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Deuterium Isotope Effects and Bonding in Carbonylvanadium Complexes

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The effects of one-bond and two-bond ^{2}H, ^{13}CO and $C^{18}O$ isotope shifts on ^{51}V shielding in various carbonyl–Cp–vanadium complexes (Cp = η^{5}-cyclopentadienyl) are reported and discussed with respect to the sensitivity of ^{51}V shifts to bond extensions, and the rovibrationally averaged values of such bond extensions. These isotope effects provide some insight into the bonding situation in these complexes. It is shown that the rate-determining step in the reaction between $V(CO)_6$ and C_5H_5D, which leads to $CpV(CO)_4$, is *not* subject to a kinetic isotope effect. The deuterium solvent isotope effects on ^{51}V shielding in $[V(CO)_6]^-$ and $[VO_4]^{3-}$ are also investigated.

KEY WORDS ^{2}H, ^{13}CO, $C^{18}O$ isotope shifts ^{51}V shielding Carbonylvanadium complexes

INTRODUCTION

The effect of isotopic substitution in the ligands and the solvation sphere of a coordination compound on the shielding of the metal centre is of interest in the context of the intrinsic shielding sensitivity of a metal nucleus towards even minor changes in its environment. The observed effects of isotopic substitution have been successfully described by and are related to the sensitivity of metal shielding to changes in the bond distances in the complex.[1,2]

In the vanadium system, isotope effects induced by ligand nuclei replacements (usually referred to as intrinsic isotope effects) have been described for the ^{13}CO and $C^{18}O$ exchange in $[V(CO)_6]^-$, $CpV(CO)_4$ (Cp = η^{5}-C_5H_5) and $Cp^*V(CO)_4$ (Cp^* = η^{5}-C_5Me_5),[1,3] $[V(^{13}CO)_5]^{3-}$ and $[HV(^{13}CO)_5]^{2-}$,[4] and further for the $^{1}H/^{2}H$ effect in $[CpV(CO)_3H]^-$,[3] and the $^{18/17}O$ effect in $[VO_4]^{3-}$.[5,6] In this paper we report on intrinsic isotope effects exerted on ^{1}H and ^{51}V shielding in $CpV(CO)_4$ and related compounds as H is substituted by D in the ligand system, providing some insight into the bonding situation in the CpV moiety. We also address the reactivity of cyclopentadienes towards $V(CO)_6$ in the light of a possible kinetic isotope effect, and finally we consider solvent isotope effects on ^{51}V shielding in $[V(CO)_6]^-$ and $[VO_4]^{3-}$.

RESULTS AND DISCUSSION

Intrinsic isotope effect

The one-bond deuterium isotope effect on ^{51}V shielding, $^{1}\Delta^{51}V(^{2/1}H)$, measured previously in $[CpV(CO)_3H]^-$, amounts to -4.7 ppm,[1,3] which compares with $^{1}\Delta^{51}V(^{13/12}CO) = -0.46$ ppm in $CpV(CO)_4$ [1,3] and -0.51 ppm in $[CpV(CO)_3H]^-$. We have now also obtained the two-bond isotope shift, $^{2}\Delta^{51}V(^{2/1}H) = -0.715(7)$ per ^{2}H, for a mixture of isotopomers of η^{5}-$\{C_5(^{1}H)_{5-n}(^{2}H)_n\}V(CO)_4$, prepared from perdeuteriated cyclopentadiene and $V(CO)_6$ in hexane (Fig. 1). The isotope shifts are strictly additive, and no differentiation for positional isomerism in the d_2 and d_3 species is observed. Within the limits of error, the $^{2}\Delta^{51}V(^{2/1}H)$ values for several related compounds (Table 1) are the same.

Nuclear shielding is a highly localized property, weighted for the most part by $1/r^3$ of the electronic distribution about the nucleus in question. Hence the bonds directed to the observed nucleus determine the shielding to a large extent. It has been shown that one-bond isotope shifts depend on the sensitivity of the nuclear shielding to extension of the bond between the observed nucleus and the substituted atom.[7] On the other hand, isotope shifts over two or more bonds serve as indices of the extent to which the nuclear shielding is sensitive to specific remote parts of the molecule connecting the observed nucleus to the point of isotopic substitution via some electronic transmission path.[8] In particular, the magnitude of the isotope shift of a metal nucleus over two or more bonds in a complex should shed some insight into the extent of communication through this electronic pathway, and thereby provide some information about the nature of the metal ligand bonding. This is based on the following. The linear terms contributing to the two-bond isotope shift are, expressed for ammine complexes,

$$^{2}\Delta M(^{2/1}H) \approx (\partial\sigma^{M}/\partial r_{MN})_e[\langle\Delta r_{MN}\rangle_H - \langle\Delta r_{MN}\rangle_D] + (\partial\sigma^{M}/\partial r_{NH})_e[\langle\Delta r_{NH}\rangle - \langle\Delta r_{ND}\rangle]$$

The generally large magnitudes of $^{2}\Delta$ values observed on ^{2}H substitution in transition metal ammine complexes have been found to be characteristic of the

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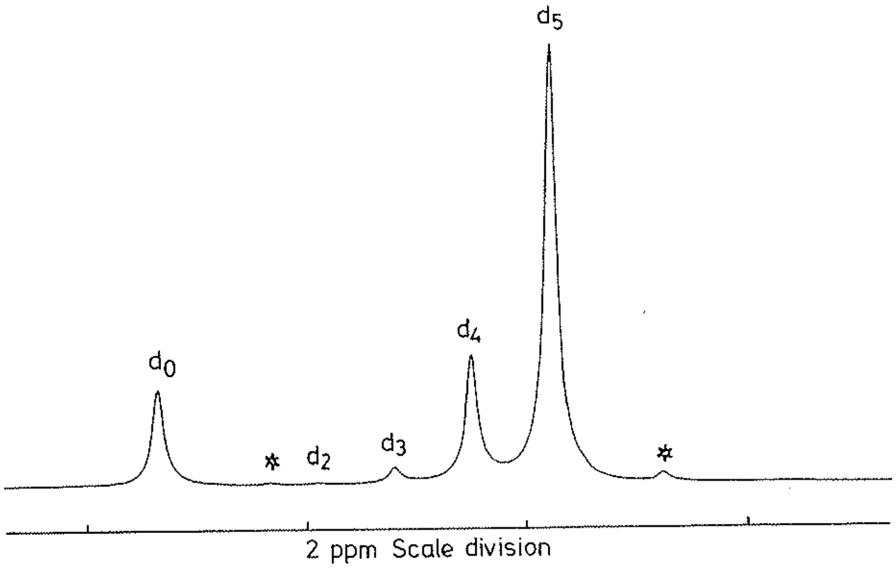


Figure 1. 94.73 MHz ^{51}V NMR spectrum of $C_5H_{5-n}D_nV(CO)_4$ (degree of deuteriation 94%) + 10% of $C_5H_5V(CO)_4$. The distribution of the isotopomers (%, by MS [NMR]) is as follows: d_0 (13.8 [13.9]), d_3 (3.4 [2.5]), d_4 (18.5 [18.8]), d_5 (64.2 [64.8]). The d_1 isotopomer is not observed. The peaks marked with asterisks are the high-field components of the natural abundance ^{13}C satellite doublets; $^1J(^{51}V,^{13}C)$ = 108 Hz.

observed large differences between the rovibrationally averaged N—H and N—D bond extensions, $[\langle\Delta r_{NH}\rangle - \langle\Delta r_{ND}\rangle]$, rather than of the much smaller difference between the MN average bond extensions in the protonated versus the deuteriated isotopomers. This is an indication that the metal shielding sensitivity to the remote N—H bond extension $(\delta\sigma^M/\partial r_{NH})_e$ dominates this isotope shift. This is indeed fortunate, since (1) a measure of $(\partial\sigma^M/\partial r_{MN})_e$ is already available in $^{15/14}$N-induced shifts of M metal shielding, and (2) the difference $[\langle\Delta r_{NH}\rangle - \langle\Delta r_{ND}\rangle]$ is a relatively localized average and is much easier to estimate than the very small, molecule specific difference in $\langle\Delta r_{MN}\rangle$ in the deuteriated versus protonated isotopomers. This means that $^2\Delta M(^{2/1}H)$, being a relatively direct measure of $(\partial\sigma^M/\partial r_{NH})_e$, can provide some information about the M—N—H electronic transmission path.

The deuterium-induced $^2\Delta^{51}V$ in the ammine complex $CpV(CO)_3N(^2H)_2Bu$ (−0.85 ppm per D) is considerably smaller than, for example, $^2\Delta^{59}Co$ in $[Co(N(^2H)_3)_6]^{3+}$ (−5.2 ppm per D).[9] This factor of 6 cannot entirely be accounted for in terms of the different shielding sensitivities of the two nuclei (^{51}V and ^{59}Co) to bond extensions of the X—Y bond in M(XY). $\partial\sigma^M/\partial\Delta r_{XY} = -2000$ ppm Å^{-1} ($[Co(CN)_6]^{3-}$) and −800 ppm Å^{-1} ($[V(CO)_6]^-$),[1] for example, are related by a factor of 2.5. Rather, the less pronounced increase of metal shielding on deuterium substitution in

Table 1. Intrinsic isotope shifts

Complex[a]	Isotope effect[b] (ppm)	
$[C_5H_5V(CO)_3(H/D)]^-$	$^1\Delta V(D)$	−0.46
$[C_5H_4DV(CO)_3H]^-$	$^2\Delta V(D)$	−0.80 (9)[c]
$C_5H_{5-n}D_nV(CO)_4$ [d]	$^2\Delta V(D)$	−0.715 (7)
η^5-{Indenyl-d_1}$V(CO)_4$	$^2\Delta V(D)$	−0.83 (5)
$C_5H_5V(CO)_3NH_{2-n}D_nBu$	$^2\Delta V(D)$	−0.85 (20)[c]
$C_5H_{5-n}D_nV(CO)_4$ [e]	$1.87(^3\Delta H + ^4\Delta H)$	-3.2×10^{-3}
$[C_5H_5V(CO)_{3-n}(^{13}CO)_nH]^-$ [f]	$^1\Delta V(^{13}CO)$	−0.51 (6)
$C_5H_5V(CO)_{4-n}(^{13}CO)_n$ [f]	$^1\Delta V(^{13}CO)$	−0.46 (2)[g]
$C_5H_5V(CO)_{4-n}(C^{18}O)_n$ [f]	$^2\Delta V(C^{18}O)$	−0.13[h]
$C_6H_4MeV(CO)_3(^{13}CO)$	$^1\Delta V(^{13}CO)$	−0.5 (5)
$C_5Me_5V(CO)_{4-n}(^{13}CO)_n$ [f]	$^1\Delta V(^{13}CO)$	−0.42 (4)[g]
{$C_5H_4C(O)Me$}$V(CO)_{4-n}(^{13}CO)_n$	$^1\Delta V(^{13}CO)$	−0.46 (5)

[a] For $\delta(^{51}V)$ values see Ref. 22.
[b] Per isotopic substitution; negative values are high-field (low-frequency) shifts.
[c] Obtained from a fit of the resonance line.
[d] Fig. 1.
[e] n = 3 (27%) and 4 (73%). $^1J(^1H^{13}C)$ = 174 Hz, which is approximately the same coupling as in other aromatics π-bonded to a metal.
[f] Fig. 2.
[g] From Ref. 1.
[h] Lower limit.

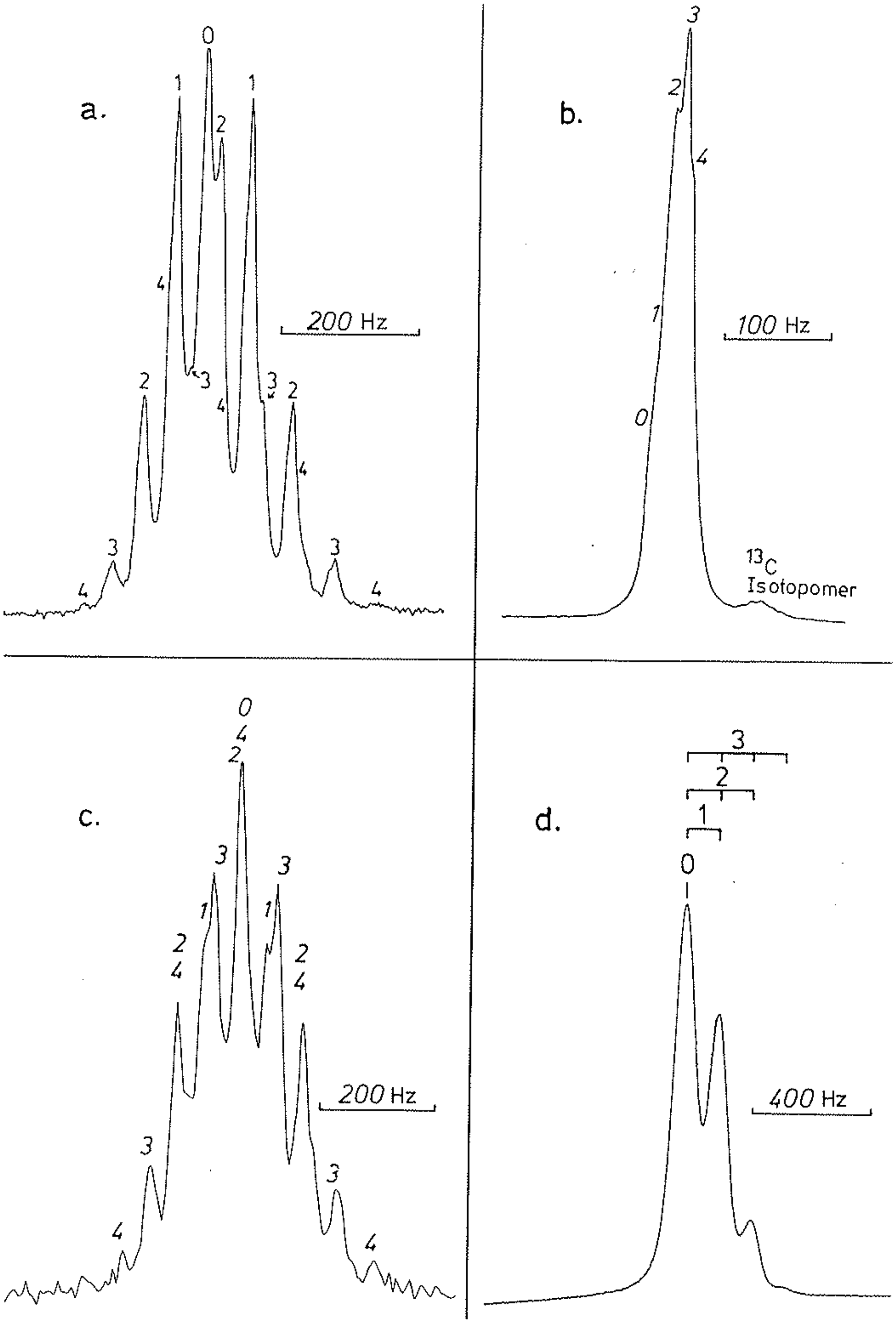


Figure 2. ^{51}V NMR spectra of (a) $C_5H_5V(CO)_{4-n}(^{13}CO)_n$, (b) $C_5H_5V(CO)_{4-n}(C^{18}O)_n$, (c) $C_5Me_5V(CO)_{4-n}(^{13}CO)_n$ and (d) $[(Ph_3P)_2N][C_5H_5V(CO)_{3-n}(^{13}CO)_nH]$ showing the distribution of isotopomers. The numerals indicate the number of (CO)* ligands present in the complex. Spectra taken at 23.7 MHz (a and c) and at 97.7 MHz (b and d).

$CpV(CO)_3NH_2Bu$ in comparison with $[Co(NH_3)_6]^{3+}$ reflects a considerably reduced metal ammine interaction in the low-valent vanadium compound. The $CpV(CO)_3NH_{3-n}R_n$ complexes are in fact rather labile as a consequence of the weak vanadium—ammine bond.[10]

In the M—N—H or the M—C—O transmission path, the sensitivity of the metal shielding to the NH or CO bond extension is understandable in terms of the significant accompanying changes in electronic distribution in the MN or MC bonds (and thus also in the M shielding), since the NH or CO bond stretch substantially affects the availability of the :N or :C donor pair to the metal orbitals.

Let us now consider the ^{51}V isotope shift on going from $C_5H_5V(CO)_4$ to $C_5D_5V(CO)_4$. In the spirit of the sigma–pi separability approximation in the Cp moiety, the CH stretch should affect the pi system only slightly. It is interesting, therefore, to observe the ^{2}H-induced ^{51}V shifts of *ca.* −0.75 ppm per ^{2}H (see Table 1). We can compare these $^2\Delta^{51}V(^{2/1}H)$ deuterium isotope effects with the two-bond isotope effects $^2\Delta^{51}V(C^{18/16}O) = -0.13$ ppm in $CpV(CO)_{4-n}(C^{18}O)_n$ (Fig. 2(b)) and $^2\Delta^{51}V(C^{18/16}O) = -0.101$ ppm in $[V(CO)_{6-n}(C^{18}O)_n]^{-1}$. Rovibrational calculations on $[M(CO)_{6-n}(C^{18}O)_n]^-$ (M = V, Nb) and $[Co(CN)_{6-n}(C^{15}N)_n]^{3-}$ have shown that $^2\Delta$ depends on the metal shielding sensitivity to r_{XY}, contributions from $\langle \Delta r_{MX} \rangle$ being much smaller.$^{1-3}$ Hence, for $^2\Delta$ induced per deuterium,

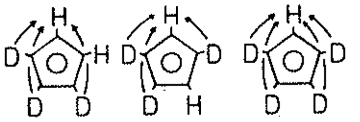
$$^2\Delta^{51}V(^{2/1}H) = \sigma^V(H) - \sigma^V(D)$$
$$\approx (\partial\sigma^V/\partial\Delta r_{CH})_e[\langle \Delta r_{CH} \rangle - \langle \Delta r_{CD} \rangle]$$

With the quantity in square brackets $\approx 5 \times 10^{-3}$ Å adapted from Ref. 8, and an experimental $^2\Delta^{51}V(^{2/1}H) = -0.715$ ppm, we arrive at $(\partial\sigma/\partial\Delta r_{CH})_e \approx -150$ ppm Å^{-1} for the derivative at the equilibrium geometry. This is indeed significantly less than $(\partial\sigma/\partial\Delta r_{CO})_e = -800$ ppm Å^{-1} for $[V(CO)_{6-n}(C^{18}O)_n]^-$ or the value of −1100 ppm Å^{-1} which is obtained for $CpV(CO)_4$ based on $\langle \Delta r_{CO} \rangle$ for the hexacarbonylvanadate. This seems to indicate a less intimate involvement of orbitals associated with CH in bonding to vanadium than is the case with the CO orbitals (where oxygen takes part in back-donation). Nevertheless, it is significantly greater than what would be expected from the zeroth-order picture of no sigma–pi polarization in the Cp moiety and negligible direct overlap between the hydrogen and metal orbitals.

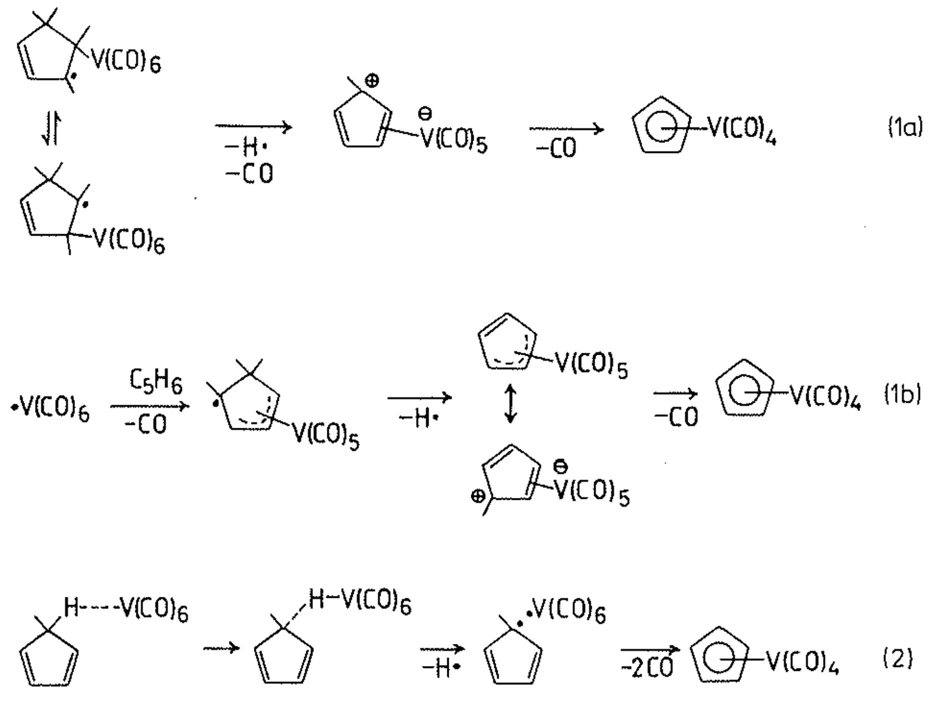
We have also determined the deuterium-induced proton shifts, $^n\Delta^1H(^{2/1}H)$, in the Cp ring for a partially deuterated sample consisting of 73% of $C_5H_4DV(CO)_4$ and 23% of $C_5H_2D_3V(CO)_4$ [by mass spectrometry (MS)], which shows a high-field shift of the ^{1}H resonance relative to $C_5H_5V(CO)_4$ of −3.2 ppb, compared with, for example, −1.6 ppb found for benzene.^{11} The proton shift reflects the concomitant effect of $^3\Delta$ and $^4\Delta$ in the tri and tetra-deuteriated complexes, viz. (cf. Scheme 1) $2^3\Delta(d_4) + 2^4\Delta(d_4) + {}^3\Delta(1,2,3\text{-}d_3) + 2^4\Delta(1,2,3\text{-}d_3) + 2^3\Delta(1,2,4\text{-}d_3) + {}^4\Delta(1,2,4\text{-}d_3) = 1.87(^3\Delta + {}^4\Delta) = -3.2$ ppb. Contributions from equilibrium isotope effects can be excluded on the grounds of the low concentration (*ca.* 0.02 M) of our sample.

Is there a kinetic isotope effect in the reaction between cyclopentadienes and hexacarbonylvanadium?

The first reaction step in the formation of η^5-$CpV(CO)_4$ from $V(CO)_6$ and C_5H_6 may be a direct attack of the radical $V(CO)_6$ [or $V(CO)_5$, since $V(CO)_6$ easily loses CO in solution] on the carbon atoms of the ring, forming a radical intermediate with a vanadium–carbon σ bond or, if $V(CO)_5$ is the reactant, an allylic bond [Eqns (1a) and (1b) in Scheme 2], followed by hydrogen abstraction and stabilization to the half-sandwich complex. Alternatively, the initiating step can be abstraction of an allyl hydrogen by $V(CO)_6$. In this case, an intermediate hydrido complex (unstable in nonpolar solvents) and, successively, the σ complex η^1-$CpV(CO)_6$ arise [Eqn (2) in Scheme 2]. A mechanism



Scheme 1



Scheme 2

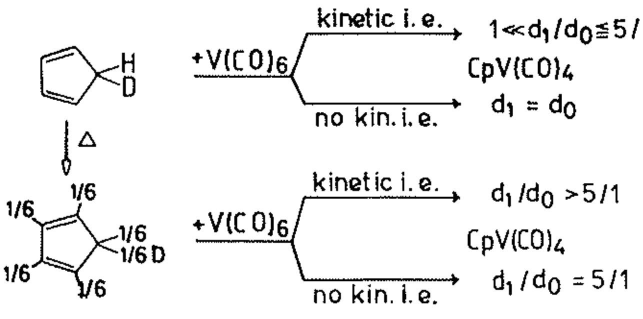
comparable to the latter has been proposed for the formation of alkenyl-substituted half-sandwich complexes obtained from the reaction between $V(CO)_6$ and 6-alkylfulvenes.[12] Justification for the intermediates depicted in Eqns (1) and (2) comes from the existence of neutral, heptacoordinated hydrido,[13] σ-alkyl-[14,15] and η^3-allylcarbonylvanadium complexes[16] stabilized by phosphines, and carbonylvanadates of the composition $[V(CO)_5(\text{alkene/alkyne})]^-$ with π-bonded organic ligands.[17]

If the rupture of one of the allylic C—H bonds in CpH is the rate-determining step, there should be a kinetic isotope effect for the reaction between C_5H_5D (with the deuterium on the methylene carbon) and $V(CO)_6$ in that the formation of $C_5H_4DV(CO)_4$ should clearly be favoured with respect to the formation of $C_5H_5V(CO)_4$ (Scheme 3). The expected ratio $CpV(CO)_4\text{-}d_1/CpV(CO)_4\text{-}d_0$ is 5:1, provided that there is no isomerization in C_5H_5D due to a 1,2-H/D shift. Isomerization of C_5H_5D, although a slow process, actually has to be considered with the reaction conditions that have to be maintained. Most of the $CpV(CO)_4$ is, however, formed before the isomerization process is terminated. On the basis of a mass spectrometric analysis of the $CpV(CO)_4$ obtained from this reaction, $d_1/d_0 \approx 1:1$; hence there is no kinetic isotope effect, and Eqn (2) does not represent the rate-determining step. An equivalent result was obtained for the formation of η^5-indenyl-$V(CO)_4$ from 1-D-indene and $V(CO)_6$.

In a further experiment we employed deuteriated cyclopentadiene containing *ca.* 60% of fully isomerized C_5H_5D. Here, the ratio d_1/d_0 should be >5:1 (Scheme 3) if there were a kinetic isotope effect, which was not the case. In all three samples investigated there were also small amounts of di- and, in the case of Cp complexes, tri-deuteriated species present in the reaction mixture, probably as a consequence of intermolecular H/D exchange accompanying intramolecular isomerization.

Solvent isotope effect

Direct comparisons of metal shielding in H_2O solution and metal shielding in D_2O solution have been reported for various metal ions.[18] These differences are largely (though not solely) intrinsic isotope effects, since the metal–aqua complexes being compared are $[M(H_2O)_x]^{n+}$ and $[M(D_2O)_x]^{n+}$. The solvent isotope effects have not been easily separable in these cases. Here we consider systems in which the solvent isotope effects are directly observable. Although the effect is small, its treatment is of some practical importance in the context of the reproducibility of metal NMR data collected in deuteriated solvents. We measured solvent isotope shift ($^s\Delta$) values in the $[M][V(CO)_6]$ and $[VO_4]^{3-}$ systems which, owing to the cubic symmetry at the vanadium centre, provide well resolved spectra. The counter ion to hexacarbonylvanadate is usually $[Et_4N]^+$. In two solvents (water and toluene), however, Na^+ and $[MeN(n\text{-decyl})_3]^+$ had to be employed in order to provide appropriate solubilities. The counter-ion effect on $\delta(^{51}V)$ is of the same order of magnitude of $^s\Delta$ and was eliminated by the sample arrangement explained in detail under Experimental. $^s\Delta^{51}V$ values are summarized in Table 2.



Scheme 3

The smallest $^s\Delta$ for $[V(CO)_6]^-$ is observed with the nonpolar toluene (−0.01 ppm per D), and the largest with water (−0.60 ppm per D). Large effects are induced by D_2O and CH_3OD (but not, to this extent, by CD_3OH). The differential hydrogen-bonding characteristics of OH versus OD in hydrogen bonding to the $[V(CO)_6]^-$ anion, as well as hydrogen-bonding to other OD, are undoubtedly responsible for this. We have also measured the solvent isotope effect for orthovanadate, $[VO_4]^{3-}$, in which the vanadium centre should be affected by solvation to a greater extent because of the smaller size and larger charge compared with $[V(CO)_6]^-$.

In comparing the $^s\Delta$ values of the two anions we must also take into account the different sensitivities of the vanadium nucleus in different oxidation states, which in these two complexes are V(V) and V(−I). From $^1\Delta^{51}V(^{13/12}CO)$ in $[V(CO)_6]^- = -0.26$ ppm[1] and $^1\Delta^{51}V(^{18/16}O)$ in $[VO_4]^{3-} = -0.19$ ppm[6] we arrive, also taking into consideration the relative mass changes for $^{13}C/^{12}C$ (7.7%) and $^{18}O/^{16}O$ (11%), at a sensitivity of the ^{51}V nucleus of about 1/2 in oxo- as compared with carbonyl-vanadate. This is, of course, only a rough estimate since the bonding situations in the two complex anions are different. Thus, under exactly identical solvation arrangements, $[V(CO)_6]^-$

Table 2. Solvent isotope effects of $\delta(^{51}V)$ induced by deuteriated solvents[a]

Complex/solvent	Counter ion	$\Sigma^s\Delta(D)$ (Hz)	(ppm)	$^s\Delta(D)^b$ (ppm)
$[VO_4]^{3-}/D_2O^c$	Na aq	−34	−1.45	−0.73
$[V(CO)_6]^-/D_2O$	Na aq	−28	−1.20	−0.60
CD_3OD	Et_4N	−13	−0.55	
CH_3OD	Et_4N	−5	−0.21	−0.21
CD_3OH	Et_4N	−7	−0.30	−0.10
THF-d_8	Et_4N	−16	−0.68	−0.09
Pyridine-d_5	Et_4N	−9	−0.38	−0.08
DMSO-d_6	Et_4N	−11	−0.46	−0.08
Acetone-d_6	Et_4N	−8	−0.34	−0.06
CD_3CN	Et_4N	−2	−0.08	−0.03
Toluene-d_8	$(decyl)_3MeN$	−2	−0.08	−0.01

[a] Ca 0.1 M. No concentration dependence of $\delta(^{51}V)$ was observed in acetone in the concentration range 0.02–0.2 M.
[b] Solvent isotope shift per D.
[c] Adjusted to pH/D14 by addition of NaOH/D.

and $[VO_4]^{3-}$ anions should have ^{51}V solvent isotope shifts of roughly 2:1. A ratio of 0.60 ppm:0.73 ppm is actually observed. Thus the solvation effects on $[VO_4]^{3-}$ are a factor of roughly 2.5 times greater, which is not surprising with three times the charge. This interpretation is consistent with the D_2O solvent isotope shifts of ^{51}V, ^{53}Cr and ^{55}Mn shielding in the isosteric anions $[VO_4]^{3-}$ ($^{s}\Delta^{51}V = -0.73$ ppm; Table 2), $[CrO_4]^{2-}$ ($^{s}\Delta^{53}Cr = -0.65$ ppm[19]) and $[MnO_4]^-$ ($^{s}\Delta^{55}Mn = -0.38$ ppm[20]). Despite the very similar intrinsic shielding sensitivities of the three nuclei[21] the $^{s}\Delta(D)$ values decrease, as one would expect from the decreasing solvation tendency as the charge of the anion decreases.

EXPERIMENTAL

All operations were conducted under argon and in highly purified solvents.

NMR measurements

^{51}V and ^{1}H NMR spectra were obtained on a Bruker AM360 PFT spectrometer. ^{51}V NMR spectra (at 94.7 MHz) were recorded for 0.02–0.1 M solutions contained in spinning 10 mm diameter tubes at a constant temperature of 298 K [the temperature coefficient of $\delta(^{51}V)$ in carbonylvanadium compounds amounts to -0.25 to -0.5 ppm K^{-1}].[1] Sweep widths between 5000 and 50 000 Hz were used, depending on the degree of resolution required (spectral resolutions were typically between 1 and 5 Hz per point). A pulse angle of 30–45° was employed and the spectra were recorded without relaxation delay.

For the determination of solvent isotope shifts the spectra were scanned at a sweep width of 3000 Hz and, to reduce chemical shift anisotropy broadening, at 23.7 MHz (Bruker WH90). Digital resolution was 0.4 Hz per point. The number of scans was restricted to *ca.* 100 to avoid line broadening due to temperature variations over a longer period of time. A 7.5 mm diameter tube containing the sample in deuteriated solvent was fitted co-axially into a 10 mm tube containing the same sample in non-deuteriated solvent; this arrangement allowed for a direct determination of the shift differences after correction for bulk susceptibility influences [δ(exterior) – δ(interior) $\approx$ 1 Hz].

Preparation of complexes

Neutral compounds. The half-sandwich complexes $Cp'V(CO)_4$ [$Cp' = C_5H_4Me$, C_5Me_5, $C_5H_4C(O)Me$] were prepared from $V(CO)_6$ and Cp′H as described previously.[22] The photo-induced replacement of CO by (CO)* (^{13}CO or $C^{18}O$) has been described elsewhere.[1,3] The (CO)* contents of the samples investigated here were as follows (by ^{51}V NMR and/or MS): $C_5H_5V(CO)_{4-n}(^{13}CO)_n$ (41%, Fig. 2(a)); $C_5H_5V(CO)_{4-n}(C^{18}O)_n$ (46%, Fig. 2(b)); $C_5Me_5V(CO)_{4-n}(^{13}CO)_n$ (43%, Fig. 2(c)); $C_5H_4C(O)MeV(CO)_{4-n}(^{13}CO)_n$, $n = 0$–3 (15%); $C_5H_4MeV(CO)_3(^{13}CO)$ (natural). For the MS analyses, the natural ^{13}C contents were taken into consideration.

$CpV(CO)_3NH_{2-n}D_nBu^n$: 3 ml of *n*-butylamine were stirred in 2 ml of D_2O for 24 h, treated with 10 g of 4A molecular sieved and distilled at room temperature. This procedure was repeated twice to yield the amine enriched in ^2H by 40%. A 100 mg amount of $CpV(CO)_4$ (0.44 mmol) was then dissolved in 20 ml of THF, cooled to 195 K (dry-ice) and irradiated[10] to produce a green solution of $CpV(CO)_3THF$. This was treated with 1 ml of the partially deuteriated butylamine, warmed to 273 K and irradiated for 5 min to complete replacement of THF by the amine. The solution is stable for *ca.* 2 days when kept at 210 K, and decomposes within a few hours at room temperature.

Anionic compounds. The hexacarbonylvanadates $[M][V(CO)_6]$ {[M] = Et_4N, $(n\text{-decyl})_3MeN$} were prepared by precipitation with [M]Br from $MeOH–H_2O$ solutions of $Na[V(CO)_6]$. In the case of the decyl salt, excess of $[Me(decyl)_3N]Br$ was removed by extraction with *n*-hexane. Analytically pure $[(decyl)_3MeN][V(CO)_6]$ was isolated as a viscous, yellow oil after drying in high vacuum; ν(CO) [toluene (cm^{-1})] = 2022 m, 1905 m, 1854 vs,br. The appearance of the two bands of medium intensity indicates highly distorted O_h symmetry on the IR time scale. The ^{51}V resonance is still very sharp, indicating nearly ideal O_h symmetry on the NMR time scale. $[P_2N][Cp(CO)_{3-n}(^{13}CO)_nH]$ [Fig. 2(d); $Cp = C_5H_5$; $P_2N = N(PPh_3)_2$] was prepared by Na–Hg reduction of $CpV(CO)^*_4$ in THF and subsequent treatment of the $Na_2[CpV(CO)_3]THF$ thus generated[23] with $[P_2N]Cl$ and H_2O.[13,24] A mixture of $[Et_4N][CpV(CO)_3H]$ and $[Et_4N][CpV(CO)_3D]$ was obtained by dissolving yellow, powdery $Na_2[CpV(CO)_3]$ in $CH_3CN–CD_3CN$ (1:1) and addition of $[Et_4N]Cl$.

Ring-deuteriated complexes

$C_5D_5V(CO)_4$. A 1.01 g (11.5 mmol) amount of NaC_5D_5, placed in a 50 ml round-bottomed flask (A) fitted with a dropping funnel and connected to a second flask (B), was cooled externally with liquid N_2. After evacuation of the complete apparatus, 4 ml of D_3PO_4 in D_2O [$c(1/3H_3PO_4) = 3$ mol/l^{-1}] were added to A via the funnel in one batch. Flask B was now cooled to dry-ice temperature, and the reaction mixture in A slowly warmed while stirring. C_5D_6 (degree of deuteriation 93%) thus condensed over to B. C_5D_6 (2.3 mmol) was then added to 400 mg (1.8 mmol) of $V(CO)_6$ dissolved in 20 ml of *n*-hexane at room temperature. After 2 h of stirring the solution was filtered, the solvent distilled off and the orange residue dried under high vacuum. Yield: 340 mg (80%) of $C_5D_5V(CO)_4$ (deuterium content 94.1%, by MS). IR [KBr (cm^{-1})]: $\nu(CD) = 2320$, $\delta_{ip}(CD) = 883$ (E_2) and 773 (E_1), $\delta_{op}(CD) = 807$ (E_2) and 588 (A_1). The ν(CO) pattern is the same as in $C_5H_5V(CO)_4$.[22,25] $C_5HD_4V(CO)_4$ was prepared accordingly by the reaction between $V(CO)_6$ and C_5HD_5, obtained by hydrolysis of NaC_5D_5 with $H_3PO_4–H_2O$. Analysis of the reaction product by MS revealed a composition according to $C_5HD_4V(CO)_4$ (73%) + $C_5H_2D_3V(CO)_4$ (23%).

'$C_5H_4DV(CO)_4$.' Cyclopentadiene-d_1 was prepared from NaC_5H_5 and D_3PO_4–D_2O as described above, yielding C_5H_5D with a vinyl-H/allyl-H ratio of 3.1:1 [by ^1H NMR in $CDCl_3$: $\delta(^1H) = 6.50$ and 6.42/2.91 ppm]. A 0.4 ml volume of C_5H_5D was added immediately after the preparation to 50 mg of $V(CO)_6$ in 5 ml of hexane. The solution was stirred for 15 min and then quenched by the addition of 2 ml of THF.[26] The solvents were removed by evaporation, and C_5H_4D was obtained by extraction of the residue with *n*-pentane. The composition of the sample, according to MS, corresponded to d_0–d_1–d_2–d_3 = 43:41:10:4%. The same preparative procedure was repeated with another sample of C_5H_5D which had been refluxed for 1 h to achieve isomerization. The composition of the carbonylvanadium complex was d_0–d_1–d_2–d_3–d_4 = 19:59:14:6:2%. Reduction with Na–Hg and subsequent treatment with $[P_2N]Cl$ in CH_3CN gave $[P_2N][C_5H_4DV(CO)_3H]$.

η^5-(Indenyl-1-d_1)$V(CO)_4$. Indene-1-d_1 was prepared by D_2O hydrolysis of indenyllithium (from freshly distilled indene and LiBu) according to a literature procedure.[27] Analysis by MS gave d_0–d_1–d_2–d_3 = 21:57:20:2%; the isomeric purity by ^1H NMR was close to 100% for the 1-d_1 isomer. The reaction with $V(CO)_6$ was carried out as described above for the Cp derivatives but employing a 5-fold molar excess of indene and a reaction time of 30 min. The composition of the complex by MS was d_0–d_1–d_2 = 48:42:10%.

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