Organometallic Photochemistry in Supercritical Fluids: the Reaction of H_2 with $[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Re and Mn) and the Formation of a 'Non-classical' Dihydrogen Complex of Manganese(I)

Steven M. Howdle and Martyn Poliakoff*

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.

U.v. photolysis of $[(cp)M(CO)_3]$ (cp = η^5-C_5H_5, M = Re and Mn) at room temperature in supercritical Xe pressurized with H_2, leads to formation of the dihydride, $[(Cp)Re(CO)_2H_2]$, and the 'non-classical' dihydrogen complex, $[(cp)Mn(CO)_2(H_2)]$, which is stabilized by the high pressure of H_2.

Photolysis of organometallics in the presence of H_2 is a convenient and fairly general method for the generation of thermally labile dihydrogen and dihydride complexes.[1] Unfortunately, the route is limited by the rather low solubility of H_2 in most common hydrocarbon solvents at room temperature. This limitation can be removed completely by carrying out the reactions in supercritical fluids, such as CO_2 or Xe.† These fluids are totally miscible with gaseous H_2 or N_2 yet, like hydrocarbon solvents, they can dissolve a wide range of neutral organometallic compounds.[2,3] Thus, for a given pressure of H_2, the supercritical environment will provide a much higher concentration of 'dissolved' H_2 than in a conventional solvent.‡

We have recently developed[3] a miniature high pressure cell§ for performing supercritical reactions at temperatures up to 100 °C. We illustrate its use with the reaction of H_2 and $[(cp)M(CO)_3]$ (cp = η^5-C_5H_5, M = Re and Mn). This reaction is of considerable interest because the electronic properties[4] of the $(cp)Mn(CO)_2$ moiety suggest that the reaction product should be a relatively stable 'non-classical' dihydrogen complex.

---

† The critical points of these substances are CO_2 (31 °C, 74 atm) and Xe (17 °C, 59 atm) (10.1 atm = *ca.* 1 MPa).

‡ In addition, supercritical Xe is totally transparent throughout the u.v., visible, and mid-i.r. regions, making it particularly easy to monitor reactions spectroscopically.

§ The stainless steel cell has a cold finger for condensing in the Xe. It has CaF_2 windows (1 cm thick) and, in these experiments, a 1.8 mm pathlength. In a typical experiment the cell contained *ca.* 3 g of Xe, 1—2 mg of $[(cp)M(CO)_3]$ and 100 atm overpressure of H_2 gas, giving *ca.* 175 atm total pressure at +25 °C. Under these conditions, the concentration of dissolved $[(cp)M(CO)_3]$ is less than 1/10 of the saturated solution and so no undissolved solid is present in the cell. A Cermax 300 W Xe lamp filtered to give u.v. light, 200—400 nm, was used for photolysis.

Safety note: experiments in supercritical fluids involve relatively high pressures of gases and should be approached with caution.

Table 1. Wavenumbers[a] cm^{-1}, of ν(C–O) i.r. bands in supercritical Xe at 25 °C.

$[(cp)Mn(CO)_3]$[b]		$[(cp)Mn(CO)_2(H_2)]$		$[(cp)Mn(CO)_2(N_2)]$[c]	
				2171.3	ν(N–N)[d]
2032.8	a_1	1991.9 (1992.3)[e]	a′	1985.0	a′
1952.3	e	1932.5 (1931.4)[e]	a″	1934.0	a″
2021.5	$\nu(^{13}C–O)$	—[f]	$\nu(^{13}C–O)$	—[f]	$\nu(^{13}C–O)$
1917.3	$\nu(^{13}C–O)$	1903.8 (1901.5)[e]	$\nu(^{13}C–O)$	1904.3	$\nu(^{13}C–O)$
$[(cp)Re(CO)_3]$		$[(cp)Re(CO)_2H_2]$[g]		$[(cp)Re(CO)_2(N_2)]$[h]	
				2146.8	ν(N–N)
2035.0	a_1	2028.4	a_1	1978.4	a′
1946.9	e	1962.0	b_1	1925.8	a″
2023.9	$\nu(^{13}C–O)$	—		—	
1012.1	$\nu(^{13}C–O)$	—		—	

[a] Spectra recorded on Nicolet 730 Fourier transform (F.t.) i.r. interferometer (16K data points, 32K transform points) error ± 0.2 cm^{-1}. [b] *ca.* 40 other i.r. bands (fundamentals, overtones *etc.*) due to $[(cp)Mn(CO)_3]$ could be observed in the range 4400—1100 cm^{-1}. [c] Reported values,[6] 2169, 1980 and 1923 cm^{-1} in hexane. [d] 2137.2 cm^{-1} $\nu(^{14}N–^{15}N)$ satellite, natural isotopic abundance. [e] Values in parentheses for $[(cp)Mn(CO)_2(D_2)]$. [f] These $\nu(^{13}C–O)$ satellites obscured by other bands. [g] Reported values (ref. 5), 2022 and 1954 in n-heptane. [h] Reported values (ref. 12), 2141, 1970, and 1915 cm^{-1} in hexane.

Figure 1 shows part of the i.r. spectra recorded after u.v. photolysis of $[(cp)Re(CO)_3]$ and $[(cp)Mn(CO)_3]$ with H_2 in supercritical Xe (scXe) at room temperature.¶ The i.r. data are summarized in Table 1. The following points are clear from these spectra. (i) The i.r. spectra of the starting materials, $[(cp)Mn(CO)_3]$ and $[(cp)Re(CO)_3]$, are almost identical. (ii) The ν(C–O) bands of the photoproducts (coloured black in Figure 1) are quite different for the two metals. The bands of the Re species appear *between* those of $[(cp)Re(CO)_3]$, while the bands of the Mn photoproduct are shifted *down* in wavenumber relative to $[(cp)Mn(CO)_3]$. (iii) The Re photoproduct can be identified from its ν(C–O) spectrum as the known[5] dihydride, $[(cp)Re(CO)_2H_2]$, formed by oxidative addition of H_2 to the Re centre. This change in oxidation state is underlined by the fact that the ν(C–O) bands of $[(cp)Re(CO)_2H_2]$ occur at substantially higher wavenumber than the corresponding bands of $[(cp)Re(CO)_2(N_2)]$ (average shift +43 cm^{-1}, see Table 1). (iv) By contrast, the ν(C–O) bands of the Mn photoproduct are very close in wavenumber to those of $[(cp)Mn(CO)_2(N_2)]$ (average shift +5 cm^{-1}), suggesting that Mn has the same oxidation state in both compounds. The photoproduct clearly contains hydrogen co-ordinated to the metal, because there is a small but definite increase (+1.5 cm^{-1}) in the separation of the two ν(C–O) bands when D_2 is used instead of H_2.‖

Thus, the evidence indicates that photolysis of $[(cp)Mn(CO)_3]$ in the presence of H_2 leads to the formation of a dihydrogen complex rather than a dihydride, equation (1).

$$[(cp)Mn(CO)_3] + H_2 \xrightarrow{\text{u.v., scXe}} [(cp)Mn(CO)_2(H_2)] + CO \quad (1)$$

$[(cp)Mn(CO)_2(H_2)]$ is surprisingly stable in scXe at room temperature under a pressure of H_2, decaying by less than 50% overnight. If, however, the H_2 is vented and the cell refilled with N_2, the compound reacts smoothly with N_2 to form the known compound[6] $[(cp)Mn(CO)_2(N_2)]$. Under the conditions used this exchange reaction was complete in less than 70 min,†† see equation (2) and Figure 2.

$$[(cp)Mn(CO)_2(H_2)] + N_2 \xrightarrow{\Delta,\text{scXe}} [(cp)Mn(CO)_2(N_2)] + H_2 \quad (2)$$

Thermal reaction with N_2 is characteristic of dihydrogen complexes[7] and our observation underlines the non-classical nature of $[(cp)Mn(CO)_2(H_2)]$, apparently the first Mn compound of this type.‡‡ In contrast to this behaviour, the dihydride, $[(cp)Re(CO)_2H_2]$, does not react thermally§§ with N_2, even over periods of many hours in the presence of high pressures of N_2 (*e.g.* 100 atm).

Complex $[(cp)Re(CO)_2H_2]$ is not formed directly from $[(cp)Re(CO)_3]$. There is initial formation of an unstable photoproduct, X, which decays in the dark without formation of $[(cp)Re(CO)_2H_2]$. Under u.v. irradiation, X rapidly reaches a low steady state concentration and $[(cp)Re(CO)_2H_2]$ is formed. This suggests that X is an intermediate in the formation of $[(cp)Re(CO)_2H_2]$.

$$[(cp)Re(CO)_3] + H_2 \xrightarrow{\text{u.v., scXe}} X \xrightarrow{\text{u.v., scXe}} [(cp)Re(CO)_2H_2] \quad (3)$$

¶ For both metals, photolysis also generates free CO which, under these conditions, gives rise to two broad i.r. absorptions (*P* and *R* branches, centred at *ca.* 2150 cm^{-1}, with unresolved rotational fine structure).

‖ This shift in ν(C–O) is not due to a solvent effect because the bands of $[(cp)Mn(CO)_3]$ are unshifted when D_2 is used instead of H_2. Despite the i.r. transparency of scXe, we were unable to observe any bands directly associated with co-ordinated η^2-H_2, probably because there are relatively strong ν(C–H) bands due to the cp group in the region *ca.* 3000—2700 cm^{-1} where ν(H–H) bands might be expected.[1c] Neither did we observe bands due to co-ordinated D_2 but the shifts in the ν(C–O) bands (see Table 1) suggest that the ν(D–D) may be masked by the much more intense ν(C–O) bands.

†† $[(cp)Mn(CO)_2(N_2)]$ can also be generated directly by u.v. photolysis of $[(cp)Mn(CO)_3]$ in the presence of N_2.

‡‡ Allowing for a solvent shift in the ν(C–O) bands, the $[(cp)Mn(CO)_2(H_2)]$ complex generated in scXe appears to be the same as the unstable species previously observed[8] but not isolated on protonation of the anion $[(cp)Mn(CO)_2]^{2-}$ in solution in tetrahydrofuran. However, this protonation experiment did not lead to any discussion on the nature of the co-ordinated H_2.

§§ There is, however, a photochemical reaction between $[(cp)Re(CO)_2H_2]$ and N_2 which produces a new ν(N–N) band at 2178.4 cm^{-1}, presumably due to a mixed dinitrogen/dihydride complex.

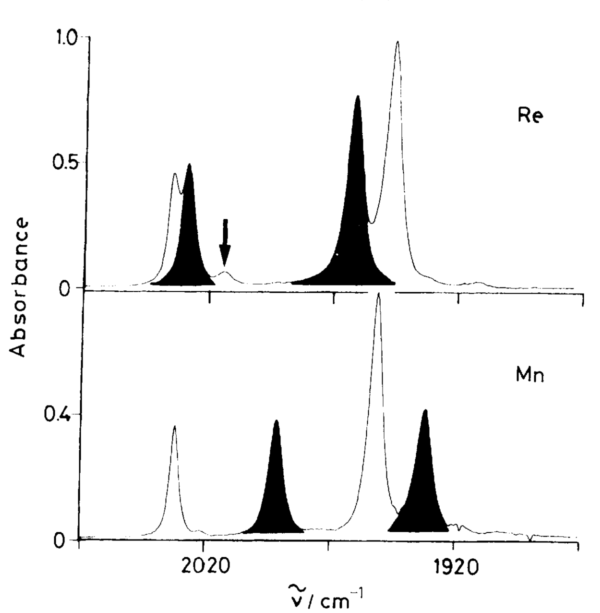


Figure 1. I.r. spectra in the ν(C–O) region, obtained after (a) 10 min u.v. photolysis of $[(cp)Re(CO)_3]$ and (b) 5 s u.v. photolysis of $[(cp)Mn(CO)_3]$ in scXe and H_2 § at 25 °C. The bands are labelled as follows: coloured, major photoproducts, $[(cp)Re(CO)_2H_2]$ and $[(cp)Mn(CO)_2(H_2)]$; Unlabelled, unreacted $[(cp)M(CO)_3]$; arrowed, primary photoproduct which rapidly reaches steady state, see text.¶¶

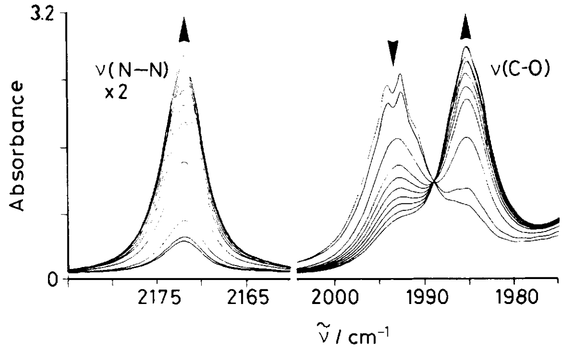
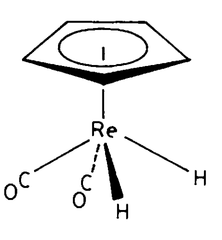
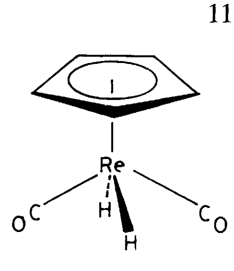


Figure 2. I.r. spectra in the ν(N–N) and part of the ν(C–O) regions showing the thermal reaction of $[(cp)Mn(CO)_2(H_2)]$ with N_2 in scXe at 25 °C. $[(cp)Mn(CO)_2(H_2)]$ was initially generated photochemically. The contents of the high pressure cell were then condensed into the cold finger of the cell, most of the H_2 was vented, the cell was repressurized with N_2 (*ca.* 100 atm) and the cold finger was warmed up. The first spectrum shown was recorded as soon as the cold finger had warmed to room temperature and subsequent spectra were taken at 10 min intervals. The band labelled ▼ is due to $[(cp)Mn(CO)_2(H_2)]$ and those labelled ▲ are due to the known compound[6] $[(cp)Mn(CO)_2(N_2)]$. Note that the ν(N–N) band has been plotted with a ×2 expansion in the ordinate scale.



cis-unstable



trans-stable

X has a ν(C–O) band, arrowed in Figure 1, at 2013.8 cm^{-1} {14.6 cm^{-1} lower than that of $[(cp)Re(CO)_2H_2]$}. By comparison with matrix isolation experiments,[9] we suggest that X is $[(cp)Re(CO)_2H_2]$ with the two H atoms *cis* rather than *trans* as found in the stable isomer of $[cpRe(CO)_2H_2]$.¶¶ It is presumably the high concentration of H_2 in the supercritical fluid, which stabilizes X sufficiently to make the subsequent photochemical generation of $[(cp)Re(CO)_2H_2]$ possible.

These experiments show that there is a clear difference in the way that the Mn and Re centres react with hydrogen; Mn forms a dihydrogen complex while Re forms a dihydride. This behaviour is reminiscent of the reactivity of these species towards $HSiR_3$ or $HSnR_3$ compounds; Re undergoes complete oxidative addition while for Mn the process is 'arrested.'[10,11] In both cases the difference is presumably due to greater electron density on the Re centre. The high 'effective' concentration of H_2 in a supercritical fluid is clearly stabilizing $[(cp)Mn(CO)_2(H_2)]$ at room temperature. Work is now in progress to carry out such reactions on a preparative scale.

We thank the S.E.R.C., E.E.C., the Donors of the Petroleum Research Fund, B.P. Venture Research Unit and I.C.I. Chemicals and Polymers Ltd. for support and the Nuffield Foundation for a Science Research Fellowship (M. P.). We are grateful to Professor J. J. Turner, Dr. M. A. Healy, Dr. R. Whyman, and Mr. J. M. Whalley for their help and advice, to Dr. R. N. Perutz for a sample of $[(cp)Re(CO)_3]$, and to Dr. A. J. Rest for communicating his results[9] in advance of publication.

Received, 17th April 1989; Com. 9/01574D

¶¶ In an Ar matrix, *cis*-$[(cp)Re(CO)_2H_2]$ has two ν(C–O) bands; the first at 1999 cm^{-1} {13 cm^{-1} lower than the corresponding band of *trans* $[(cp)Re(CO)_2H_2]$} and the second at 1927 cm^{-1}, which allowing for the solvent shift would probably be masked in our scXe experiment. The formation of the intermediate X explains at least partly why the photolysis time required to generate $[(cp)Re(CO)_2H_2]$ was much longer than that needed for $[(cp)Mn(CO)_2(H_2)]$, which is apparently formed directly from $[(cp)Mn(CO)_3]$. For both metals, prolonged photolysis eventually results in complete destruction of the parent $[(cp)M(CO)_3]$.

References

1 See, *e.g.*, M. J. Mirbach, in 'High Energy Processes in Organometallic Chemistry,' ACS Symp. Ser. No. 333, ed. K. S. Suslik, 1987, p. 110; (b) 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; (c) M. Poliakoff, J. J. Turner, and R. K. Upmacis, *J. Am. Chem. Soc.*, 1986, **108**, 3645.

2 M. McHugh and V. Krukonis 'Supercritical Fluid Extraction,' Butterworth, Boston, 1986.

3 M. Poliakoff, S. M. Howdle, M. A. Healy, and J. M. Whalley, in Proc. Int. Symp. Supercritical Fluids, ed. M. Perrut, *Soc. Chim.*, France, 1988, p. 967.

4 R. H. Morris, K. A. Earl, R. L. Luck, N. J. Lazarowych, and A. Sella, *Inorg. Chem.*, 1987, **26**, 2674.

5 J. K. Hoyano and W. A. G. Graham, *Organometallics*, 1982, **1**, 783.

6 D. Sellmann, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 919.

7 See, *e.g.*, R. H. Crabtree and D. G. Hamilton, *Adv. Organomet. Chem.*, 1989, **28**, 299.

8 V. S. Leong and N. J. Cooper, *Organometallics*, 1988, **7**, 2080.

9 A. J. Rest, A. K. Capen, M. A. Ollino, W. A. G. Graham, and L. Sturgeoff, to be published.

10 W. A. G. Graham, *J. Organomet. Chem.*, 1986, **300**, 81.

11 U. Schubert, E. Kunz, B. Harkers, J. Willnecker, and J. Meyer, *J. Am. Chem. Soc.*, 1989, **111**, 2752; U. Schubert, *Adv. Organomet. Chem.*, 1989, **30**, in the press.

12 D. Sellmann, *J. Organomet. Chem.*, 1972, **36**, C27.