Journal of Organometallic Chemistry, 388 (1990) 95–104
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20686

Carbonylvanadates, hydrido- and alkyl-carbonylvanadium complexes containing alkylated oligophosphines as ancillary ligands

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(Received December 7th, 1989)

Abstract

The ionic complexes *cis*-$[Et_4N][V(CO)_4p_m]$ (p_m = *m*-dentate phosphine: $Cy_2PCH_2CH_2PCy_2$; $RP(CH_2CH_2CH_2PR'_2)_2$ with R/R′ = Me/Me, Me/Et, Et/Et; $P(CH_2CH_2CH_2PEt_2)_3$] have been prepared. Isomers with 6- and 10-membered chelate rings are present in the case of p_3 (^{51}V NMR evidence). Ion exchange on silica gel yields $HV(CO)_4p_2$, $HV(CO)_3p_m$ ($m = 3$, 4), which, for $m = 4$, can be converted photochemically into *cis*-$[HV(CO)_2p_4]$. The ^1H NMR pattern in the hydride region is indicative of a face-capped octahedron with a restricted mobility of the capping H^-. Reaction between $[Et_4N][V(CO)_4dppe]$ and RI (R = Me, i-Pr, t-Bu, $SiMe_3$) leads to $RV(CO)_4dppe$ ($\delta(^{51}V)$ -1032 to -1235 ppm relative to VCl_3). In the case of t-BuI and Me_3SiI, $HV(CO)_4dppe$ is also formed. The reaction with t-BuCl in the presence of D_2O yields $DV(CO)_4dppe$.

Introduction

Hepta-coordinated complexes with a basic hexa-coordinated $M(CO)_np_m$ unit (p_m is a phosphine coordinating through *m* P atoms, $n + m = 6$; M = V, Nb, Ta) have recently attracted interest in respect of their structural characteristics and chemical reactivity. The seventh ligand attached to $M(CO)_np_m$ can be a halide and pseudohalide [1], methyl [2], SiH_3 [3] and R_3E^{14} (E^{14} = Ge, Sn, Pb; [4]) or the hydrido ligand [5–7]. A face-capped (distorted) octahedron, with the seventh ligand in the capping position, has been found in the case of $Ph_3PbV(CO)_6$ [4f] and $HV(CO)_3\{(Me_2PCH_2)_3Si\text{-t-Bu}\}$ [7]. This is also the structure in solution for various other complexes of the composition $HM(CO)_np_m$ [5,6], while $HV(CO)_4dppe$ (dppe $= Ph_2PCH_2CH_2PPh_2$), in the crystalline solid state, has been found to provide an example of the pentagonal bipyramid [5c]. Halide complexes, on the other hand, exhibit a solution and solid state structure derived from the capped trigonal prism (cf. [1a] and references therein).

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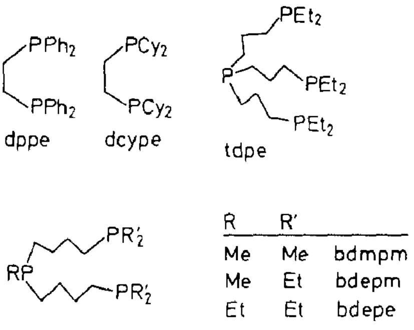


R	R'	
Me	Me	bdmpm
Me	Et	bdepm
Et	Et	bdepe

Scheme 1

Most hydrido complexes $HM(CO)_n p_m$ that have been investigated to date contain oligodentate phosphine ligands carrying phenyl substituents on the P atoms [5,6]. The main reason for using phenylphosphines as supporting ligands is that they impart stability but this also implies a certain inertness. Although some reactions are known, such as the formation of η^3-allyl complexes with butadienes [8] or η^5-Cp complexes with pentafulvenes [9], the metal–hydrogen bond is rather stable and even survives UV irradiation [6]. In order to obtain material for the study of the potential reactivity of hydrido complexes of the group 5 metals, we have synthesized various complexes with 2-, 3- and 4-dentate alkylphosphines (Scheme 1). For comparison, several new alkyl and silyl complexes, stabilized by dppe, have also been prepared. Included in the present study are the precursor complexes $[Et_4N][V(CO)_n p_m]$, the ^{51}V NMR features of which reveal an interesting coordination behaviour commonly not observed with long-chain oligodentate phosphines.

Results and discussion

Carbonylphosphinevanadates(− 1)

These were obtained by UV irradiation of THF solutions containing $[Et_4N][V(CO)_6]$ and the phosphine in about equimolar amounts. All the products, formed by successive replacement of carbon monoxide, can be detected by their IR (CO stretching region) and ^{51}V NMR patterns. The 2-, 3- and 4-dentate phosphines readily form tetracarbonylvanadates (in the *cis* configuration). A third CO is not easily removed, and a fourth not at all: with the tetradentate tdep, the final product of reaction after several hours of irradiation is a mixture of *cis*-$[V(CO)_4tdpe]^-$ and *mer*-$[V(CO)_3tdpe)]^-$. Similar observations have been reported for tri- and tetra-dentate phenylphosphines [6a,10]. Since, for the preparation of the hydrido complexes, the tetracarbonyls are as effective as the tricarbonyls, no efforts were made to achieve complete conversion. IR and ^{51}V NMR data are listed in Table 1. The IR spectra are in accord with the idealized local symmetries C_{4v}($[V(CO)_5p_m]^-$) and C_{2v}(*cis*-$[V(CO)_4p_m]^-$, *mer*-$[V(CO)_3p_m]^-$). The ^{31}P NMR spectra exhibit very broad (up to one kHz) signals in the region associated with coordinated phosphorus functions [5a,5b,10]. The large width is caused by unresolved coupling of the spin-1/2 nucleus ^{31}P to the spin-7/2 nucleus ^{51}V.

The various degrees of substitution are easily distinguishable from the ^{51}V NMR spectra (shown in Fig. 1 for the complexes formed with bdepm), both from the

Table 1

CO-stretching frequencies and ^{51}V NMR data for the complexes $[Et_4N][V(CO)_np_m]$

p_m [a]	n	ν(CO)(cm)$^{-1}$ [b]	$\delta(^{51}V)$ [c] (ppm/i)	$J(^{51}V-^{31}P)$ [d] (Hz)
	6	1888sh 1849vs	−1956	
PMe(al)$_2$	5	1959w 1852m 1809s	−1882	218(d)
dppe	4	1903m 1799s 1780vs 1747sh	−1790	unresolved
dcype	4	1878s 1760sh 1740vs 1710sh	−1857	unresolved
bdmpm	5	1955w 1853m 1810s	−1883	208(d)
	4	1888s 1770vs 1755sh 1740sh	−1803/1	218(t)
			−1808/4	208(t)
bdepm	5	1953w 1853m 1808s	−1885/1	(d)
			−1891/5	208(d)
	4	1887s 1773vs 1755sh 1730sh	−1807/1	208(t)
			−1812/1.2	208(t)
	3	1910m 1812s 1680m,vbr	−1677	208(q)
bdepe	5	1955w 1853m 1806s	−1884/1	(d)
			−1892/4	218(d)
	4	1882s 1770vs 1750sh 1730sh	−1811/1	218(t)
			−1815/0.5	208(t)
	3	1905m 1814s 1685sh	−1684	199(q)
tdep	5		−1905 [e]	
	4	1883s 1772vs 1755sh 1730sh	−1818 [f,e]	
			−1826	209(t)
	3	1910m 1815s 1680sh	−1695	203(q)

[a] al = allyl; for other abbreviations see Scheme 1. [b] All data in THF, except of the dcype complex (Nujol). [c] At 298 K and in CD_3CN, relative $VOCl_3$. /i indicates the relative intensities of signals belonging to isomers. [d] The multiplicities of the signals are given in parentheses. [e] Incompletely resolved. [f] Signal of very weak intensity.

chemical shifts $\delta(^{51}V)$ and the coupling patterns originating from one-bond coupling between ^{51}V and ^{31}P. Increasing substitution of the strong acceptor CO by the weaker phosphine induces a deshielding of the ^{51}V nucleus (The decrease in symmetry also contributes to the deshielding effect.) This phenomenon has been thouroughly investigated earlier [11] and traced back to a decrease in the HOMO-LUMO gap ΔE, which leads to an increase in the paramagnetic deshielding parameter σ'(para) in the overall shielding term σ' according to eq. 1:

$$\sigma' = \sigma'(\text{dia}) + \sigma'(\text{para}) = \sigma'(\text{dia}) + \text{const}\,\overline{\Delta E^{1}}\langle r^{-3}\rangle_{3d}\overline{C_{3d}^{2}} \qquad (1)$$

In this operation σ'(dia) is the practically constant diamagnetic shielding contribution, r the distance of the 3d electrons from the vanadium nucleus, and C the LCAO coefficient of relevant MOs.

In the clearly distinct regions for mono- and di-substitution, there are neighbouring and partly overlapping groups of signals, indicating the presence of isomers in the case of $[V(CO)_5p_m]^-$ and *cis*-$[V(CO)_4p_m]^-$. There are two doublets for pentacarbonylvanadates, which can be traced back to coordination via the central PMe and the terminal PEt$_2$ groups, respectively. Since, both statistically and for steric reasons, coordination of the terminal P functions is favoured, the more intense doublet is associated with PEt$_2$. Steric crowding at the vanadium centre, as in the case of PMe coordination, leads to poorer overlap between vanadium-d and

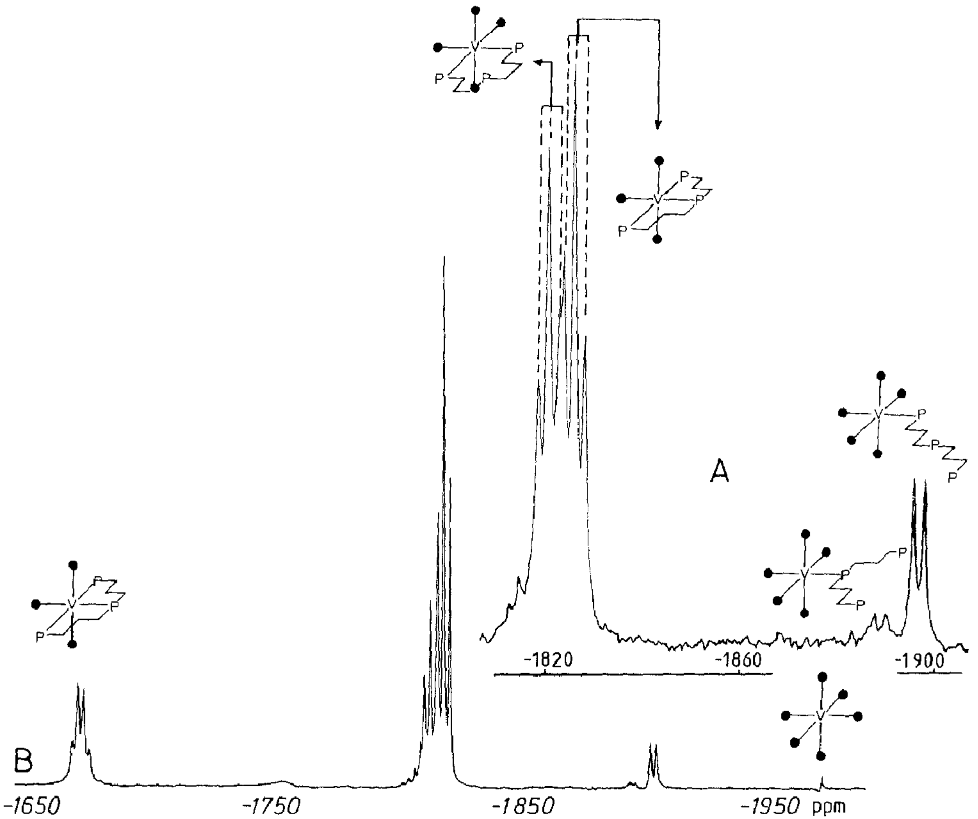


Fig. 1. 94.73 MHz {^{1}H}^{51}V NMR spectrum of the complexes formed in THF between [Et$_4$N][V(CO)$_6$] and bis(3-diethylphosphinopropyl)methylphosphine (bdepm). A represents the original solution (THF-d_8): expanded section for the tri- and tetra-carbonylvanadates. B (CD$_3$CN) illustrates the situation after working up with one of the two isomers of *cis*-[V(CO)$_4$bdemp]$^-$ substantially diminished.

phosphorus orbitals and hence, according to eq. 1, to a decrease in $\overline{\Delta E}$ and σ' [11a]. A steric effect acting in the same direction is observed in all but the chelate-5 ring structures: Strains, which may arise from angle distortions (e.g in 4-membered rings) or from torsional strains in larger ring systems [11a,11b,12] give rise to deshielding effects. The low-field (high-frequency) triplet in the spectrum of *cis*-[V(CO)$_4$bdepm]$^-$ (Fig. 1), and similarly in the spectra of other complexes (see Table 1 for details and data), is therefore allocated the 10-membered chelate ring. The formation of this system is statistically disfavoured, and we can offer no explanation at present for the large amount of this isomer present in the reaction mixture.

Hydrido complexes

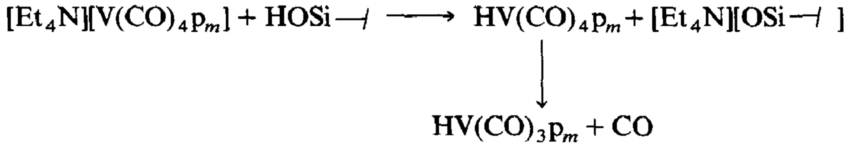
Ion exchange chromatography of the ionic precursor complexes [Et$_4$N][V(CO)$_4$p$_m$] on silica gel yield (eq. 2) the hydrido complexes HV(CO)$_4$p$_m$ and, if m is > 2 and the THF solutions are allowed to stand for a while, HV(CO)$_3$p$_m$. Upon UV irradiation, the complex with the tetradentate tdpe looses a fourth CO ligand to form *cis*-[HV(CO)$_2$tdpe], the *cis* configuration being indicated by the IR spectrum (2 ν(CO) of about equal intensities). Spectroscopic data are summarized in Table 2.

Table 2

Spectroscopic data for hydrido complexes

Complex [a]	ν(CO) [b] (cm^{-1})	$\delta(^{51}V)$ [c] (ppm)	$\delta(^{1}H)/J(HP)$ [d] (ppm/Hz)
$HV(CO)_n p_m$			
$n = 4$, p_m = dppe [e]	1990s 1878vs,br	−1690	−4.91(t)/51
dcype	1975m 1880sh 1857vs 1811m	−1745	−5.52(t)25 [g]
bdmpm	1979m 1865s	−1716	
bdepm	1980m 1664s		
bdepe	1979m 1865s		
tdep	1979m 1862s		
$n = 3$, p_m = bdmpm	1931w 1835s 1810vs	−1582	−5.61 [f]
bdepm	1931w 1834s 1800vs	−1606	−6.14(td) [h]/47 and 14
bdepe	1930w 1835s 1798vs	−1581	−5.70 [f]
tdep	1928w 1835s 1800vs	−1606	
$n = 2$, p_m = tdep	1791s 1769s	−1393	

[a] See Scheme 1 for abbreviations. [b] In THF, except for $HV(CO)_4$dcype (Nujol). [c] In THF-d_8/THF 1/2, relative to $VOCl_3$. Coupling not resolved. [d] In THF-d_8/THF 1/2 at 298 K. t = triplet, td = triplet of doublets; the second entry for $J(^1H-^{31}P)$ is the (smaller) doublet coupling to the bridge-head P. [e] From ref. 5a. [f] Not resolved. [g] −5.58 (t) ppm at 220 K. [h] −6.27 ppm at 220 K (cf. Fig. 2).



$$\begin{tikzcd}[Et_4N][V(CO)_4p_m] + HOSi{-}\!\dashv \arrow[r] & HV(CO)_4p_m + [Et_4N][OSi{-}\!\dashv\ ] \arrow[d] \\ & HV(CO)_3p_m + CO\end{tikzcd} \qquad (2)$$

The patterns of IR bands are very similar to those observed for the corresponding complexes with phenylphosphines [5], and so are the $\delta(^{51}V)$ values. There is again the typical down-field (high-frequency) shift as the number of CO groups decreases, although the trend for the hydrido complexes with V^1 is less pronounced than for the anionic V^{-1} complexes, where π back-donation is more essential to maintain stability. The resonance signals are broadened (several hundred Hz) to the extent that coupling to ^1H and ^{31}P is no longer resolved. The broadening is a consequence of the presence of various isomers in solution, generated by varying the position of the hydride ligand (see below). Owing to the greater basicity of alkyl- than of phenyl-phosphines, the ^1H nucleus of the hydrido ligand is more shielded in the former by ca. 0.6 to 1.6 ppm, and shielding increases as the number of alkylphosphosphine groups attached to vanadium increases. The coupling pattern for $HV(CO)_3$bdepm (Fig. 2) and $HV(CO)_4$dcype are consistent with a model of restricted fluctionality developed previously [5,6], and represented for the special case of *fac*-$[HV(CO)_3$bdepm] in Fig. 2. According to this model, the H^- is in capping positions of a $M(CO)_n p_m$ octahedron, migrating between all those faces which are not edge-spanned by the back-bone of the phosphine. For the other hydrido complexes, only broad and unstructured resonances are observed.

Alkyl and silyl complexes

Among the few examples which had been characterized previously were $MeV(CO)_4$diars (diars = *o*-phenylenebis(dimethylarsine)) [2], $[\eta^5-C_5H_5V(Me)$-

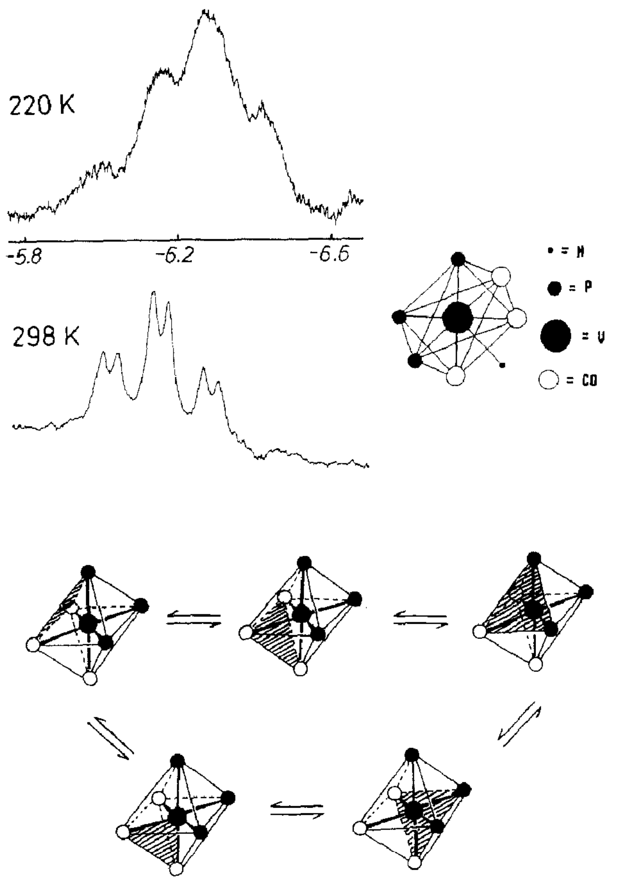
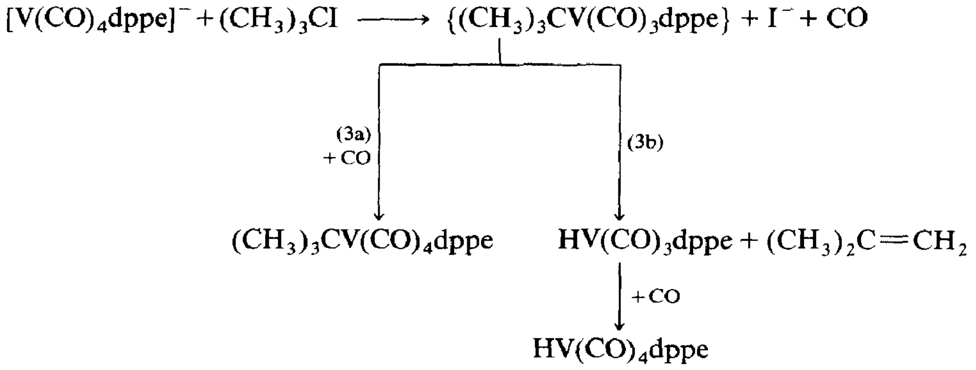


Fig. 2. 360 MHz variable temperature ^1H NMR spectra of HV $(CO)_3$bdepm (in THF-d_8) in the hydride region. The scheme indicates "allowed" (only dashed faces are available for H^-) positional isomers. Cf. refs. 5 and 6 for details.

$(CO)_3]^-$ [12], and the labile $H_3SiV(CO)_6$ [3]. We obtained complexes of composition $RV(CO)_4$dppe with R = Me, i-Pr, t-Bu and Me_3Si by treating $[Et_4N]$-$[V(CO)_4$dppe] with the appropriate alkyl or silyl iodides. In the case of t-BuI and Me_3SiI, considerable amounts of $HV(CO)_4$dppe (62 and 45%, respectively) were formed as by-products via β-elimination of isobutene (detected in the gas phase by IR) and $(Me_2SiCH_2)_2$ (detected by MS). The overall reaction between $[Et_4N]$ $[V(CO)_4$dppe] and t-BuI can be formulated as shown in eq. 3:



$$[V(CO)_4\text{dppe}]^- + (CH_3)_3CI \longrightarrow \{(CH_3)_3CV(CO)_3\text{dppe}\} + I^- + CO$$

$$\xrightarrow[+CO]{(3a)} (CH_3)_3CV(CO)_4\text{dppe}$$

$$\xrightarrow{(3b)} HV(CO)_3\text{dppe} + (CH_3)_2C{=}CH_2 \xrightarrow{+CO} HV(CO)_4\text{dppe}$$

Table 3

Spectroscopic data for alkyl- and silyl complexes, and $\delta(^{51}V)$ values for related complexes

Compound	$\delta(^{51}V)$ [a] (ppm)	Ref.	$\nu(CO)$ [b] (cm^{-1})
$HV(CO)_4dppe$	−1695	5	
$Ph_3PbV(CO)_5PPh_3$	−1665 [c]	4c	
$Ph_3SnV(CO)_5PPh_3$	−1651 [c]	4c	
$Me_3SiV(CO)_4ddpe$	−1235		1920s 1820vs
$Me_3CV(CO)_4dppe$	−1096		1920s 1845vs
$Me_2HCV(CO)_4dppe$	−1048 [d]		1933s 1850sh 1836vs
$MeV(CO)_4dppe$	−1032		1934s 1850sh 1834vs
η^5-(Fluorenyl)$V(CO)_4$	−1118	14	
η^3-$C_3H_5V(CO)_3dppe$	−1420 [c]	[e]	
η^7-$C_7H_7V(CO)_3$	−1485	14	
η^5-$C_5H_5V(CO)_4$	−1534	14	
$[\eta^6$-$(C_6H_5Me)V(CO)_4]^+$	−1660	14	
$[\eta^2$-$HC{\equiv}CBu)V(CO)_5]^-$	−1636 [f]	16	
$[\eta^2$-$H_2C{=}CHPr)V(CO)_5]^-$	−1788 [f]	16	

[a] In THF/THF-d_8 2/1, relative to $VOCl_3$ and at room temperature. Spectra were obtained at 94.7 MHz or [i-$PrV(CO)_4dppe$] 21.1 MHz. [b] In THF. [c] In a comparison of the δ values account should be taken of the fact that replacement of each CO by $RP(Ph)_2$ leads to a deshielding of ca. 100–200 ppm. [d] Triplet; $J(PV)$ 210 Hz. [e] Obtained by treating $[Et_4N][V(CO)_4dppe]$ with 3-bromopropene. For a systematic treatment of η^3-allylcarbonylvanadium complexes see ref. 15. [f] The values given in the table have been extrapolated to 300 K (cf. [16]).

As an explanation for the simultaneous formation of the alkyl and the hydrido complexes, and the resistance of the alkyl complexes towards further elimination, we suggest that an intermediate state is involved with the coordination number lower by 1, i.e. $RV(CO)_3dppe$ or $RV(CO)_4(\eta^1$-dppe), which either directly or after β-elimination regains its stable coordination geometry (eq. 3).

This reaction also casts light on the formation of $HV(CO)_4dppe$ from t-BuCl and $[V(CO)_4dppe]^-$ in hexane/water suspension [13]. Rather than by direct attack of H_3O^+, the hydrido complex may be formed through an elimination reaction, as represented in reaction path b in eq. 3, with water acting as a weak ligand to stabilize the intermediate state. If the reaction is carried out in D_2O, $D(VO)_4dppe$ is obtained, with a degree of deuteration of 75%.

The IR patterns for the new complexes in the CO stretching region (Table 3) are very similar to those of the corresponding hydrido compounds in that there are 2 resonances (a relatively sharp one of medium intensity at 1920–1935 cm^{-1}, and a rather broad one at ca. 1830 cm^{-1} with a poorly resolved high-frequency shoulder), but shifted to lower wave numbers by 40–70 cm^{-1}. On the basis of this similarity, we assume that the solution structure and fluctional behaviour are comparable to those of the corresponding hydrido complexes (vide supra).

As for the hydrido complexes, the ^{51}V resonances are usually too broad to be resolved, except in the case of i-$PrV(CO)_4dppe$, for the signal is a triplet with $^1J(^{31}P-^{51}V)$ 210(15) Hz, which is comparable to the pattern found for various other carbonylphosphinevanadium complexes [11] including those listed in Table 1. It is of interest to compare the shielding of the ^{51}V nucleus in the σ alkyl complexes with that in (i) other seven-coordinate complexes and (ii) other carbonylvanadium complexes containing vanadium–carbon bonds. The $\delta(^{51}V)$ values are listed in Table 3. In the seven-coordinate complexes $ZV(CO)_{6-m}p_m$ ($m = 1$ or 2) the shielding increases in the sequence $Z = \text{alkyl} < SiMe_3 < PbPh_3 \approx SnPh_3 < H$, following the sequence of increasing ligand polarizability. This is the normal dependence for metal shielding, which is generally observed in low-valent $[M(d^n)]$ complexes. Owing to the many factors influencing metal shielding in a group of complexes as heterogeneous as the set of organovanadium compounds listed in Table 3, direct comparison between the chemical shifts $\delta(^{51}V)$ cannot be made unambiguously. Nonetheless we can group together σ alkyl complexes with rather low shielding of the vanadium nucleus, half-sandwich complexes capable of π back-donation to some extent with medium shielding values, and η^2-alkene and -alkyne complexes with a comparatively high back-bonding potential and relatively large shielding.

Experimental

General

All procedures were carried out under nitrogen in oxygen-free, highly purified solvents. For the photochemical reactions a high pressure mercury lamp (Philips HPK 125) was used, equipped with a water-cooled quartz immersion well. The lamp was placed close to the reaction vessel which consisted of a Duran (borosilicate) Schlenk tube, fitted with a gas inlet to allow passage of a weak N_2 stream via a filter plate during the reaction to remove CO. Silica gel for chromatography (Kieselgel 60, Merck, 70–230 mesh ASTM) was activated under high vacuum for 2 h and treated with N_2; column dimensions 6 × 10 cm.

VCl_3, $PEtCl_2$, $P(Bu)_3$, dppe, dcype, $SPCl_3$, Me_3SiI, and alkyl iodides were obtained from commercial sources, $PMeCl_2$ and bdmpm were kindly supplied by Prof. L. Dahlenburg, University of Hamburg. The following compounds were prepared by published procedures: $[Et_4N][V(CO)_6]$ [17], $[Et_4N][V(CO)_4dppe]$ [18], $PMe(allyl)_2$ and $PEt(allyl)_2$ [19], $P(allyl)_3$ [19,20], $Et_2P(S)P(S)Et_2$ [21], $PHEt_2$, bdmpe and tdep [19]. Bis(3-diethylphosphinopropyl)ethylphosphine, $EtP(CH_2CH_2CH_2PEt_2)_2$ (bdepe), which has not previously been reported was prepared by a procedure analogous to that used for bdepm [19]. Thus a mixture of 5.8 g (64 mmol) $PHEt_2$, 4.1 g (29 mmol) $PEt(allyl)_2$ and 0.1 g azo-2,2′-bis(isobutyronitrile) (AIBN) was irradiated for 48 h at room temperature and the product isolated by distillation under high vacuum (50 ° C). $\delta(^{31}P)$ −27.5 (central P) and −22.7 ppm (terminal Ps).

IR spectra for all but the dcype complexes were recorded with THF solutions in 0.1 mm KBr cuvettes; for $[Et_4N][V(CO)_4dcype]$ and $HV(CO)_4dcype$ KBr or Nujol mulls were used. ^1H NMR: AM 360 spectrometer (Bruker) in THF-d_8. $^{31}P\{^1H\}$ NMR: 80 MHz, WP 60 spectrometer (Bruker), 10 mm vials, $CDCl_3$. $^{51}V\{^1H\}$ NMR: 94.73 MHz (Bruker AM 360), 10 mm vials. THF-d_8/THF 1/2, CD_3CN or mixtures of THF and CD_3CN (solution shifts are within the experimental uncertainty of ca. ±1 ppm), 298(1) K; standard: $VOCl_3$. Typical measuring parameters: sweep width 125 kHz, time domain 8.2 K, pulse width 10 μs, no relaxation delay, 20,000 scans.

cis-$[Et_4N][V(CO)_4MeP(CH_2CH_2CH_2PMe_2)_2]$. A solution of 0.35 g (1 mmol) $[Et_4N][V(CO)_6]$ and 0.25 g (1 mmol) bdmpm in 20 ml of THF was irradiated for 3 h with a weak N_2 stream through the solution. The colour changed from yellow to orange-red. The progress of the reaction was monitored by IR spectroscopy, and the irradiation time was optimized to provide for maximum generation of the tetracarbonylvanadate. The solution was rigorously stirred with 20 ml of n-hexane to yield a red oil. This was washed with three 5 ml portions of hexane and dried under high vacuum for 2 h. Yield: 0.53 g (0.84 mmol), 84%, of a viscous red oil, containing small amounts of pentacarbonyl- and tricarbonyl-vanadate (by ^{51}V NMR).

The carbonylvanadates containing bdepm, bdepe, tdep, dcype and $PMe(allyl)_2$ were prepared similarly. Red oils in yields of 68–80% were isolated in the case of complexes containing bdepm, bdepe and tdep. Pure orange coloured microcrystals of *cis*-$[Et_4N][V(CO)_4MeP(CH_2CH_2CH_2PEt_2)_2]$ were obtained when a solution of the red "crude" oil in 5 ml of THF + 3 ml of hexane/toluene 1/1 was kept for several weeks at 245 K. In the case of *cis*-$[Et_4N][V(CO)_4Cy_2PCH_2CH_2PCy_2]$ the irradiation time was 5 h, and yellow-orange needles were isolated (yield: 88%). $[Et_4N][V(CO)_5PMe(allyl)_2]$, obtained from the reaction between 1.75 g (5 mmol) $[Et_4N][V(CO)_6]$ and 0.64 g (5 mmol) $PMe(allyl)_2$, was separated from unchanged hexacarbonylvanadate by fractional precipitation with hexane ($[Et_4N][V(CO)_6]$ is less soluble in THF/hexane). Yield: 1.36 g (3.2 mmol) 64%, of a yellow, microcrystalline powder.

$HV(CO)_3MeP(CH_2CH_2CH_2PMe_2)_2$. A solution of 330 mg (0.60 mmol) of $[Et_4N][V(CO)_4bdmpm]$ in 10 ml of THF was placed on a column of silica gel. Elution with 150 ml of THF during 20 min yielded a yellow-orange solution containing the hydrido complexes $HV(CO)_n$bdmpm ($n = 3$ (main product) and 4). During work-up of the mixture, the tetracarbonyl complex was almost quantitatively converted into the tricarbonyl complex. The solution was evaporated to dryness and the residual red oil dissolved in 15 ml of n-hexane. The solution was kept at 195 K, and $HV(CO)_3$bdmpm crystallized out within ca. 1 h. The supernatant liquid was decanted and the product stored at dry-ice temperature. Melting point: ca. 240 K. Yield: 210 mg (0.54 mmol), 89%.

The complexes $HV(CO)_3$bdepm (red), $HV(CO)_3$bdepe/$HV(CO)_4$bdepe (yellow-brown) and $HV(CO)_3$tdep (red) were prepared similarly in yields of 80–92%.

cis-$[HV(CO)_4Cy_2PCH_2CH_2PCy_2]$. A solution of 500 mg (0.70 mmol) of $[Et_4N][V(CO)_4dcype]$ in 10 ml of THF was chromatographed on silica gel. The deeply yellow eluant was concentrated to 20 ml. Treatment with 20 ml of hexane yielded yellow micro-crystalline $HV(CO)_4$dcype, which was washed twice with 5 ml portions of hexane and dried in high vacuum for 4 h. Yield: 320 mg (0.57 mmol) 82%.

cis-$[HV(CO)_2P(CH_2CH_2CH_2PEt_2)_3]$. A solution of 140 mg (0.25 mmol) of $HV(CO)_3$tdep was dissolved in 10 ml of THF and irradiated for 6 h. CO was removed by passing N_2 through the solution. The originally yellow-orange solution turned red and finally red-brown. Small amounts of brownish decomposition products were filtered off and the filtrate evaporated to dryness. The red-brown oil thus obtained was dissolved in 5 ml of n-hexane and the solution was kept at 195 K to allow precipitation as a powder of the red $HV(CO)_2$tdpe, which turned back to an oil above 240 K. Yield: 50 mg (0.09 mmol) 38%.

cis-$[DV(CO)_4Ph_2PCH_2CH_2PPh_2]$. This compound was prepared in the way described for $HV(CO)_4$dppe [13] from 2.75 g (3.9 mmol) of $[Et_4N][V(CO)_4dppe]$ suspended in a mixture of t-BuCl, D_2O (99.8%) and hexane. Yield: 1.7 g (3.0 mmol) 77%. Degree of deuteration (by ^1H NMR), 75%.

cis-$[(CH_3)_2HCV(CO)_4Ph_2PCH_2CH_2PPh_2]$. A solution of 2.59 g (3.7 mmol) of

$[Et_4N][V(CO)_4dppe]$ in 80 ml of THF was cooled to dry-ice temperature and treated with 0.50 ml (0.85 g, 5.0 mmol) of i-PrI. The mixture was allowed to warm to room temperature during 6 h. The brown suspension was filtered to remove $[Et_4N]I$ and the violet filtrate evaporated to dryness. The residue was dissolved in 5 ml of CH_2Cl_2 and transferred to a small column (2.5 × 3 cm) of silica gel. Elution with CH_2Cl_2/hexane 3.5/1 gave a violet solution, which was evaporated to dryness to yield 1.1 g (2.3 mmol, 64%) of i-PrV$(CO)_4$dppe as a violet-brown air-sensitive powder. Analysis: Found C, 65.2; H, 5.4; P, 10.5; V, 8.2. $C_{33}H_{31}O_4P_2V$ (604.50) calcd.: C, 65.57; H, 5.17; P, 10.25; V, 8.43%.

MeV(CO_4)dppe was prepared analogously in a yield of 64%. Reaction between $[Et_4N][V(CO)_4dppe]$ and t-BuI or $(Me_3)_3Si$ under the same conditions described above gave a mixture of the alkyl or silyl complex with the hydrido complex.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (grant Re 431/6-3).

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