

# 'Non-classical' Dihydrogen Complexes of Vanadium: the Spectroscopic Characterization of $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3(\text{H}_2)]$ in Solution at both Cryogenic and Room Temperatures

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UV photolysis of  $[\text{cpV}(\text{CO})_4]$  ( $\text{cp} = \eta^5\text{-C}_5\text{H}_5$ ) and  $\text{H}_2$  provides IR evidence for the formation of  $[\text{cpV}(\text{CO})_3(\eta^2\text{-H}_2)]$  both in n-heptane solution at  $25^\circ\text{C}$  and in liquid xenon solution at  $-78^\circ\text{C}$ , where the  $\nu(\text{H-H})$  IR band of co-ordinated dihydrogen (and its HD isotopomer) can be observed; time-resolved IR (TRIR) studies provide information about the reactivity of these species at room temperature.

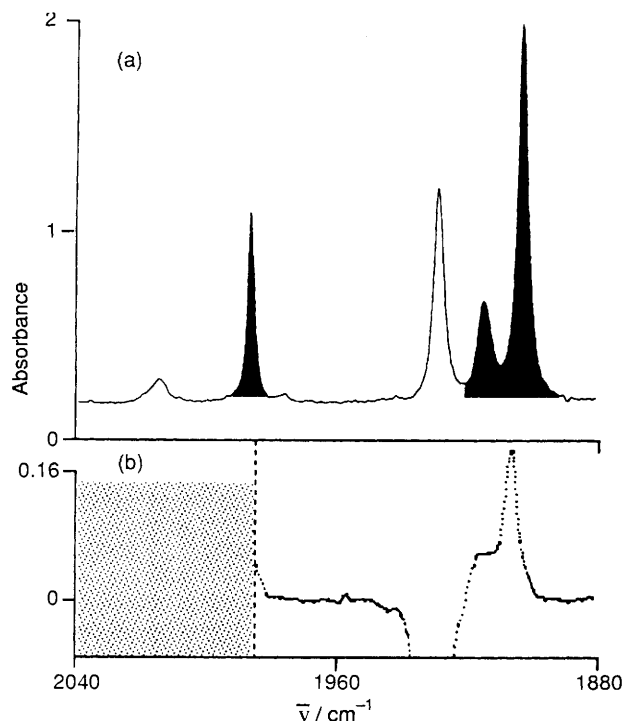
Transition metal complexes containing the  $\eta^2\text{-H}_2$  ligand, so-called 'non-classical' dihydrogen complexes, are now so numerous<sup>1</sup> that they can no longer be considered unusual. Nevertheless, the majority of these compounds involve metals in Groups 6 or 8 and most have centres which, formally at least, have  $d^6$  electron configurations. Until now, no dihydrogen compounds have been reported for vanadium, where the d-electron count will usually be lower.

UV photolysis of metal carbonyl complexes in the presence of  $\text{H}_2$  has proved to be a relatively general route for the generation and spectroscopic identification of labile non-classical dihydrogen complexes in solid matrices,<sup>2</sup> in liquid Xe (IXe) solution,<sup>3</sup> or in supercritical fluids<sup>4</sup> [equation (1)]. Such studies become particularly valuable when they are supported

by time-resolved IR (TRIR) experiments, which provide information about the reactivity of these species in conventional solvents at room temperature.<sup>5</sup> Photolysis of  $[\text{cpV}(\text{CO})_4]$  ( $\text{cp} = \eta^5\text{-C}_5\text{H}_5$ ) is a well established route to  $[\text{cpV}(\text{CO})_3\text{L}]$  complexes<sup>6</sup> and here we show that a similar route leads to the previously unknown compound  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$ .



UV photolysis of  $[\text{cpV}(\text{CO})_4]$  and  $\text{H}_2$  in IXe<sup>+</sup> at  $-78^\circ\text{C}$ , gives rise to three new bands in the  $\nu(\text{C-O})$  region of the IR spectrum [coloured in Figure 1(a)]. These bands, which are not observed in the absence of  $\text{H}_2$ , have positions and relative intensities similar to those of known  $[\text{cpV}(\text{CO})_3\text{L}]$  species,<sup>6</sup> particularly  $[\text{cpV}(\text{CO})_3(\text{N}_2)]$ , see Table 1. The three bands are due to a single compound and one band shows small but



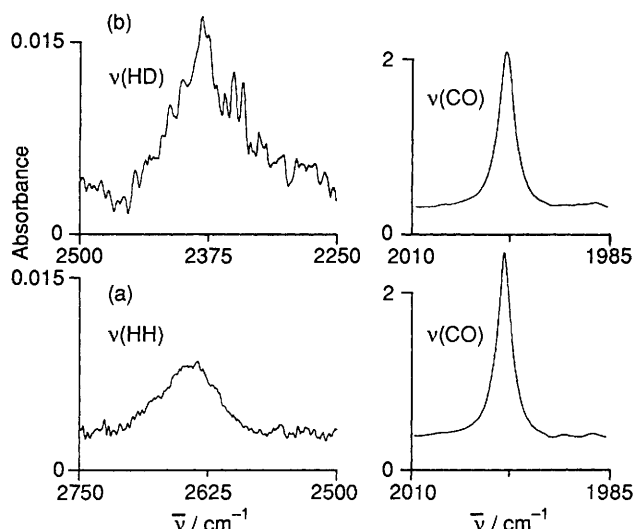
**Figure 1.** IR spectra in the  $\nu(\text{C-O})$  region showing formation of  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  in solution. (a) FTIR spectrum obtained after UV photolysis of  $[\text{cpV}(\text{CO})_4]$  ( $9 \times 10^{-5} \text{ M}$ ) and  $\text{H}_2$  (200 psi) in IXe solution at  $-78^\circ\text{C}$ . Bands are assigned as follows: coloured,  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$ ; uncoloured, residual  $[\text{cpV}(\text{CO})_4]$  starting material. (b) TRIR spectrum corresponding to  $10 \mu\text{s}$  after UV photolysis of  $[\text{cpV}(\text{CO})_4]$  ( $7 \times 10^{-4} \text{ M}$ ) and  $\text{H}_2$  (2 atm.) in n-heptane at  $25^\circ\text{C}$ ; the positive bands are due to  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  and the truncated negative peak is due to  $[\text{cpV}(\text{CO})_4]$  destroyed by the UV flash. (The heavier points are data points and the lighter ones computer interpolation; the shaded area indicates the region outside the wavenumber limit of the TRIR apparatus.)

**Table 1.** Wavenumbers,<sup>a</sup>  $\text{cm}^{-1}$ , of  $\nu(\text{C-O})$  IR bands of  $[\text{cpV}(\text{CO})_4]$ ,  $[\text{cpV}(\text{CO})_3(\text{N}_2)]$ , and  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  in liquid Xe at  $-78^\circ\text{C}$  and n-heptane at  $25^\circ\text{C}$ .

$[\text{cpV}(\text{CO})_4]^b$	$[\text{cpV}(\text{CO})_4]^c$	$[\text{cpV}(\text{CO})_3(\text{N}_2)]^{b,d}$	$[\text{cpV}(\text{CO})_3(\text{N}_2)]^{c,e}$
2032.3 $a_1$	2029.3 $a_1$	1997 $a'$	2199.5 $\nu(\text{N-N})$
1931.8 $e$	1934.8 $e$	1908 $a'(\text{sh})$	1995.2 $a'$
		1916 $a''$	1911.4 $a'(\text{sh})$
			1915.4 $a''$
		$[\text{cpV}(\text{CO})_3(\text{H}_2)]^{b,d}$	$[\text{cpV}(\text{CO})_3(\text{H}_2)]^c$
		2642 $\nu(\text{H-H})$	2380 $\nu(\text{H-D})^f$
		1997 $a'$	1998.4 $a'$
		1917 $a'(\text{sh})$	1919.0 $a'$
		1908 $a''$	1917.7 (HD), 1915.8 ( $\text{D}_2$ ) <sup>g</sup>
			1903.4 $a''$

<sup>a</sup> Spectra recorded on Nicolet 730 FTIR interferometer (16K data points, 32K transform points), wavenumber  $\pm 0.2 \text{ cm}^{-1}$ . <sup>b</sup> n-Heptane solution. <sup>c</sup> IXe solution. <sup>d</sup> TRIR spectrum, band positions  $\pm 2 \text{ cm}^{-1}$ . <sup>e</sup> Cf. 2210.3, 1995.6, 1911.9, and (1875.1)  $\text{cm}^{-1}$ , reported for matrix isolated  $[\text{cpV}(\text{CO})_3(\text{N}_2)]$  (R. B. Hitam and A. J. Rest, *Organometallics*, 1989, 8, 1598). The matrix band in parentheses does not agree with our solution data and it is possible that this band, which was relatively weak, was due to some other species. <sup>f</sup> If the isotopic shift were the same as for  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  and  $[\text{Cr}(\text{CO})_5(\text{D}_2)]$ , the  $\nu(\text{D-D})$  band of  $[\text{cpV}(\text{CO})_3(\text{D}_2)]$  would be predicted at  $1955 \text{ cm}^{-1}$  where it would be masked by the much more intense  $\nu(\text{C-O})$  bands. <sup>g</sup> These changes in the wavenumber are a chemical effect rather than a solvent effect because, within experimental error, the bands of the parent  $[\text{cpV}(\text{CO})_4]$  compound are not shifted when HD or  $\text{D}_2$  are used.

<sup>†</sup> The UV photolysis source was a Philips HPK 125W medium pressure Hg lamp with a Balzer's 367 nm narrow band interference filter; typical photolysis times were 10 min. In dilute solution (*i.e.*  $5 \times 10^{-5} \text{ M}$   $[\text{cpV}(\text{CO})_4]$ ) up to ca. 80% conversion can be achieved. In more concentrated solutions (*i.e.* those illustrated in Figure 2) the overall conversion is less, presumably due to secondary photolysis.



**Figure 2.** FTIR spectra in lXe solution at  $-78\text{ }^{\circ}\text{C}$ , showing the bands assigned to (a) the  $\nu(\text{H-H})$  vibration of  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  and (b) the  $\nu(\text{H-D})$  vibration of  $[\text{cpV}(\text{CO})_3(\text{HD})]$ . In both cases, the bands are compared to the least intense  $\nu(\text{C-O})$  band, the high wavenumber  $\nu'$  vibration. As in other dihydrogen complexes,<sup>3</sup> the  $\nu(\text{H-D})$  band is rather more intense relative to the  $\nu(\text{C-O})$  band than is the  $\nu(\text{H-H})$  band. Note that the 'fine structure' on the  $\nu(\text{H-D})$  band is caused by atmospheric  $\text{CO}_2$  in the optical path of the interferometer and has no chemical significance. The initial concentrations of  $[\text{cpV}(\text{CO})_4]$  were (a)  $3 \times 10^{-4}\text{ M}$  ( $\text{H}_2$  200 psi) and (b)  $1.5 \times 10^{-3}\text{ M}$  (HD 120 psi).

reproducible shifts in wavenumber when HD or  $\text{D}_2$  are used in place of  $\text{H}_2$ , see Table 1, suggesting that the compound does indeed contain hydrogen and therefore may be  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$ .

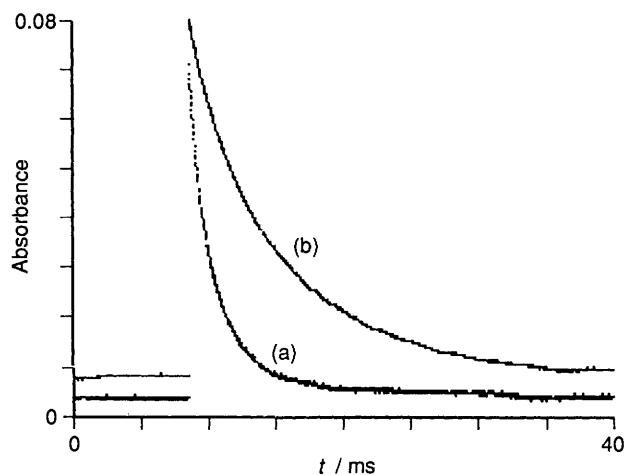
Although several spectroscopic criteria have been used to deduce the presence of  $\eta^2\text{-H}_2$  groups, the observation of an IR band associated with the  $\nu(\text{H-H})$  vibration is one of the more conclusive. When larger quantities of the new compound are generated (by using a higher initial concentration of  $[\text{cpV}(\text{CO})_4]$ ), a very weak and rather broad IR band can be observed at  $2642\text{ cm}^{-1}$ , see Figure 2(a). This band shifts to  $2380\text{ cm}^{-1}$  when the experiment is repeated with HD, see Figure 2(b). The ratio of wavenumbers (HD/ $\text{H}_2$ ,  $0.901 \pm 0.007$ ) is somewhat less than expected for isolated HD and  $\text{H}_2$  diatomics but the ratio is identical to that observed<sup>3b</sup> (0.899) for the  $\nu(\text{H-H})$  and  $\nu(\text{H-D})$  bands of  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$ . The HD isotopomer of a 'classical' dihydride cannot give rise to an IR band shifted in this way and there is little doubt that the bands are due to the  $\nu(\text{H-H})$  and  $\nu(\text{H-D})$  vibrations of a non-classical dihydrogen compound. §

TRIR experiments in n-heptane solution¶ show that the

‡ The  $\nu(\text{H-D})$  band is close in wavenumber to that of  $\text{CO}_2$  dissolved in lXe. This meant that great care had to be taken to avoid the presence of  $\text{O}_2$  in the solution because even small traces of air dissolved in lXe will give rise to  $\text{CO}_2$  when the solution is photolysed. A band due to residual  $\text{CO}_2$  in the solution has been removed by computer subtraction.

§ Although weak bands of  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  can be observed in the region  $<1000\text{ cm}^{-1}$ , the bands due to  $\nu(\text{M-H}_2)$  vibrations which are expected in this region have not yet been identified.

¶ For further details of the TRIR equipment in Nottingham (pulsed 308 nm XeCl excimer laser, cw CO IR laser, HgCdTe detector) see ref. 5b.



**Figure 3.** TRIR kinetic traces, measured at  $1908.2\text{ cm}^{-1}$  in n-heptane at  $25\text{ }^{\circ}\text{C}$ , showing the variation in the rate of decay of  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  under (a) 0.5 and (b) 2 atm pressure of  $\text{H}_2$ .

same species,  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$ , is also formed by photolysis of  $[\text{cpV}(\text{CO})_4]$  and  $\text{H}_2$  at room temperature [equation (2), Figure 1(b)]. Under these conditions  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  is relatively labile, decaying to reform  $[\text{cpV}(\text{CO})_4]$  || at a rate which decreases with increasing pressure of  $\text{H}_2$ , see Figure 3. The lifetime of  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  is significantly shorter than that of  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  under similar conditions.<sup>7</sup>



In lXe solution,  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  undergoes a smooth thermal exchange reaction with  $\text{D}_2$  (complete in *ca.* 10 min at  $-78\text{ }^{\circ}\text{C}$ ) to form  $[\text{cpV}(\text{CO})_3(\text{D}_2)]$  without the formation of any  $[\text{cpV}(\text{CO})_3(\text{HD})]$ . Photolysis of  $[\text{cpV}(\text{CO})_4]$  with a mixture of  $\text{H}_2/\text{D}_2$  results in the formation of  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  and  $[\text{cpV}(\text{CO})_3(\text{D}_2)]$  but not  $[\text{cpV}(\text{CO})_3(\text{HD})]$ , while photolysis in the presence of HD leads only to the formation of  $[\text{cpV}(\text{CO})_3(\text{HD})]$ . This contrasts with the  $[\text{Cr}(\text{CO})_6]/\text{H}_2/\text{D}_2$  system<sup>3b</sup> where prolonged photolysis did result in H/D exchange, probably<sup>8</sup> via  $[\text{Cr}(\text{CO})_4(\text{H}_2)(\text{D}_2)]$ . As with other dihydrogen complexes,<sup>3,5</sup>  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  reacts thermally with  $\text{N}_2$  in lXe to give the corresponding dinitrogen complex,  $[\text{cpV}(\text{CO})_3(\text{N}_2)]$ , which can also be generated directly from  $[\text{cpV}(\text{CO})_4]$  by photolysis in the presence of  $\text{N}_2$  (see Table 1).

There is still some argument over the bonding in these species but formation of a dihydrogen complex rather than a dihydride is probably determined by a delicate balance between the acceptor and donor properties of the metal centre.<sup>1,8</sup> Both the wavenumber and the width of the  $\nu(\text{H-H})$  band of  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  are interesting in this context. The lowering of the frequency of the  $\nu(\text{H-H})$  vibration of the  $\eta^2\text{-H}_2$  relative to that of unco-ordinated  $\text{H}_2$  (*ca.*  $4400\text{ cm}^{-1}$ )<sup>9</sup> might be expected to indicate the strength of this back-donation and, hence, of the  $\text{M}-(\eta^2\text{-H}_2)$  interaction. However, this is clearly not the case;  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  has a lower frequency for  $\nu(\text{H-H})$  ( $2642\text{ cm}^{-1}$ ) than either  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  ( $3030\text{ cm}^{-1}$ )<sup>2,3</sup>

|| Although the dihydride  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  has been postulated as an intermediate in the formation of  $[\text{cp}_2\text{V}_2(\text{CO})_5]$  (E. O. Fischer and R. J. J. Schneider, *Chem. Ber.*, 1970, **103**, 3686), our TRIR experiments in the presence of  $\text{H}_2$  provide no evidence for the formation of dinuclear species.

or  $[\text{W}(\text{CO})_5(\text{H}_2)]$  ( $2711\text{ cm}^{-1}$ )<sup>3b,9</sup> yet is thermally the most labile of the three compounds. On the other hand, the  $\nu(\text{H}-\text{H})$  band of  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  is significantly broader (*ca.*  $90\text{ cm}^{-1}$  FWHM) than those of the two  $[\text{M}(\text{CO})_5(\text{H}_2)]$  compounds (*e.g.*  $40\text{ cm}^{-1}$  for W).<sup>3,9</sup> Although the origins of broadening of  $\nu(\text{H}-\text{H})$  are still not completely clear,<sup>2,3,9</sup> it is believed to be the consequence of rotation of the  $\eta^2\text{-H}_2$  group.<sup>10</sup> Thus, the greater line-width in  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$  may reflect a lower barrier to rotation and, perhaps, a weaker  $\text{M}-(\eta^2\text{-H}_2)$  interaction.

$[\text{cpV}(\text{CO})_3(\text{H}_2)]$  is the first dihydrogen complex of vanadium but, almost certainly, it is not unique<sup>††</sup> because, already, we have preliminary evidence for another vanadium dihydrogen complex. Photolysis of  $[\text{V}(\text{CO})_6]$  and  $\text{H}_2$ , both in  $\text{IXe}$  and in *n*-heptane, generates a new species, probably  $[\text{V}(\text{CO})_5(\eta^2\text{-H}_2)]$ , with  $\nu(\text{C}-\text{O})$  bands close in wavenumber to those of  $[\text{V}(\text{CO})_5(\text{N}_2)]$ . Work is now in progress to characterize these species and also to study the intermediates involved in formation of  $[\text{cpV}(\text{CO})_3(\text{H}_2)]$ .

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<sup>††</sup> Sweany has reported the formation of matrix isolated  $[\text{cpW}(\text{CO})_2(\text{H}_2)\text{H}]$ , presumably with a similar  $d^4$  configuration (R. L. Sweany, *J. Am. Chem. Soc.*, 1986, **108**, 6986).