Dihydride *versus* Dihydrogen Complex; The Photochemical Reaction of $[(\eta^5\text{-}C_5H_5)M(CO)_4]$ (M = V, Nb and Ta) with Hydrogen in Solution at both Cryogenic and Room Temperatures

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UV photolysis of $[cpM(CO)_4]$ (cp = η^5-C_5H_5; M = V, Nb and Ta) and H_2 has been studied by IR spectroscopy both in n-heptane solution at 25 °C and in liquid Xenon solution at −110 to −45 °C; for V, the reaction leads to formation of the non-classical complex $[cpV(CO)_3(\eta^2\text{-}H_2)]$ while, for Ta, the dihydride $[cpTa(CO)_3H_2]$ is formed; for Nb, there is a temperature dependent equilibrium between the classical $[cpNb(CO)_3H_2]$ and non-classical $[cpNb(CO)_3(\eta^2\text{-}H_2)]$ compounds, which presents an unusual opportunity to study the formation of these species using nanosecond Time-resolved IR spectroscopy (TRIR).

Despite the ever-increasing number of so-called 'non-classical' dihydrogen complexes,[1] their structures and chemistry continue to be pleasingly unpredictable. (Recent examples include evidence for η^1-H_2 coordination,[2] very long H–H bonds[3] and even a 16-electron configuration[3b]). A particularly fruitful route to such compounds has been the UV photolysis of transition metal carbonyl complexes in fluid solution under a pressure of hydrogen, particularly in liquid xenon (lXe), where the low temperatures have stabilized a whole series of otherwise highly labile compounds.[4] In addition, the absence of IR bands due to lXe itself has allowed several of these compounds to be identified unambiguously by observation of the ν(H–H) IR band which is frequently obscured in more conventional solvents. Recently, we reported the synthesis,[5] by this route, of $[cpV(CO)_3(\eta^2\text{-}H_2)]$ (cp = η^5-C_5H_5), the first non-classical dihydrogen complex of vanadium,[†] [eqn. (1)].

$$[cpV(CO)_4] + H_2 \xrightarrow{UV} [cpV(CO)_3(\eta^2\text{-}H_2)] + CO \quad (1)$$

In this Communication, we describe the analogous reactions of the Group 5 congeners, Nb and Ta. Fig. 1 compares IR spectra of the reaction products obtained by UV photolysis[‡] of $[cpM(CO)_4]$ (M = V, Nb and Ta) in lXe doped with H_2. A number of points are clear from Fig. 1. (*i*) Although the ν(C–O) bands of the three complexes $[cpM(CO)_4]$ are almost identical in frequency and relative intensity (see Table 1), the IR spectra of the products are different for the three metals. (*ii*) The spectrum in Fig. 1(*a*) has previously been assigned to $[cpV(CO)_3(\eta^2\text{-}H_2)]$ with a weak band, assigned to ν(H–H) of η^2-H_2, at 2642 cm^{-1}. There are no bands assignable to a dihydride species. (*iii*) The IR bands for the Ta product, Fig. 1(*c*), show the formation of a previously unknown classical dihydride, $[cpTa(CO)_3H_2]$ (*i.e.* the ν(C–O) bands are shifted to higher wavenumber relative to those of the parent $[cpTa(CO)_4]$, indicating oxidation of the metal centre and there is no IR band attributable to a ν(H–H) vibration of an η^2-H_2 group). A dihydride should also display two bands due to ν(M–H) vibrations but all attempts to detect these bands have, so far, proved unsuccessful.[§] Formation of a dihydride compound by a third row element is consistent with previously observed trends[6] in Group 8 and is presumably due to greater back-bonding to H_2 by the heavier element.[1] (*iv*) Qualitatively at least, the IR spectrum for Nb, Fig. 1(*b*), is the sum of those for Ta and V. There are two sets of bands; a set of three bands, coloured black in Fig. 1(*b*), is similar to those of the dihydride $[cpTa(CO)_3H_2]$, Fig. 1*c*; the other set, uncoloured in Fig. 1(*b*), is very close to those of the non-classical dihydrogen species $[cpV(CO)_3(\eta^2\text{-}H_2)]$, including a weak band at 2600 cm^{-1} assignable to ν(H–H) vibration of $[cpNb(CO)_3(\eta^2\text{-}H_2)]$.

Thus reaction of $[cpNb(CO)_4]$ with H_2 leads to a mixture of classical and non-classical dihydrogen complexes [eqn. (2)].

$$[CpNb(CO)_4] + H_2 \xrightarrow{UV} [cpNb(CO)_3(\eta^2\text{-}H_2)] + [cpNb(CO)_3H_2] \quad (2)$$

The amount of $[cpNb(CO)_3H_2]$ can be increased reversibly at the expense of $[cpNb(CO)_3(\eta^2\text{-}H_2)]$ by raising the tempera-

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[†] Very recent matrix isolation experiments (Z. L. Xiao, R. H. Hauge and J. L. Margrave, *J. Phys. Chem.*, 1991, **95**, 2696) show that V atoms react with H_2 to form a dihydride $V(H)_2$.

[‡] The UV photolysis source for the lXe experiments was a Philips HPK 125W medium Pressure Hg lamp with a <300 nm glass cut-off filter. For further details of the TRIR equipment in Nottingham (pulsed 308 nm XeCl excimer laser, Edinburgh Instruments cw CO IR laser (or Mütek tunable IR diode laser), 77K HgCdTe detector, 125 nsec time-resolution) see ref. 4*c*.

[§] In lXe solution, ν(M–H) bands are generally much less intense and considerably broader than ν(C–O) absorptions. Thus it is probable that, in both the Ta and Nb systems, these bands are masked by the much more intense ν(C–O) absorptions. Such problems of overlap should not occur with ν(M–D) bands of the corresponding deuterides but, sadly, such bands are even weaker than those due to ν(M–H) and our attempts to observe them have been equally unsuccessful.

Table 1 Wavenumbers,[a] cm^{-1}, of ν(C–O) IR bands of $[cpM(CO)_4]$, $[cpM(CO)_3(\eta^2\text{-}H_2)]$ and $[cpM(CO)_3H_2]$ in liquid Xe at −78 °C and n-heptane at 25 °C

$[cpV(CO)_4]^{b,c}$	$[cpNb(CO)_4]^{b,c}$	$[cpTa(CO)_4]^{b,c}$	
2032.3 (2029.4)	2038.5 (2037.0)	2036.0 (2033.5)	a_1 ν(C–O)
1934.1^d (1931.8)	1933.5^d (1931.9)	1925.6^d (1923.0)	e ν(C–O)
$[cpV(CO)_3(\eta^2\text{-}H_2)]^{b,c}$	$[cpNb(CO)_3(\eta^2\text{-}H_2)]^{b,c}$		
2642	2600		ν(H–H)
1998.4 $(1998)^e$	2007.7$(^g)$		a′ ν(C–O)
1919.1 $(1913.8)^f$	1915.0 $(1912)^e$		a′ ν(C–O)
1904.4 $(1905.3)^f$	1902.4 $(1904)^e$		a″ ν(C–O)
	$[cpNb(CO)_3(H)_2]^{b,c}$	$[cpTa(CO)_3(H)_2]^{b,c}$	
	2053.0$(^g)$	2053.4^g	a′ ν(C–O)
	2006.0$(^g)$	2001.8^g	a″ ν(C–O)
	1966.1 $(1969)^e$	1958.4 $(1960)^e$	a′ ν(C–O)

[a] Spectra recorded on Nicolet 730 FTIR interferometer (16K data points, 32K transform points wavenumbers ± 0.2 cm^{-1}. [b] lXe solution. [c] Wavenumbers in parentheses for n-heptane solution. [d] Relative absorbance a_1 : e; V, 1 : 6.2; Nb, 1 : 6.0; Ta, 1 : 5.5. [e] CO laser TRIR spectrum, band positions ± 2 cm^{-1}. [f] IR semiconductor diode laser TRIR, band positions ± 0.5 cm^{-1}. [g] Bands in n-heptane outside the range of the CO TRIR laser.

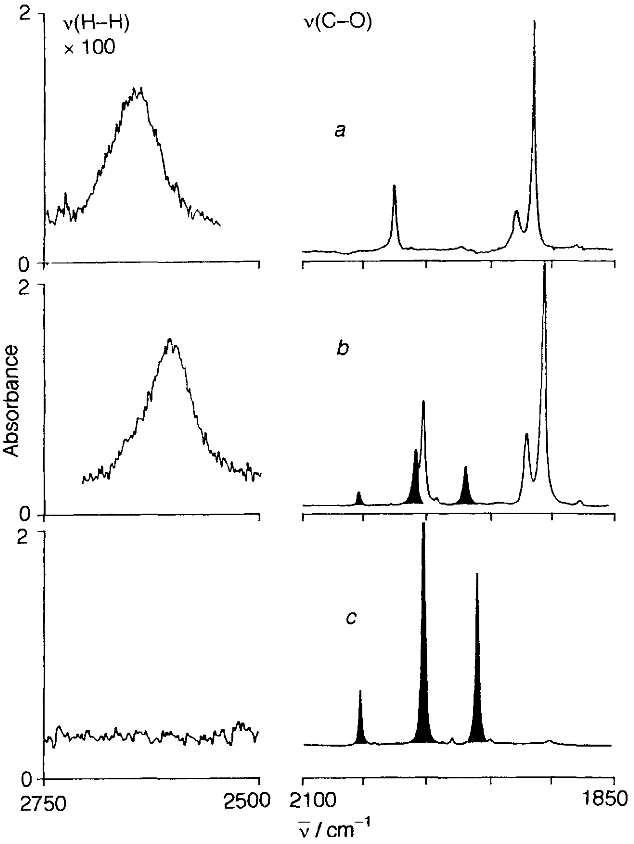

Fig. 1 IR spectra in the ν(C–O) and ν(H–H) regions showing the absorptions of products, formed by UV photolysis of $[cpM(CO)_4]$ (M = V, Nb and Ta) with H_2 in lXe solution. Bands coloured black are assigned to dihydrides while those which are unmarked are due to dihydrogen complexes. In each spectrum bands due to any unreacted $[cpM(CO)_4]$ have been removed by computer subtraction. Spectra were obtained as follows (*a*) after 2 min photolysis of $[cpV(CO)_4]$ (6×10^{-4} mol dm^{-3}) and H_2 (180 psi) at −78 °C; (*b*) after 5 min photolysis of $[cpNb(CO)_4]$ (3.4×10^{-4} mol dm^{-3}) and H_2 (140 psi) at −78 °C; (*c*) after 5 min photolysis of $[cpTa(CO)_4]$ (1.9×10^{-4} mol dm^{-3}) and H_2 (140 psi) at −77 °C. (Note the expanded absorbance and contracted wavenumber scales in the ν(H–H) region.)

ture of the solution after the photolysis has stopped, see Fig. 2*a*. This indicates a thermal equilibrium between the two species [eqn. (3)].

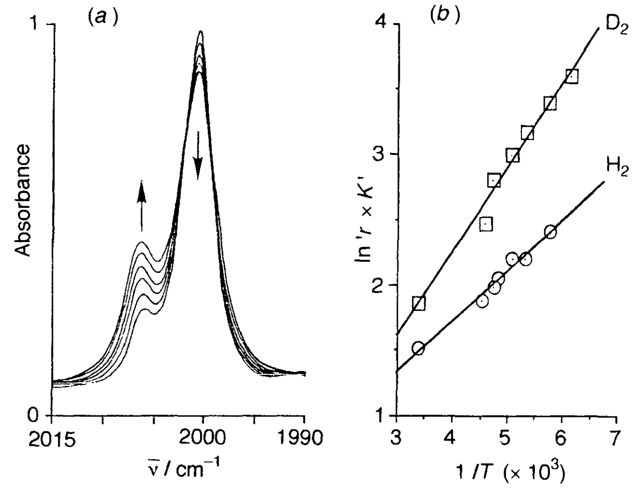

Fig. 2 (*a*) FTIR spectra of part of the ν(C–O) region showing the reversible change in equilibrium between $[cpNb(CO)_3(\eta^2\text{-}H_2)]$ and $[cpNb(CO)_3H_2]$ as the temperature of lXe solution is raised from −110 to −45 °C; the band due to $[cpNb(CO)_3H_2]$ (marked ↑) increases with a corresponding decrease in the band of $[cpNb(CO)_3(\eta^2\text{-}H_2)]$ (marked ↓). (NB The spectra have been plotted to remove the slight change in frequencies (*ca.* 1 cm^{-1}) of the IR bands, which occurs as the temperature is raised. The wavenumber scale refers to −110 °C. (*b*) Van't Hoff plot relating the variation of equilibrium constant, *K*, for the hydrogen and deuterium complexes as a function of reciprocal temperature. The true equilibrium constant, *K* [for definition, see eqn. (3)], cannot be measured from our spectra since the extinction coefficients of the various species are unknown. However, by measuring the absorbance of the non-overlapping IR bands of the two species at 1902.4 and 1966.1 cm^{-1} (see Table 1 and Fig. 1*b*), we obtain a value '$r \times K$' where *r*, the unknown ratio of the extinction coefficients, does not affect the gradients of the plots. For both H_2 and D_2, the highest temperature point was measured using TRIR at room temperature in n-heptane.

$$[cpNb(CO)_3H_2] \rightleftharpoons [cpNb(CO)_3(\eta^2\text{-}H_2)];$$

$$\Delta H^{\circ}_{(H_2)}\; K = \frac{[cpNb(CO)_3(\eta^2\text{-}H_2)]}{[cpNb(CO)_3H_2]} \quad (3)$$

Quantitative analysis of the temperature dependence of this equilibrium, Fig. 2*b*, leads to a value of $\Delta H^{\circ}_{(H_2)}$ of only -3.5 ± 0.5 kJmol^{-1} {*i.e.* $[cpNb(CO)_3H_2]$ is only marginally higher in energy than $[cpNb(CO)_3(\eta^2\text{-}H_2)]$}. When the experiment is repeated with D_2, the enthalpy difference, $\Delta H^{\circ}_{(D_2)}$, is slightly

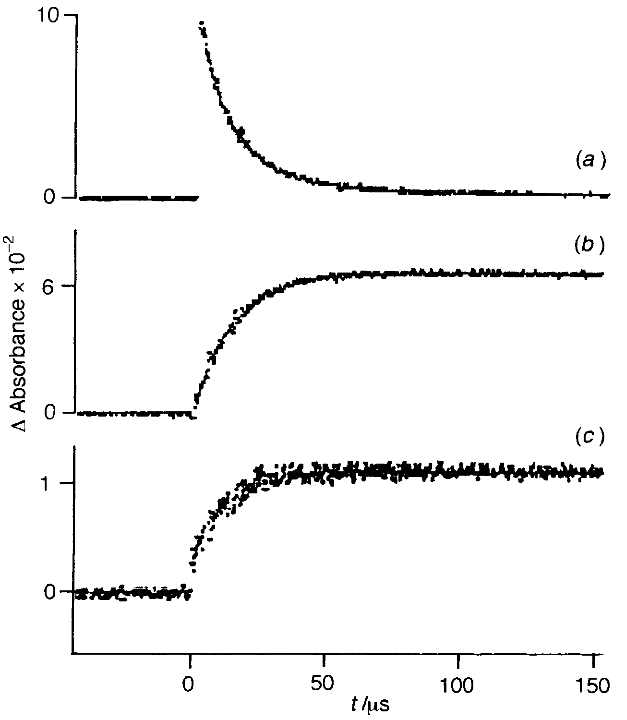

Fig. 3 TRIR kinetic traces obtained with $[cpNb(CO)_4]$ (7×10^{-4} mol dm^{-3}) in n-heptane at 25 °C, 2 atm pressure of H_2 showing (*a*) the formation and decay of $[cpNb(CO)_3]$ measured at 1888 cm^{-1} (*b*) the formation of $[cpNb(CO)_3(\eta^2\text{-}H_2)]$ measured at 1903 cm^{-1} and (*c*) the formation of $[cpNb(CO)_3H_2]$ measured at 1967 cm^{-1}

larger -5.5 ± 0.5 $kJmol^{-1}$, presumably the consequence of a small net change in zero point energy.

Our lXe experiments provide no information about the rate of interconversion of the classical and non-classical dihydrogen species, because the equilibrium is established faster than the temperature of the solution can be changed. However, an indication of this rate can be obtained from fast time-resolved IR (TRIR) spectroscopy which allows rates of formation to be measured directly for both $[cpNb(CO)_3(\eta^2\text{-}H_2)]$ and $[cpNb(CO)_3H_2]$ during the UV photolysis of $[cpNb(CO)_4]$ in n-heptane solution at room temperature. This is the first dihydrogen/dihydride system to be studied by TRIR and Fig. 3 shows the appropriate kinetic traces. Surprisingly, the two compounds, classical and non-classical, are formed at identical rates from the formally unsaturated $[cpNb(CO)_3]$ intermediate¶ and reach their final equilibrium concentrations <50 μs after the UV flash. Similar TRIR results were obtained for $[cpNb(CO)_4]/D_2$. Thus, the addition of H_2 to $[cpNb(CO)_3]$ appears to be the rate determining step with equilibration between dihydrogen and dihydride extremely fast,|| [eqn. (4)]. This contrasts sharply with $[W(CO)_3P(Pr^i{}_3)_2(\eta^2\text{-}H_2)]$, one of the first compounds shown to exhibit a dihydrogen/dihydride equilibrium,[7] where the rate of interconversion at 25 °C was slow even on an NMR timescale.

$$[cpNb(CO)_3] + H_2 \xrightarrow{slow} [cpNb(CO)_3(\eta^2\text{-}H_2)] \overset{fast}{\rightleftharpoons} [cpNb(CO)_3H_2] \quad (4)$$

The ν(H–H) vibration of $\eta^2\text{-}H_2$ would appear to be closely related to the reaction coordinate which should interconvert dihydrogen complex and dihydride.[8] One might therefore expect differences between the ν(H–H) IR bands of $[cpNb(CO)_3(\eta^2\text{-}H_2)]$, which interconverts, and $[cpV(CO)_3(\eta^2\text{-}H_2)]$ which apparently does not. However, the differences are surprisingly small (*cf.* Fig. 1*b* and 1*c*); their halfwidths are similar (V *ca.* 70 cm^{-1} and Nb *ca.* 50 cm^{-1}), the frequency for Nb is only 42 cm^{-1} lower than for V and the ν(H–H) bands of both metals are lower in frequency than that[7a] of $[W(CO)_3(PPr^i{}_3)_2(\eta^2\text{-}H_2)]$, 2690 cm^{-1}.

The Nb complexes, $[cpNb(CO)_3(\eta^2\text{-}H_2)]/[cpNb(CO)_3H_2]$, are relatively labile decomposing over a period of 2 h even at −70 °C in lXe. $[cpTa(CO)_3H_2]$ is rather less reactive with a half-life of 5 min at room temperature in supercritical** Xe under 100 atm pressure of H_2, conditions under which $[cpNb(CO)_3(\eta^2\text{-}H_2)]/[cpNb(CO)_3H_2]$ are too short-lived to be detected at all by FTIR spectroscopy. Experiments are in progress to explore the properties of these compounds further.

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References

1 For general reviews of these species see *e.g.* G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120; R. H. Crabtree and D. G. Hamilton, *Adv. Organometal. Chem.*, 1989, **28**, 299.

2 F. A. Cotton and R. L. Luck, *Inorg. Chem.*, 1991, **30**, 767.

3 (*a*) L. Brammer, J. A. K. Howard, O. Johnson, T. F. Koetzle, J. L. Spencer and A. M. Stringer, *J. Chem. Soc., Chem. Commun.*, 1991, 241; (*b*) B. Chaudret, G. Chung, O. Eisenstein, S. A. Jackson, F. J. Lahoz and J. A. Lopez, *J. Am. Chem. Soc.*, 1991, **113**, 2314.

4 e.g. (*a*) R. K. Upmacis, G. E. Gadd, M. Poliakoff, M. B. Simpson, J. J. Turner, R. Whyman and A. F. Simpson, *J. Chem. Soc., Chem. Commun.*, 1985, 27; (*b*) S. A. Jackson, P. M. Hodges, F-W. Grevels, M. Poliakoff and J. J. Turner, *J. Am. Chem. Soc.*, 1990, **112**, 1221; (*c*) *J. Am. Chem. Soc.*, 1990, **112**, 1234.

5 M. T. Haward, M. W. George, S. M. Howdle and M. Poliakoff, *J. Chem. Soc., Chem. Commun.*, 1990, 913.

6 R. H. Crabtree and D. G. Hamilton, *J. Am. Chem. Soc.*, 1986, **108**, 3124.

7 (*a*) G. J. Kubas, C. J. Unkefer, B. I. Swanson and E. Fukushima, *J. Am. Chem. Soc.*, 1986, **108**, 7000; (*b*) G. Rattan, K. Khalsa, G. J. Kubas, C. J. Unkefer, L. S. van der Sluys and K. A. Kubat-Martin, *J. Am. Chem. Soc.*, 1990, **112**, 3855.

8 For a more detailed discussion of ν(H–H) bands, see J. J. Turner, M. Poliakoff, S. M. Howdle, S. A. Jackson and J. G. McLaughlin, *Faraday Disc.*, 1988, **86**, 271.

¶ $[cpNb(CO)_3]$ has not been observed previously but its behaviour (*e.g.* reaction with CO to reform $[cpNb(CO)_4]$) and the similarity of its ν(C–O) spectrum to that reported for matrix-isolated $[cpV(CO)_3]$ (R. B. Hitam and A. J. Rest, *Organometallics*, 1989, **8**, 1598) are sufficient for its identification. There is increasing evidence that many, if not most, coordinatively unsaturated 16-electron intermediates are solvated by hydrocarbon solvents (see *e.g.* ref. 4*b*) and almost certainly $[cpNb(CO)_3]$ should be formulated as $[cpNb(CO)_3(\text{n-heptane})]$.

|| An alternative explanation is that $[cpNb(CO)_3(\eta^2\text{-}H_2)]$ and $[cpNb(CO)_3H_2]$ are not formed sequentially as indicated in eqn. (4) but rather originate independently from a commoner precursor, for example $[cpNb(CO)_3(\eta^1\text{-}H_2)]$. If this were the case, however, it seems unlikely that the two species would be formed initially in precisely their correct equilibrium concentrations.

** *Safety note*: Experiments with supercritical fluids involve high pressures of gases and should be approached with caution; for details of such experiments, see S. M. Howdle, M. A. Healy and M. Poliakoff, *J. Am. Chem. Soc.*, 1990, **112**, 4804 and references cited therein.