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SYNTHESIS AND NMR-SPECTROSCOPY CHARACTERISTICS OF CARBONYLHYDRIDOVANADIUM COMPLEXES STABILIZED BY OLIGOTERTIARY PHOSPHINES

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Summary

Hydridocarbonylvanadium complexes are stabilized by the tri- and tetratertiary phosphines (L) $PhP(CH_2CH_2PPh_2)_2$ (p_3), $MeC(CH_2PPh_2)_3$ (cp_3), $[Ph_2PCH_2CH_2PPhCH_2]_2$ (p_4) and $P(CH_2CH_2PPh_2)_3$ (pp_3). The stable complexes $HV(CO)_3L$ and the labile intermediates $HV(CO)_4L$ have been prepared by chomatography of the anionic parent compounds on silica gel. Irradiation of $HV(CO)_3pp_3$ and $HV(CO)_3p_4$ affords *cis*-$[HV(CO)_2pp_3]$ and *trans*-$[HV(CO)_2p_4]$, respectively. The complexes are characterized by their IR, ^1H, ^{31}P and ^{51}V NMR spectra. A model of restricted dynamic behaviour based on the face-capped octahedron is proposed on the basis of the hydride NMR pattern. The dinuclear ligand-bridged $\{HV(CO)_4\}_2\mu$-p_4 is obtained by treatment of $[Et_4N]_{2n}$-$[\{V(CO)_4\}_{2n}(\mu\text{-}p_4)_n]$ with t-BuCl/H_2O. An improved synthesis for the $[\eta^5\text{-}C_5H_5\text{-}VH(CO)_3]^-$ anion is described; ^1H and ^{51}V NMR data indicate that the local symmetry of the $\{VH(CO)_3\}$ moiety is probably C_{3v}.

Introduction

Hydrido complexes of vanadium are of interest because of their ability to transfer hydrogen to organic molecules. Thus, η^3-allyl complexes are obtained from the reaction between $HV(CO)_6$ or $HV(CO)_4Ph_2P(CH_2)_2PPh_2$ and butadiene or isoprene [1,2]. A recent review surveys various hydride transfers to organic halogen compounds involving the anionic $[\eta^5\text{-}C_5H_5VH(CO)_3]^-$ [3].

Hydrido complexes derived from $HV(CO)_6$ [4] are thermally unstable unless at least two CO-groups are replaced by phosphines or arsines. Several compounds of the type $HV(CO)_4LL$, prepared from $[Et_4N][V(CO)_4LL]$ by the use of proton-active agents have been described (LL = o-$C_6H_4(AsMe_2)_2$ [5], $Me_2PCH_2CH_2PMe_2$ [5], $Ph_2PCH_2CH_2PPh_2$ [6], $Ph_2PCH_2PPh_2$ [2], $Ph_2AsCH_2CH_2PPh_2$ [2]). The complexes $HV(CO)_4Ph_2P(CH_2)_nPPh_2$ (n = 1—4) are easily accessible in good yields by ion exchange chromatography of the anionic parent compounds on silica gel [7]. We have now extended this method to complexes of tri- and tetra-tertiary phosphines. The hydrido complexes thus obtained, containing three or two CO-groups, are surprisingly stable even in solution. Their ^1H-NMR spectra suggest a fluxional behaviour related to that discussed for the isoelectronic compounds $HTa(CO)_2(Me_2PCH_2CH_2PMe_2)_2$ [8] and $[HM(CO)_2(PP)_2]^+$ (M = Cr, Mo, W) [9—12] with a mono-capped octahedral structure.

For the oligotertiary ligands employed in this work, we will use the following abrivations:

$Ph_2As(CH_2)_2PPh_2$, asp; $Ph_2P(CH_2)_nPPh_2$ (n = 1—4), $p_2(n)$; $PhP(CH_2CH_2PPh_2)_2$, p_3; $MeC(CH_2PPh_2)_3$, cp_3; $(Ph_2PCH_2CH_2PPhCH_2)_2$, p_4; $P(CH_2CH_2PPh_2)_3$, pp_3; generals, p_m, where m denotes the total number of P-atoms. The spectra of the complexes $HV(CO)_4p_2(n)$ and $HV(CO)_3p_3$ were considered in two earlier reports [7,13]. They are included here in a comprehensive and partly revised presentation.

Results and discussion

$[Et_4N][\eta^5\text{-}C_5H_5VH(CO)_3]$

While $Na_2[\eta^5\text{-}C_5H_5V(CO)_3]$ is converted into $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ by strong acids [14,15], the use of moderately protonactive agents yields the hydrido complex $[\eta^5\text{-}C_5H_5VH(CO)_3]^-$ (I). I can be obtained from a THF/H_2O suspension [3]. We find that I is also formed in acetonitrile, from which it can be isolated in almost quantitative yields as the tetraethylammonium salt $[Et_4N]$-$[\eta^5\text{-}C_5H_5VH(CO)_3]$. The complex forms an orange yellow, micro-crystalline powder which is relatively air-stable and only slightly soluble in THF. The yellow solutions in CH_3CN become dark brown during two days, and amines are generated. The IR spectrum in CH_3CN [1889s, 1775vs cm^{-1}] is about identical to that reported by Bergman et al. for $[(Ph_3P)_2N][\eta^5\text{-}C_5H_5VH(CO)_3]$ [3].

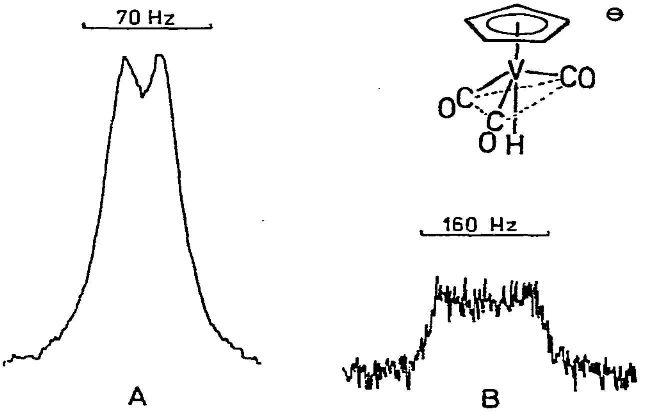


Fig. 1. 23.66 MHz ^{51}V NMR spectrum (A) and 270 MHz ^1H NMR spectrum (B) of $[\eta^5\text{-}C_5H_5VH(CO)_3]^-$. Presumed local symmetry of the $\{HV(CO)_3\}$ moiety is C_{3v}.

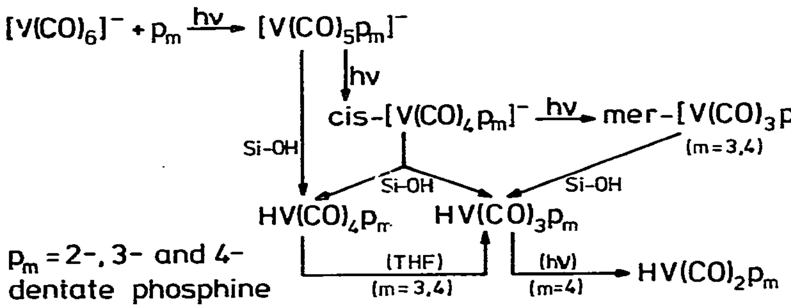
Although the absorption band at 1775 cm^{-1} is comparatively broad and may thus hide two accidentially degenerate absorptions (3 : 4 geometry), there is strong evidence for axial symmetry (3 : 3 : 1 geometry, i.e. C_{3v} for the $\{VH(CO)_3\}$ moiety) from the NMR spectra. As shown in Fig. 1, the ^{51}V NMR spectrum exhibits a doublet $[\delta(^{51}V) = -1730$ ppm, $^1J(^{51}V-^1H) = 20.3 \pm 0.2$ Hz, half-width (^1H-decoupled) = 60 Hz]. The ^1H NMR spectrum shows a broad signal for the H^- corresponding to the unresolved eight-line system $[\delta(^1H) = -6.33$ ppm, half width ca. 163 Hz] characteristic of a dipolar nucleus coupling wih a quadrupolar nucleus $[I(^{51}V) = 7/2]$ at a point where coupling is not averaged to zero by rapid quadrupolar relaxation [16]. Hence, to allow scalar coupling, relaxation times have to be sufficiently long. This is accomplished only by a small electric field gradient tensor, i.e. sufficiently high symmetry. The local symmetry is therefore very probably C_{3v}; the structure of the anion I thus differs from that of the complex η^5-$C_5H_5WH(CO)_3$, for which a square pyramidal ligand arrangement (local C_s symmetry) with rapid exchange of CO and H^- sites via an intermediate of 3 : 3 : 1 geometry was proposed [17].

Mononuclear carbonylhydridophosphine complexes

Preparation and properties

The preparations of the neutral species of general formula $HV(CO)_np_m$ were carried out according to Scheme 1 below.

SCHEME 1



Synthesis and spectroscopic characteristics of the parent compounds $[Et_4N]$-$[V(CO)_np_m]$ have been described in ref. 18 (n = 3, 4; p_m = cp_3, pp_3), [19] (n = 4, p_m = p_2; n = 3 or 4, p_m = p_4), and [20] (n = 3, 4; p_m = p_3).

The initial step for the conversion of the anionic species into the neutral hydrido complexes is the replacement of tetraethylammonium by hydrogen in an ion exchange process with participation of the silanol groups of the silica gel carrier [7]. For monosubstituted complexes $[Et_4N][V(CO)_5p_m]$, this reaction is slow. If there are free phosphorus atoms available in the initially formed hydrido complexes, the compounds can be stabilized by CO-elimination and chelation. This second step is fast for the reaction $HV(CO)_5p_m \rightarrow HV(CO)_4p_m$ and slow (several hours to days at room temperature) for $HV(CO)_4p_m \rightarrow HV(CO)_3p_m$. For that reason, no monosubstituted hydridocomplex and no pure $HV(CO)_4p_m$ with $m > 2$ could be isolated. For preparation of the treblysubstituted complexes $HV(CO)_3p_m$ ($m = 3, 4$), it is unnecessary to obtain pure starting reagents, since a mixture of $[V(CO)_4p_m]^-$ and $[V(CO)_3p_m]^-$ will afford the same final product. For $m = 4$, the conversion $HV(CO)_3p_m \rightarrow HV(CO)_2p_m$ is ineffective. However, UV irradiation of $HV(CO)_3p_4$ and $HV(CO)_3pp_3$ yields *trans*-$HV(CO)_2p_4$ and *cis*-$HV(CO)_2pp_3$, respectively.

There is an increase in stability with a decrease in the number of CO groups (and an increase in the number of ring systems in which vanadium is incorporated). While the $HV(CO)_4p_2(n)$ compounds are rather sensitive to oxygen and tend to decompose in solution to yield the paramagnetic $V(CO)_4p_2(n)$ [6], the trisubstituted species can be refluxed in THF without degradation, and crystalline powders of $HV(CO)_2p_4$ and $HV(CO)_2pp_3$ may be exposed to air for about a minute without visible decomposition.

Spectra

NMR data, including those for $[\eta^5\text{-}C_5H_5VH(CO)_3]^-$ and $\{HV(CO)_4\}_2\mu\text{-}p_4$ (see next section), are listed in Table 1. The complexes are arranged in order of

TABLE 1

^1H, ^{31}P AND ^{51}V NMR DATA ON CARBONYLHYDRIDOVANADIUM COMPLEXES

Complex	$\delta(^{51}V)$ [a] (ppm)	$\delta(^{31}P)$ [b] (ppm)	^1H NMR data (hydride region)		
			Multiplicity (Spin System)	$^2J(^1H—^{31}P)$ (Hz)	$\delta(^1H)$ (ppm)
$[\eta^5\text{-}C_5H_5VH(CO)_3]^-$(I)	−1730 [c]	—	[d]	—	−6.33
$HV(CO)_4pp_3$ (II)	[e]	+87, +76 −15,6	triplet (A_2X)	25.0	−5.32
$HV(CO)_4cp_3$ (III)	−1608	[e]	triplet (A_2X)	26.1	−5.20
$\{HV(CO)_4\}_2\mu\text{-}p_4$ (IV)	−1685	+68	[triplet] [f] ([ABX])	[23.0, 27.0]	−5.20
$HV(CO)_4asp$ [g]	−1663	+72	doublet (AX)	25.9	−5.08
$HV(CO)_4p_2(1—4)$ [g]	−1555 −1690	+12 to +72	triplet (A_2X)	21.9 to 26.7	−4.91 to −5.15
$HV(CO)_3p_4$(V)	−1665	+96, +84, +80 −15.1, −18.0	[quartet] [f, k] (ABCX)	29.2, 21.4, 32.1	−5.08
$HV(CO)_3cp_3$ (VI)	−1528 [h]	+27 −28.0	broad signal	[j]	−5.06
$HV(CO)_3p_3$ [g]	−1640	ca. +90 [i]	[sextet] [f] (A_2BX)	39.7, 20.0	−4.54
$HV(CO)_3pp_3$ (VII)	−1690	+99, +83 −15.6	[sextet] [f] (A_2BX)	39.7, 20.0	−4.54
cis-$HV(CO)_2pp_3$ (VIII)	−1541	ca. +100 [i]	quartet of doubl. (A_3BX)	36.7, 9.6	−3.84
trans-$HV(CO)_2p_4$ (IX)	−1658	+111, +98	triplet of tripl. (A_2B_2X)	113.0, 17.7	−3.62

[a] Ca. 0.1 *M* THF or THF/CH_3CN at 298 K; negative shifts are upfield from $VOCl_3$. [b] Ca. 0.1 *M* THF or THF/CH_3CN at 200 K relative to H_3PO_4 80%. Positive shift values (downfield from H_3PO_4) correspond to coordinated P-atoms and are considerably broadened. Literature shift values for unligated P-atoms are: PPh_2, −12.9 to −13.5; PPh, −16.6; P, −17.4 to −17.8 [27, 28] at room temperature. The upfield shift for ca. 200 K amounts to 1.5 to 2.5 ppm. [c] Doublet, $^1J(^{51}V—^1H)$ 20.3 ± 0.2 Hz. [d] Unresolved octet (see text). [e] No reliable data obtained. [f] For details see text. [g] From ref. 7. [h] Quartet, $^1J(^{51}V—^{31}P)$ 180 Hz. [i] Very broad signal. [j] Quartet in DMF-d_7 at 223 K, $^2J(^1H—^{31}P)$ (experimental) ca. 20 Hz. [k] In DMF-d_7.

TABLE 2

IR-SPECTRA (CO-STRETCHING REGION) OF CARBONYLHYDRIDOVANADIUM COMPLEXES

Complex	ν(CO) (cm^{-1}) in 0.01—0.02 *M* THF			
I	1889m	1775vs		
$HV(CO)_4p_2(2)$	1990s	1878vs(br)		
$HV(CO)_4p_2(3)$	1990s	1909w	1867vs	1831w
$HV(CO)_4p_4$	1990s	1879vs		
II	1991m	1877vs		
III	1987m	1866vs		
IV	1990m	1877vs	1905w(sh)	1845w(sh)
$HV(CO)_3p_3$	1927(sh)	1920s	1835(sh)	1820s
V	1905s	1806m		
VI	1908s	1825s(br)	1810(sh)	
VII	1922m	1911m	1819vs	
VIII	1829m	1772m		
IX	1884vw	1764s		

decreasing shielding of the hydride. IR-spectroscopic CO-stretching frequencies are summerized in Table 2. Except for VIII and IX, configuration assignment on the basis of IR data cannot be carried out unambiguously.

^{51}V NMR Spectra. The ^{51}V nucleus in the hydrido complexes is less shielded than in the anionic compounds (ca. —1760 to —1830 ppm for *cis*-$[V(CO)_4p_m]^-$ in unstrained structures and ca. —1720 ppm for *mer*-$[V(CO)_3p_m]^-$ [18,19]). The additional down-field shift for VI and VIII relative to that for other complexes listed in Table 1 may indicate that the bi- and tricyclic structural units in those systems span facial instead of meridional positions in the basic octahedron, thus giving rise to a threefold symmetry axis. Under ideal C_{3v} point symmetry, the vanadium-3*d* orbital set splits into 2*e* + a_1. However, because of the chelate structures, the degeneracy of the *e*-orbitals will be partly raised and the lowest unoccupied state stabilized. Consequently the paramagnetic contribution to the overall shielding is increased and so the chemical shift is decreased (for a detailed discussion see e.g. ref. 21). The small ^{31}P-coordination shift of VI (39 ppm) suggests ring strains resulting in hindered or diminished σ- (and perhaps also π-) overlap between vanadium and phosphorus, an effect that will add to the low-field shift of the ^{51}V signal. Similar effects have been observed for the pairs $HV(CO)_4p_2(1)$ [$\delta(^{51}V)$ = —1593, $\Delta(\delta_p)$ = 37 ppm]/ $HV(CO)_4p_2(2)$ [—1690, 82] [7] and η^5-$C_5H_5V(CO)_2p_2(1)$ [—870, 78]/η^2-$C_5H_5V(CO)_2p_2(2)$ [—1110, 127] [19], and in various platinum, manganese and group VIb complexes containing ditertiary chelating phosphines [22—25].

Generally, the vanadium signals are broad and unstructured (half widths range from ca. 500 to ca. 2000 Hz, corresponding to spin-lattice relaxation times of 2 to 0.5 ms). An exception is VI, which exhibits a 1 : 3 : 3 : 1 quartet with a vanadium-phosphorus coupling constant of 180 Hz. This is the magnitude expected for phenylalkylphosphine complexes of vanadium [26]. The comparatively narrow lines (half width 67 Hz) again indicate axial symmetry and relatively slow relaxation processes.

^{1}H NMR Spectra. Correspondingly, the hydride resonance of VI is broad (in THF solution and at room temperature) and scalar relaxation is considerably

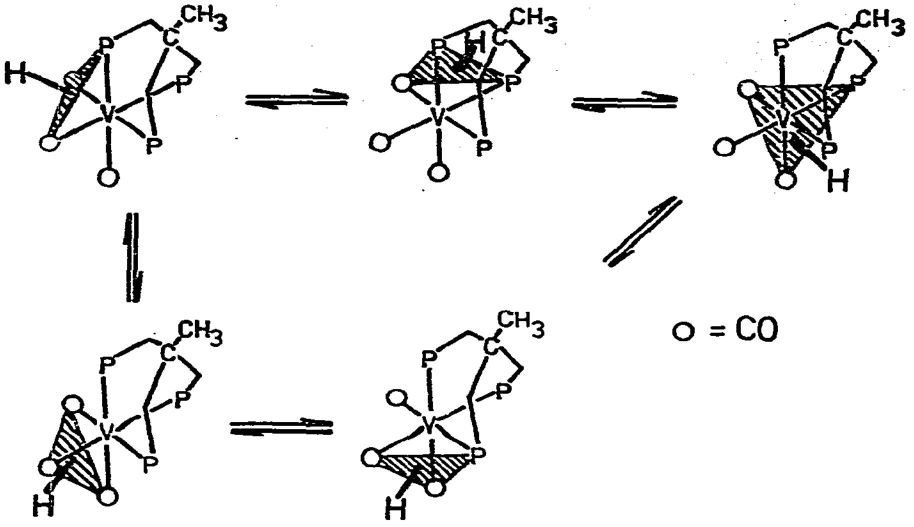


Fig. 2. Pseudo-rotation of H^- about the C_3 axis in $HV(CO)_3\{MeC(CH_2PPh_2)_3\}$ (VI).

depressed, i.e., the vanadium-hydrogen coupling constant cannot be indirectly obtained from the overall line-width. The IR spectrum of VI shows three CO-stretching frequencies (cf. Table 2), suggesting a structure in which the H^- ligand occupies definite positions in the polyhedron (local symmetry $< C_{3v}$), which are averaged out on the NMR time scale to correspond to a rotation of H^- about the C_3 axis as illustrated in Fig. 2. Complete decoupling of the ^1H and ^{51}V nuclei is achieved by increasing the relaxation rate through variation of the solvent (DMF instead of THF) and lowering the temperature to 223 K. Under these conditions, a quartet [$^2J(^1H—^{31}P)$ ca. 20 Hz] is observed.

The spectral data for the complexes II to IV and VII—IX indicate dynamic behaviour for these molecules. The ^1H and ^{51}V nuclei are completely decoupled, and the pattern observed in the hydride region of the ^1H-NMR spectra reflects coupling between H^- and bonded phosphorus atoms only. Three consistent trends are noted for these spectra: First, shielding of the hydride decrease with increasing CO substitution (II > VII > VIII; IV > V > IX). Second, complexes belonging to the same substitution class have similar shift values and coupling constants regardless of the nature of the coordinated phosphine group (II ~ III ~ IV ~ $HV(CO)_4p_2(n)$; V ~ VI ~ VII); this implies that ^1H NMR parameters are essentially independent of the chemical non-equivalence of the phosphorus groups bonded to vanadium. Third, the smallest $^2J(HP)$ couplings are observed for coupling of H^- to a bridge-head phosphorus in a tricyclic structure and the largest to phosphorus atoms not at a bridge-head (compare VIII, VII and II).

The particular role of the bridge-head phosphorus can best be understood on the basis of a structural model which takes into account the limited dynamic behaviour of the molecule. In this model, the P atoms and CO groups are octahedrally arranged as in the geometries found for $HTa(CO)_2(Me_2PCH_2CH_2PMe_2)_2$ [8] and $[HM(CO)_2(PP)_2]^+$ (M = Cr, Mo, W; PP = symmetrical and non-

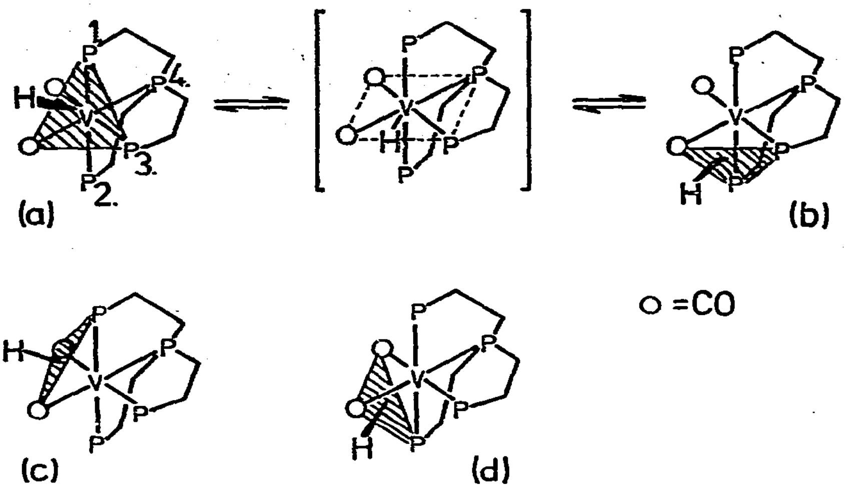


Fig. 3. The four possible positions of H^- in *cis*-$[HV(CO)_2\{P(CH_2CH_2PPh_2)_3\}]$ on the basis of a partially dynamic model involving the pentagonal bipyramid as a transitory state (see text).

symmetrical ditertiary phosphine) [9—12]. The hydride ligand, capping octahedral faces, changes sites in the manner illustrated in Figs. 2 and 3. H^- positions over faces where at least one of the octahedral edges is spanned by a $P(CH_2)_2P$ backbone of the chelate structure are excluded. The reason for that restriction is obvious when the mechanism of site exchange involves the cycle mono-capped octahedron $\rightleftharpoons$ pentagonal bipyramid, as discussed for the pairwise exchange observed for $[HMo(CO)_2(Ph_2PCH_2CH_2PPh_2)_2]^+$ [10], and illustrated in Fig. 3 for the migration of H^- from position (a) to position (b). The possible existence of the pentagonal bipyramidal intermediate is supported by a X-ray structural investigation which showed that of $HV(CO)_4Ph_2PCH_2CH_2PPh_2$ [13] has such a structure (H^- is in the $VP_2(CO)_2$ plane and situated between P and CO).

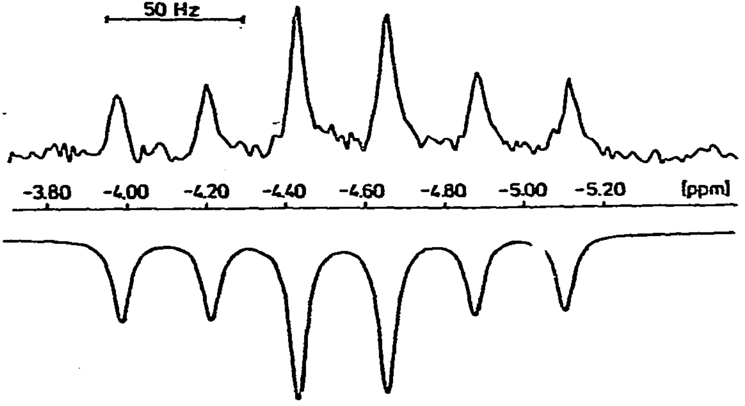
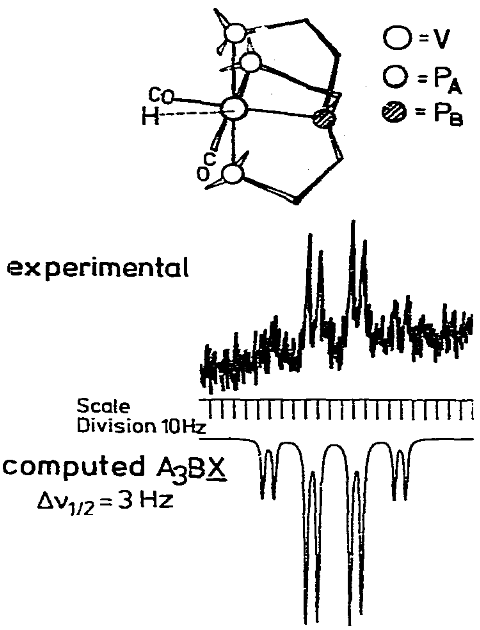


Fig. 4. Experimental (above) and computed (A_2BX, half-width $\Delta\nu_{1/2}$ = 4.5 Hz) 90 MHz ^1H NMR spectrum (hydride region) of $HV(CO)_3\{P(CH_2CH_2PPh_2)_3\}$ (V). An identical spectrum is obtained for $HV(CO)_3\,Ph_2P(CH_2CH_2PPh_2)_2$.



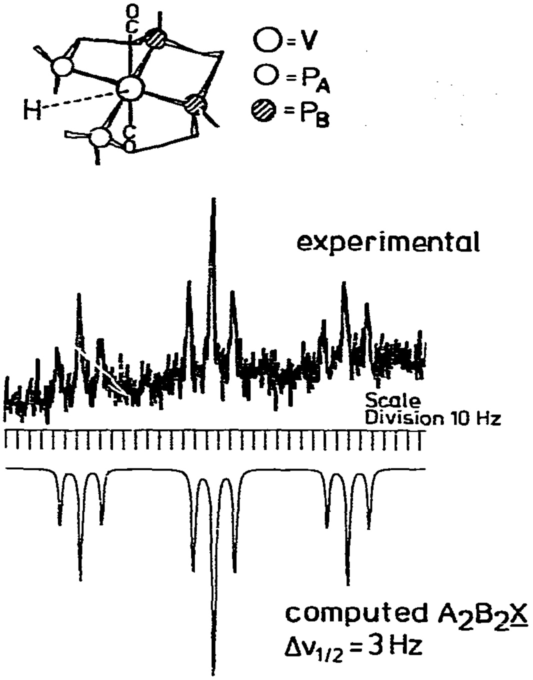


Fig. 5. 90 MHz ^1H NMR spectrum (hydride region) of *cis*-$[HV(CO)_2\{P(CH_2CH_2PPh_2)_3\}]$ (VIII).

Fig. 6. 90 MHz ^1H NMR spectrum (hydride region) of *trans*-$[HV(CO)_2\{Ph_2PCH_2CH_2PPhCH_2\}_2]$ (IX).

The computed coupling constants listed in Table 1 are in accord with this model. Figs. 4—7 show experimental and computed ^1H NMR spectra (hydride region) for VII, VIII, IX and V. It is noteworthy that the trisubstituted complexes containing ligands as different as pp_3 and p_3 give identical spectra, whereas the line patterns for the two trisubstituted complexes of the linear phosphines p_3 and p_4 are markedly different.

Taking the hydrogen-phosphorus coupling constant in the unstrained com-

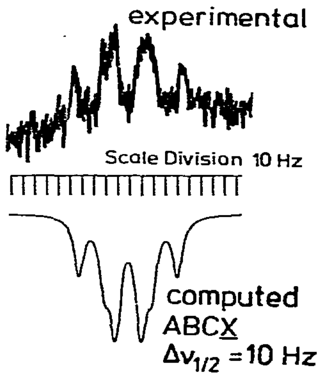


Fig. 7. 90 MHz ^1H NMR spectrum (hydride region) of $HV(CO)_3\{Ph_2PCH_2CH_2PPhCH_2\}_2$ (V).

plexes $HV(CO)_4p_2(2)$ [$^2J(HP) = 26.0$ Hz] and $HV(CO)_4$asp [$^2J(HP) = 25.9$ Hz] as a "normal" value, a semiquantitative prediction can be made of the spin system and approximate magnitude of the coupling constants in other hydridophosphinevanadium complexes. In our model of restricted fluxionality, the H^- in ditertiary phosphine complexes can migrate between six different octahedral sites, in four of which the two phosphorus atoms are mutually *cis* and *trans* to the hydride. The two remaining positions are *trans* for either phosphorus. The coupling constant in $HV(CO)_4p_2$ complexes (A_2X spin system) is then expressed according to $J = 1/6(4t + 2c) = 26$ Hz (where t stands for *trans* coupling and c for *cis* coupling). Among the various t/c pairs which are solutions to this equation, the best agreement with the available experimental $^2J(HP)$ values is obtained for $c = 60$ and $t = 9$ Hz. As an example, the calculation of coupling constants is shown for VIII, for which the matrix

$$\begin{array}{c|cccc} & 1 & 2 & 3 & 4 \\ \hline (a) & c & t & c & t \\ (b) & t & c & c & t \\ (c) & c & t & t & t \\ (d) & t & c & t & t \end{array}$$

can be constructed. (a) to (d) refer to the four allowed positions, 1 to 4 to the four P-atoms as labelled in Fig. 3. P^4 is the bridge-head atom which is trans to H^- in all four cases. The three other P-atoms are equivalent, each being twice *cis* and twice *trans* to H^-. Hence, a A_3BX spin system with $J(AX) = 1/4(2t + 2c) = 34.5$ Hz and $J(BX) = 9$ Hz ($B \equiv P^4$) arises, which is in good agreement with the computed coupling constants 36.7 and 9.6 Hz (Table 1). The calculations for the other complexes is carried out accordingly, but the agreement is not always as good as for VIII.

The ^1H NMR spectrum of V (Fig. 7) differs from the spectra of other hydrido complexes in that the signals are broadened to such an extent that the spectrum is only partly resolved. The considerable line width (ca. 10 Hz) may be caused by a still effective quadrupolar interaction on the part of the vanadium nucleus when exchange of H^- sites becomes sufficiently slow. The ^{31}P NMR spectrum of this complex indicates three inequivalent coordinated phosphorus atoms, the lowest shielding value, +96 ppm, probably corresponding to the bridge-head phosphorus [24,27]. The computed ^1H NMR spectrum (ABCX) agrees with this. If, in a first approximation ($A \approx C$, see Table 1), the spin system is A_2BX [$J(AX) = 31$ Hz, $J(BX) = 21$ Hz], then good agreement between experimental ^1H NMR results and those calculated with our partially fluxional model is obtained only for a facial configuration of V.

$\{HV(CO)_2\}_2\mu$-p_4 (IV)

While $HV(CO)_4p_m$ ($m = 3, 4$) complexes are unstable with respect to elimination of a third CO group, IV does not undergo any changes in solution, which suggests that there are no uncoordinated phosphorus atoms present for the formation of a bicyclic system. In keeping with this, no ^{31}P signals corresponding with unligated PPh or PPh_2 groups are observed. On these grounds, IV is formu-

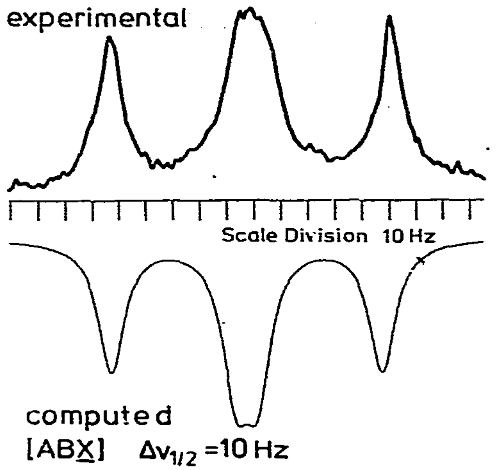


Fig. 8. 90 MHz ^1H NMR spectrum (hydride region) of $\{HV(CO)_4\}_2(\mu\text{-}\{Ph_2PCH_2CH_2PPhCH_2\}_2)$ (IV).

lated as a dinuclear, ligand-bridged complex. Since the starting material is insoluble in THF, IV is prepared in a t-BuCl/heptane/H_2O suspension according to

$$[Et_4N]_{2n}[\{V(CO)_4\}_{2n}(\mu\text{-}p_4)_n] + 2n\{H^+\} \rightarrow n\{HV(CO)_4\}_2\mu\text{-}p_4 + 2n\{Et_4N^+\}$$

The compound forms a deep yellow, micro-crystalline powder. The ^1H NMR spectrum is shown in Fig. 8. Although the spin system is complex (AA'BB'XX' at the best) a good first order fit is obtained for a computation based on ABX. IR, ^{51}V and ^{31}P NMR spectra are similar to those for $HV(CO)_4p(n)$ (n = 2 and 3).

Experimental

General

All procedures were carried out under nitrogen in oxygen-free solvents. A short column (10 × 2.5 cm, capacity approximately 0.5 mmol) filled with silica gel (Silicagel 60 purss. 70—230 mesh ASTM, Merck) was used for the ion exchange and chromatography operations. The silica gel was dried under high vacuum at room temperature for one hour and treated with N_2 and THF. For details of the irradiation and preparation of $[Et_4N][V(CO)_ncp_3]$ and $[Et_4N]$-$[V(CO)_npp_3]$ (n = 3, 4) see ref. 18, for the preparation of $[Et_4N][V(CO)_np_4]$ and $[Et_4N]_{2n}[\{V(CO)_4\}_{2n}(\mu\text{-}p_4)_n]$ ref. 19. The preparation of $HV(CO)_4asp$, $HV(CO)_4p_2(n)$ and $HV(CO)_3p_3$ was published recently [7].

IR, ^{31}P and ^{51}V NMR spectra were obtained as described in ref. 18. ^1H NMR: ca. 0.1 *M* THF or THF/CH_3CN solutions in rotating 5 mm diameter vials, Bruker WH 90 spectrometer ($[\eta^5\text{-}C_5H_5VH(CO)_3]^-$: Bruker 270) relative to TMS.

Analytical data and some of the properties of the complexes are summarized in Table 3.

TABLE 3

ANALYSES AND PROPERTIES OF ISOLATED COMPLEXES

		Empirical Formula (Molecular Mass)	Analysis found (calcd.) (%)				
			C	H	N	P	V
I	yellow powder	$C_{16}H_{26}NO_3V$	57.5	8.0	4.4	—	15.1
		(331.33)	(58.00)	(7.91)	(4.23)		(15.37)
IV	yellow powder	$C_{50}H_{44}O_8P_4V_2$	59.4	4.9	—	12.4	9.9
		(998.68)	(60.13)	(4.44)		(12.41)	(10.20)
VI	yellow crystals or powder	$C_{44}H_{40}O_3P_3V$	68.8	5.3	—	11.9	5.6
		(760.67)	(69.48)	(5.30)		(12.22)	(6.70)
VII	red needles	$C_{45}H_{43}O_3P_4V$	66.9	5.7	—	15.2	6.8
		(806.68)	(67.00)	(5.37)		(15.36)	(6.32)
VIII	red crystalline powder	$C_{44}H_{43}O_2P_4V$	67.6	6.0	—	15.4	6.6
		(778.68)	(67.87)	(5.57)		(15.91)	(6.54)
IX [a]	red needles	$C_{44}H_{43}O_2P_4V$	67.5	5.5	—		
		(778.68)	(67.87)	(5.57)			

[a] C and H values only because of low yields

Preparation of Complexes

$HV(CO)_np_m$ ($n = 3, 4$; $p_m = cp_3, pp_3, p_4$) (II, III, V—VII). As a typical procedure, a description of the preparation of $HV(CO)_3cp_3$ is given below.

350 mg $[Et_4N][V(CO)_6]$ [19] (1 mmol) and 660 mg cp_3 (1.05 mmol) dissolved in ca. 100 ml THF were irradiated for four hours. The dark red solution, containing $[Et_4N][V(CO)_4cp_3]$ and $[Et_4N][V(CO)_3cp_3]$ was concentrated to ca. 10 ml by evaporation under vacuum at room temperature, and treated with 20-ml n-heptane. After 15 min of stirring, the pasty or powdery red precipitate was separated from the supernatant solvent by decantation or filtration and (without further purification) dissolved in 4 ml CH_3CN/THF 3/2. This solution was transferred to the silica gel column and chromatographed with THF (ca. 3 ml/min), affording about 150 ml of yellow to orange eluant. The solution was allowed to stand at room temperature for two days, then concentrated to 20 ml, treated with an equal volume of heptane, and kept at 250 K for several days. Orange crystals separated out, and these were filtered off and dried under high vacuum (4 hours). From the concentrated filtrate, further product was obtained by addition of excess heptane.

For preparation of the disubstituted complexes $HV(CO)_4p_m$, pure *cis*-$[Et_4N]$-$[V(CO)_4p_m]$ has to be used as starting material. The hydrido complex is precipitated with heptane immediately after elution from the column. The compounds isolated usually contain small amounts of $HV(CO)_3p_m$.

cis-$HV(CO)_2pp_3$ (VIII). A solution of 400 mg $[Et_4N][V(CO)_6]$ (1.15 mmol) and 800 mg pp_3 (1.2 mmol) in 100 ml THF was irradiated for 2 hours. The solution, which contained $[V(CO)_4pp_3]^-$ and $[V(CO)_3pp_3]^-$, was concentrated to 5 ml, transferred to a silica gel column and chromatographed with ca. 100 ml THF. The eluant $[HV(CO)_4pp_3$ and $HV(CO)_3pp_3]$ was transferred back to the irradiation apparatus, irradiated for 1 hour and treated with 10 ml heptane. After standing for one hour, the solution was filtered and the filtrate evaporated to 15 ml, whereupon VIII precipitated.

trans-$HV(CO)_2p_4$ (IX). The preparation of IX is carried out as described for

VIII. However, the product obtained by concentration of the THF/heptane solution was impure. Red needles of pure $HV(CO)_2p_4$ were formed in the mother liquor after standing at room temperature for one day, and these were filtered off and dried under high vacuum.

$\{HV(CO)_4\}_2\mu\text{-}p_4$ (IV). A suspension of 150 mg $[Et_4N]_{2n}[\{V(CO)_4\}_{2n}(\mu\text{-}p_4)_n]$ in a mixture of 10 ml t-BuCl, 5 ml n-heptane and 15 ml H_2O (oxygen-free) was stirred magnetically for 3 hours. The yellow precipitate was filtered off, washed with 5 ml heptane and 5 ml water, and dried under high vacuum.

$[Et_4N][\eta^5\text{-}C_5H_5VH(CO)_3]$ (I). A solution of 3.4 g $Na_2[\eta^5\text{-}C_5H_5V(CO)_3]$ (13.8 mmol) (obtained by reduction of 4 g $\eta^5\text{-}C_5H_5V(CO)_4$ [15]) in 20 ml CH_3CN was treated with a solution of 4.7 g $[Et_4N]Cl$ (28.5 mmol) in 20 ml CH_3CN. The mixture was stirred magnetically overnight to afford a dark brown solution and a grey precipitate. The solution was filtered, and the filtrate evaporated to dryness at room temperature to yield yellow I. This was washed with two 25 ml portions of oxygen-free water and dried under high vacuum (6 hours). I is slightly soluble in THF and readily soluble in CH_3CN, in which it slowly decomposes.

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