**a**), 3-methyl-2-butyl (**c**). $n = 4$; p$_m$ = impp; alkyl = methyl, 3,3-dimethyl-1-butyl (**a**).

(ii) $n = 3$; p$_m$ = bdmpm; alkyl = 1-trimethylsilyl-3-methyl-2-butyl (**g**), $n = 3$; p$_m$ = bdmpi, alkyl = 3,3-dimethyl-1-butyl (**a**).

(iii) $n = 2$; p$_m$ = 2 dmpe; alkyl = 2,4,4-trimethyl-1-pentyl (**e**), 3-methyl-2-butyl (**c**), 3,3-dimethyl-1-butyl (**a**).

Yields were between 63 and 85%. The complexes (1,1-dimethyl-2-methyl-1-propyl)V$(CO)_4$dppe (**3f**-dppe) and (3,3-dimethyl-1-butyl)V$(CO)_4$dmpe (**3a**-dmpe) have been identified spectroscopically only. In the case of the ppb complexes, the solvent was acetonitril and irradiation times amounted to 12 h. The reaction with methylene-cyclopropane (**f**) was carried out at −30°C.

b and **d**, when reacted with HV$(CO)_4$dppe, yield MeV$(CO)_4$dppe (**3m**-dppe), *i.e.* the intermediates (2,3-dimethyl-1-butyl)V$(CO)_4$dppe and (1,3-dimethyl-1-butyl)V$(CO)_4$dppe undergo methyl shift to the metal centre and concomitant elimination of the remaining organic fragment.

3.2.4. $^{13}CH_3V(CO)_3(impp)$

0.78 g (1.46 mmol) of [Et_4N][V$(CO)_4$impp] were dissolved in 50 ml of THF, cooled to dry-ice temperature and treated with 0.12 ml (272 mg, 1.90 mmol) of $^{13}CH_3I$. Slow warming to room temperature overnight resulted in a colour change from orange-red to red-brown and precipitation of [Et_4N]I. After filtration,

TABLE 7. Elemental analyses of selected alkyl complexes

Compound	Empirical formula; molecular mass	Analysis calc. (found)(%)			
		C	H	P	V
3a-dppe	$C_{36}H_{37}O_4P_2V$; 646.58	66.87 (66.97)	5.77 (5.55)	9.58 (9.38)	7.88 (8.02)
3a-bdmpi	$C_{22}H_{44}O_3P_3V$; 500.45	52.80 (52.60)	8.86 (8.83)	18.57 (18.52)	10.18 (10.01)
3c-dmpe	$C_{19}H_{43}O_2P_4V$; 478.39	47.70 (48.22)	9.06 (9.54)	25.90 (24.96)	10.65 (10.58)
3m-bdmpm	$C_{14}(^{13}C)H_{30}O_3P_3V$; 403.27	44.70 (44.39)	7.73 (7.66)	23.04 (22.41)	12.63 (12.90)

the solvent was evaporated, the residue redissolved in methylene chloride and washed through a 3 cm silica gel column with a 3.5/1 mixture of CH_2Cl_2/hexane. Subsequent evaporation to dryness yielded a brown–red product which was washed several times with hexane and finally dried in high vacuum (yield, 0.44 g, 1.1 mmol = 75%) $^{13}CH_3V(CO)_3$bdmpm was prepared analogously from $[Et_4N]V(CO)_3$bdmpm with a 73% yield.

Analyses for selected compounds are summarized in Table 7.

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