Flash Photolysis of Cr(CO)6 in H2-saturated Cyclohexane Solution: I.R. Spectroscopic Evidence for a Cr(CO)5(H2) Complex at Room Temperature

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Flash photolysis of Cr(CO)6 in H2-saturated cyclohexane solution leads to the formation of Cr(CO)5(H2) as a relatively stable transient ($k = 2.5\,s^{-1}$ at room temperature); Cr(CO)5(H2) is identified by kinetic i.r. spectroscopy, including D2 isotope effects.

The first examples[1] of molecular dihydrogen complexes [*trans*-M(CO)3(PR3)2(H2); M = Mo or W; R = cyclohexyl or Pr^i] have recently been reported as stable compounds. Until now,[2] however, binary dihydrogen complexes of the type M(CO)$_x$(H2) are unknown and important questions relating to their structure and stability remain unanswered. Flash photolysis with i.r. detection has proved to be a powerful technique

for the study of unstable metal carbonyl species, *e.g.*, Cr(CO)5(C6H12),[3] Cr(CO)5(N2),[4] and Mn(CO)5.[5] It provides important structural information not accessible from u.v.–visible spectroscopy and should be particularly well suited to potential molecular dihydrogen complexes. We present here the first evidence for the binary molecular dihydrogen complex Cr(CO)5(H2) at room temperature and normal

pressure, thus complementing the evidence for this compound at low temperature presented in the preceding communication.[2]

The i.r. monitored flash photolysis equipment[6] and modified sample preparation procedures[4] have been described previously. Flash photolysis (xenon pulse, $t_{\frac{1}{2}}$ $ca.$ 1.5 μs) of 6 × 10^{-4} M $Cr(CO)_6$ in H_2-saturated cyclohexane solution generated $Cr(CO)_5(C_6H_{12})^3$ (ν_{CO} 1960 and 1937 cm^{-1}) as the first detectable photoproduct [equation (1)].

$$Cr(CO)_6 \xrightarrow[C_6H_{12}]{hv} Cr(CO)_5(C_6H_{12}) + CO \qquad (1)$$
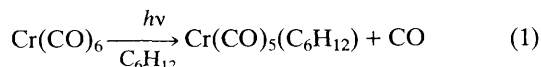
The decay of this complex followed first-order kinetics [k = 19 000 s^{-1}, Figure (1a)]. Concurrent with the disappearance of $Cr(CO)_5(C_6H_{12})$, a prominent band appeared at 1974 cm^{-1} [Figure 1(b)] and a much weaker band at 2092 cm^{-1}. We assign these new features in the i.r. spectrum (Figure 2) to $Cr(CO)_5(H_2)$, formed through reaction of $Cr(CO)_5(C_6H_{12})$ with H_2 [equation (2)].

$$Cr(CO)_5(C_6H_{12}) + H_2 \rightarrow Cr(CO)_5(H_2) + C_6H_{12} \qquad (2)$$
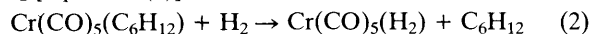
$Cr(CO)_5(H_2)$ is itself thermally unstable, and it decayed with a rate constant of 2.5 s^{-1} (at [H_2] $ca.$ 5 × 10^{-3} M;† monitored at all points shown in Figure 2).

This study is restricted to the CO stretching region of the i.r. spectrum. Therefore, we have no direct spectroscopic evidence that the new complex (Figure 2) contains H_2. However, experiments with D_2 revealed significant kinetic differences. Under the same conditions as above, $Cr(CO)_5(D_2)$ was formed with a rate constant of 10 000 s^{-1} and disappeared with a rate constant of 0.5 s^{-1} [$cf.$ 19 000 and 2.5 s^{-1}, respectively, for $Cr(CO)_5(H_2)$]. This may represent a dissociation rate constant for $Cr(CO)_5(H_2)$, through loss of H_2, which is approximately one order of magnitude higher than the corresponding rate constant for $Cr(CO)_5(D_2)$. Furthermore, in our experience $Cr(CO)_5(C_6H_{12})$ $only$ decays with k > 1000 s^{-1} in the presence of an added scavenger, $e.g.$, N_2^4 or H_2O.[3] The rate constant, k = 19 000 s^{-1}, for the reaction of $Cr(CO)_5(C_6H_{12})$ with H_2 can be compared with k = 18 000 s^{-1} for reaction with N_2^4 and k = 43 000 s^{-1} for reaction with CO[3] (all rate constants measured at a pressure of $ca.$ 1.3 bar of gas). In addition, the transient i.r. spectrum shown in Figure 2 is not observed in solutions free of H_2 and is quite different from previously investigated $Cr(CO)_5L$ species.[3,4,6]

By comparing the spectrum of $Cr(CO)_5(H_2)$ in liquid xenon[2] with that in Figure 2, there is no doubt we are observing the same species. We assign the weak band at 2092 cm^{-1} to the high-frequency a_1 vibration expected for a square-pyramidal $Cr(CO)_5$ skeleton. The stronger band at 1974 cm^{-1} probably represents a superposition of the e and the low-frequency a_1 vibrations. Direct evidence for this comes from D_2 isotopic studies in liquid xenon[2] where the shape of this band was clearly affected by D_2 substitution. Such small shifts, however, are not detectable under our somewhat lower resolution conditions (typically 7 cm^{-1} in Figure 2). Indeed, the transient i.r. spectra of $Cr(CO)_5(H_2)$ and $Cr(CO)_5(D_2)$ are the same within experimental error. Under higher resolution ($ca.$ 4 cm^{-1}) there was still no indication of the a_1 vibration becoming even partially resolved. It is likely, therefore, that in cyclohexane solution the e and low-frequency a_1 vibrations are nearly coincident.

Our observations favour a molecular dihydrogen complex rather than a hydride which would be expected to display CO

stretching vibrations at higher frequencies[8] than those encountered in this study. By analogy with the $W(CO)_3$-$(PPr^i_3)_2(H_2)$ complex[1] it is likely that the H_2 ligand of $Cr(CO)_5(H_2)$ is bonded side-on.

The rate constants (at [H_2] = $ca.$ 5 × 10^{-3} M†) for formation of $Cr(CO)_5(H_2)$ (k = 19 000 s^{-1}) and its disappearance (k = 2.5 s^{-1}) are similar to those of the N_2 analogue:[4] k = 18 000 and 1.7 s^{-1} for the respective processes. This suggests that $Cr(CO)_5(H_2)$ and $Cr(CO)_5(N_2)$ have similar stabilities. Moreover, this correlation provides further support for the molecular dihydrogen complex nature of the new transient. Notably, the transient i.r. spectra of $Cr(CO)_5(H_2)$ (ν_{CO} 2092 and 1974 cm^{-1}; Figure 2) and $Cr(CO)_5(N_2)$ (ν_{CO} 2086, 1976, and 1966 cm^{-1}, ν_{NN} 2240 cm^{-1}) are easily distinguishable which is not possible in flash photolysis experiments with u.v.–visible detection where both transients uniformly peak at 370 nm.[9] This again shows the value of i.r.-monitored flash photolysis as an analytical technique.
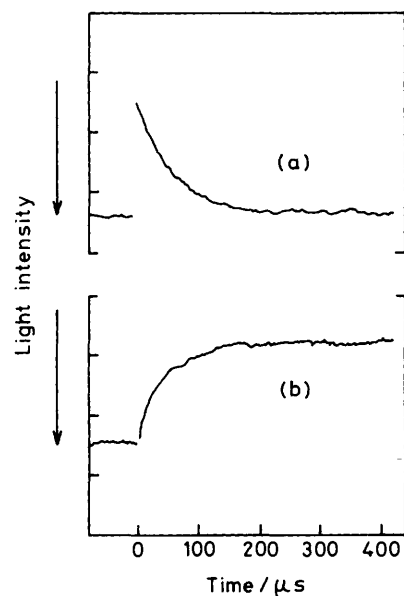

Figure 1. (a) The decay of $Cr(CO)_5(C_6H_{12})$ at 1960 cm^{-1} together with (b) the concurrent grow-in of $Cr(CO)_5(H_2)$ at 1974 cm^{-1} in H_2-saturated cyclohexane solution at room temperature.
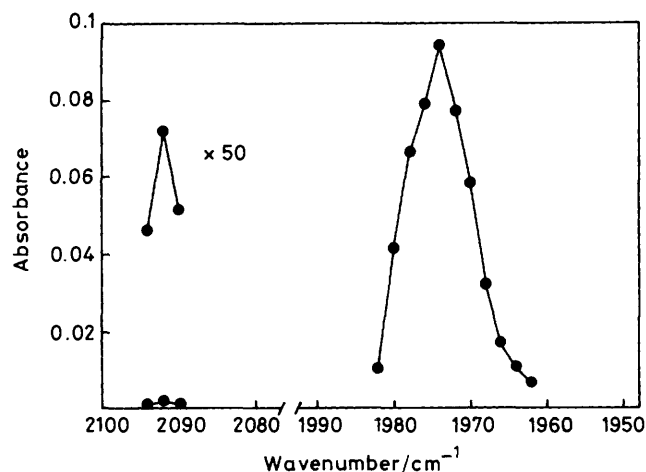

Figure 2. Transient i.r. spectrum of $Cr(CO)_5(H_2)$ in H_2-saturated cyclohexane solution at room temperature. The weak high-frequency a_1 vibration is also shown on ×50 expansion.

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