Photolysis of Group 6 Metal Carbonyl Alkene Complexes in Liquefied Noble Gases: I.R. Evidence for Very Labile Dinitrogen and Dihydrogen Adducts

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Broad-band u.v. photolysis of [(*trans*-cyclo-octene)$_x$M(CO)$_{6-x}$] (x = 1 or 2, M = Cr or W) in liquid Kr or Xe solution doped with N_2 or D_2 leads to formation of thermally labile complexes in which an alkene and either N_2 or D_2 are co-ordinated to the same metal centre; in each case the presence of the alkene appears to weaken the M–N_2 or M–D_2 bond.

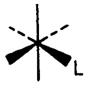
Ten years ago it was postulated that compounds such as $[Ru(H_3)(PMePh_2)_4]^+$ might contain dihydrogen co-ordinated to the metal without rupture of the H–H bond.[1] However, it was only recently that the first conclusive evdence was reported[2] for a transition metal complex containing co-ordinated molecular dihydrogen, η^2-H_2. These so-called non-classical hydrogen complexes now appear to be relatively widespread. Already over twenty compounds have been characterised by *X*-ray diffraction,[2,3] i.r. spectroscopy,[2,4] or n.m.r. measurements.[2,3,5] Many contain carbonyl ligands and all but a few[4b,g] involve d^6 metal centres. This prompts speculation that such compounds may be intermediates in photochemical hydrogenation,[6] particularly of dienes, catalysed by group 6 metal carbonyl compounds.

In this communication, we report the preliminary observation of compounds apparently containing both alkenes and η^2-H_2 co-ordinated to the same metal centre. The compounds have been generated by u.v. photolysis of metal carbonyl alkene complexes, dissolved in liquid Xe or liquid Kr doped with D_2. This route has already proved successful for the low-temperature synthesis of non-classsical hydrogen complexes in spectroscopic quantities, equation (1). Examples include $[M(CO)_5(H_2)]$ M = Cr, Mo, and W,[4a,c] $[Fe(CO)(NO)_2(H_2)]$, and $[Co(CO)_2(NO)(H_2)]$[4b] The total absence of i.r. absorptions due to the solvent allowed observation of bands associated with η^2-H_2, η^2-HD, or η^2-D_2, bands which would normally be obscured in conventional solvents.

Our aim has been to generate $[M(CO)_{5-x}(\text{alkene})_x(H_2)]$ complexes (x = 1 or 2) so that their thermal stabilities can be compared with the corresponding $[M(CO)_5(H_2)]$ and $[M(CO)_4(H_2)_2]$ species. We were initially somewhat hampered by the fact that alkene complexes of group 6 metals are themselves thermally rather unstable and easily lose the alkene ligand on photolysis. Fortunately, this problem was overcome by using the recently synthesised[7,8] complexes of *trans*-cyclo-octene (tr-cyo), (**1**) and (**2**), which are stabilised by relief of ring strain in the co-ordinated ligand.†


(1)

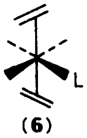

(2)



(3)

(4)

(5)



(6)

a; L = N_2
b; L = D_2

(**1**)—(**6**) = Cr; (**1′**)—(**6′**) = W

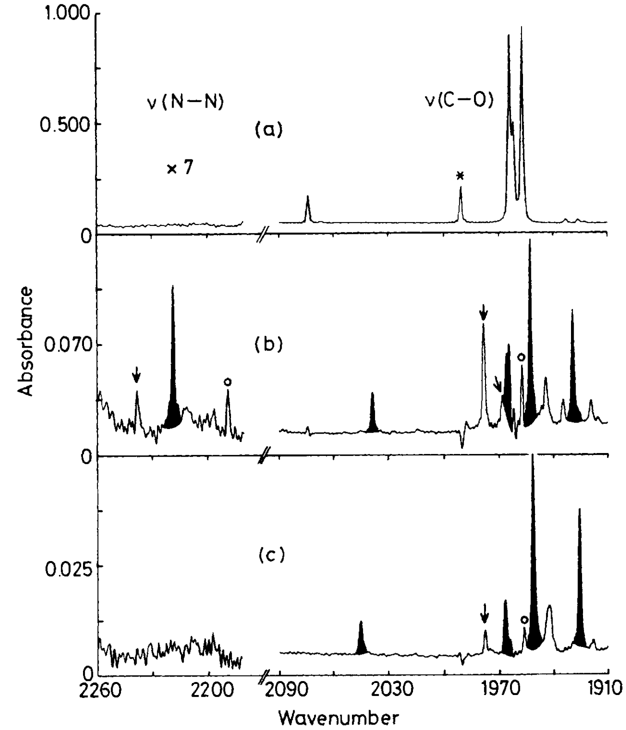


Figure 1. I.r. spectra in the ν(N–N) and ν(C–O) stretching regions. (a) $[Cr(CO)_5(\text{tr-cyo})]$, (**1**), in liquid Kr at −130 °C, approx. conc. 3 × 10^{-5} M (asterisk marks a trace impurity of $[Cr(CO)_6]$). (b) Spectra obtained after 30 s u.v. photolysis of (**1**) in the presence of dissolved N_2. Bands are labelled as follows: black, *cis*-$[Cr(CO)_4(\text{tr-cyo})(N_2)]$, (**4a**); arrowed, $[Cr(CO)_5(N_2)]$, (**3a**): circled, probably *trans*-$[Cr(CO)_4(\text{tr-cyo})(N_2)]$, (**5a**). (c) Spectra obtained after photolysis of (**1**) under 70 psig (0.5 MPa) pressure of D_2. Bands are labelled as follows: black, *cis*-$[Cr(CO)_4(\text{tr-cyo})(D_2)]$, (**4b**); arrowed, $[Cr(CO)_5(D_2)]$, (**3b**); circled, probably *trans*-$[Cr(CO)_4(\text{tr-cyo})(D_2)]$, (**5b**). Note that the bands of unreacted (**1**) have been removed from spectra (b) and (c) by computer substraction. In both spectra (b) and (c) there are unlabelled bands which are due to unidentified compounds containing neither N_2 or D_2.

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† Compounds (**1**), (**1′**) and (**2′**) proved to have comparable solubility to the corresponding $[M(CO)_6]$ species both in liquid Xe and in liquid Kr. However there are necessarily several i.r. bands due to tr-cyo in the region 3000—2900 cm^{-1}, where η^2-H_2 might be expected to absorb, and most experiments were therefore performed using D_2, which, when co-ordinated, might be expected to absorb ~2200 cm^{-1}. Full experimental details can be found in refs. 4a,b,c.

Table 1. I.r. wavenumbers (cm^{-1}) in liquefied noble gases.[a]

	L = CO		L = *cis*-D$_2$	L = *cis*-N$_2$			L = *trans*-D$_2$	L = *trans*-N$_2$	
[(tr-cyo)M(CO)$_4$L]	**(1)**		**(4b)**	**(4a)**			**(5b)**	**(5a)**	
M = Cr[b]	2074.1	a$_1$		2218.9	a′	ν(N–N)		2188.9	a′ ν(N–N)
	1991.2	a$_1$[c]	2045.3	2038.8	a′		1956.3	1957.3	(b$_1$ + b$_2$)
	1964.1	b$_1$	1966.8	1966.0	a′				
	1961.9	a$_1$	1951.6	1952.8	a″				
	1957.0	b$_2$	1925.8	1929.5	a′				
	(1′)		**(4′b)**	**(4′a)**			**(5′b)**	**(5′a)**	
M = W[d]	2080.9	a$_1$		2198.6	a′	ν(N–N)		2170.6	a$_1$ ν(N–N)
	[e]		2052.6	2043.0	a′				
	1966.6	b$_1$	1963.6	1962.1	a′				
	1954.7	a$_1$	1955.5	1954.9	a″				
	1946.9	b$_2$	1920.8	1922.3	a′				
[(tr-cyo)$_2$M(CO)$_3$L]	**(2′)**		**(6′b)**	**(6′a)**					
M = W[d]				2205.0	a′	ν(N–N)			
	1985.0	b$_2$	2025.0	2021.3	a′				
	1950.5	e	1941.2[f]	1941.0	a″				
			1938 sh	1935.6	a′				

[a] [W(CO)$_5$(N$_2$)] (**3′a**) occurs at 2222.3 cm^{-1} [ν(N–N)], 2087.4 (a$_1$), 1970.9 (e), and 1964.1 (a$_1$) in liquid Xe at −80 °C. Bands due to [M(CO)$_5$L] (**3a**), (**3b**), and (**3′b**) can be found in refs. 4c and 9. [b] LKr, −120 °C. [c] Not observed in LKr, value in LXe at −90 °C. [d] LXe −98 °C. [e] Not observed. [f] A change in band shape was observed from D$_2$ to H$_2$ products presumably as a result of the shoulder moving to higher wavenumber in the H$_2$ product (~1 cm^{-1}).

$$[\mathrm{M(CO)}_x] + \mathrm{H_2} \xrightarrow[\text{liq. Xe}]{\text{u.v.}} [\mathrm{M(CO)}_{x-1}(\mathrm{H_2})] + \mathrm{CO} \qquad (1)$$

$$(\mathbf{1}) + \mathrm{N_2} \xrightarrow{\text{u.v.}} (\mathbf{4a})\ [+\ (\mathbf{5a})] + \mathrm{CO} \qquad (2)$$

$$(\mathbf{6'b}) + \mathrm{N_2} \xrightarrow{\Delta} (\mathbf{6'a}) + \mathrm{D_2} \qquad (3)$$

Figure 1 illustrates i.r. spectra obtained in experiments with [Cr(CO)$_5$(tr-cyo)], (**1**), dissolved in liquid Kr at −130 °C. The ν(C–O) spectrum of (**1**) [Figure 1(a)] shows that the tr-cyo ligand imposes local C_{2v} symmetry on the M(CO)$_5$ moiety, consistent with the solid state structure where the C=C bond is found to eclipse a *trans* pair of CO groups.[8] Figure 1(b) shows the new i.r. bands generated by u.v. photolysis of (**1**) in the presence of dissolved N$_2$. The strongest bands, coloured black, can be reasonably assigned to the previously unknown compound‡ *cis*-[Cr(CO)$_4$(tr-cyo)(N$_2$)], (**4a**), since the frequencies are similar to those of the known compounds [Cr(CO)$_4$(C$_2$H$_4$)$_2$][8a] and [Cr(CO)$_4$(N$_2$)$_2$].[9] The rather weaker bands (arrowed) are due to the known species[9] [Cr(CO)$_5$(N$_2$)]. (**3a**). Weak absorptions (circled) at 2189 and 1957.4 cm^{-1} are probably the ν(N–N) and ν(C–O) band of *trans*-[Cr(CO)$_4$(tr-cyo)(N$_2$)], (**5a**), but the spectroscopic evidence is not conclusive. This spectrum confirms that on photolysis of (**1**), the predominant process is substitution of CO, equation (2).

Figure 1(c) shows the new i.r. bands obtained by photolysis of (**1**) in the presence of D$_2$. The strongest bands, coloured black, are similar in frequency and intensity to those of the dinitrogen complex, (**4a**) [coloured black in Figure 1(b)]. However, the bands cannot be due to (**4a**) because there are no bands in the ν(N≡N) region. These new ν(C–O) bands are only observed when D$_2$ (or H$_2$) is present in the solution and are due to a single compound, since they are always observed with the same relative intensity. The fact that there are four bands means that the compound must contain at least four CO groups, and their wavenumbers relative to those of (**1**) and (**4a**) (see Figure 1 and Table 1) indicate that the Cr centre is still in the zero oxidation state. Even at −120 °C the compound is thermally unstable ($t_{\frac{1}{2}}$ = 1 h) but its lifetime is increased by increasing pressures of D$_2$ above the cell. The most probable structure for the new compound is *cis*-[Cr(CO)$_4$(tr-cyo)(D$_2$)], (**4b**). It is also possible, by analogy

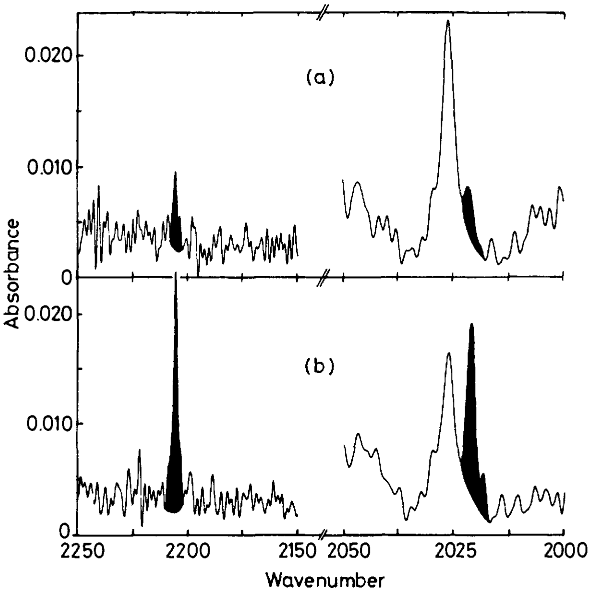

Figure 2. I.r. spectra of ν(N–N) and part of ν(C–O) regions showing the thermal reactions of [W(CO)$_3$(tr-cyo)$_2$(D$_2$)], (**6′b**), (uncoloured bands) with trace N$_2$ to form [W(CO)$_3$(tr-cyo)$_2$(N$_2$)], (**6′a**), (bands coloured black). (a) Spectra generated by 1 min u.v. photolysis of (**2′**) in liquid Xe at −97 °C. (b) Spectrum after 15 min in the dark.

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‡ These bands are due to *mononuclear* products because very similar spectra are observed in solid N$_2$ matrices at 12 K, where there is little chance of polynuclear species being formed.

with (**5a**), to assign tentatively a weak band at 1956 cm^{-1} to *trans*-[$Cr(CO)_4$(tr-cyo)(D_2)].

Similar experiments with $W(CO)_5$(tr-cyo), (**1′**), and *trans*-[$W(CO)_4$(tr-cyo)$_2$], (**2′**), dissolved in liquid Xe have provided i.r. evidence in the ν(C–O) region for the formation of the D_2 complexes, (**4′b**) and (**6′b**) (see Table 1). Unfortunately, none of the D_2 compounds of either Cr or W could be generated in sufficiently high concentrations to allow the detection of i.r. bands associated with co-ordinated η^2-D_2 (or η^2-H_2). However, each of the compounds [(**3b**), (**4b**), or (**6′b**)] reacts thermally with traces of N_2 to give the corresponding dinitrogen complex [(**3a**), (**4a**), or (**6′a**)]. The i.r. spectra in Figure 2 illustrate the evidence for one such reaction, equation (3).

It has been suggested[10,5b] that thermal reaction with N_2 is highly characteristic of non-classical hydrogen complexes but is quite unusual for metal dihydride compounds, which are normally more stable than the corresponding N_2 complexes. There are still too few examples to make reaction with N_2 a definitive test for η^2-H_2 but given our other evidence, it should be taken as strong corroboration.

Perhaps the most striking aspect of this work is the fact that the alkene–hydrogen complexes are thermally much less stable than the corresponding carbonyl–hydrogen compounds. Thus, *cis*-[$Cr(CO)_4$(tr-cyo)(D_2)], (**4b**), has a half-life of ~1 hour at −120 °C in liquid Kr, while [$Cr(CO)_5(H_2)$], (**3b**), is indefinitely stable in liquid Xe at −70 °C. Similarly, the dinitrogen–alkene complex, (**4a**), is thermally less stable than [$Cr(CO)_5(N_2)$], (**3a**).

This labilizing by alkenes of H_2 or N_2 co-ordinated to d^6 metals was not anticipated, and contrasts sharply with d^8 species, *e.g.* [(η^5-C_5H_5)$Rh(C_2H_4)(N_2)$], which is thermally stable in liquid Xe at these temperatures.[12] So far, there is no simple theoretical rationalisation apart from the general observation that co-ordination of an alkene is likely to increase electron density at the metal centre. This would weaken any interaction between the metal and poor σ-donors such as H_2 or N_2. We are now examining other alkene and diene complexes to see whether the labilization of H_2 is general,§ or the result of the steric bulk of the *trans*-cyclooctene ligand.

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§ Preliminary data[11] suggest that diene–H_2 complexes may be thermally more stable than the species described here.

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