

## The Photochemistry of Some Transition Metal Carbonyl Compounds in a 2-Methyltetrahydrofuran Matrix

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*Photolysis of some carbonyl halides of Mn and cyclopentadienylmetal carbonyl halide derivatives of Fe, Mo and W in a 2-methyltetrahydrofuran (MTHF) matrix at about 77 K leads to extrusion of CO, which becomes matrix-trapped, and formation of an unsaturated derivative characterised by i.r. spectroscopy; at ca. 30 K the Mo and W compounds readily undergo a reaction not involving loss of CO, the precise nature of which is uncertain. Photolysis at 77 K of the dimers  $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ ,  $M = \text{Mo}, \text{W}$  results in i.r. changes compatible with metal-metal bond homolysis, whilst that of  $\text{Re}(\text{CO})_5\text{X}$  (unlike  $\text{Mn}(\text{CO})_5\text{X}$   $X = \text{Cl}, \text{Br}$ ) does not involve loss of CO.*

### Introduction

For many years there has been interest in the photochemistry of metal carbonyls  $\text{M}(\text{CO})_n$  in solution, particularly in the co-ordinatively unsaturated primary photochemical product  $\text{M}(\text{CO})_{n-1}$  and its reactions [1]. Turner [2] and others [3, 4] have reported evidence that the equilibrium geometry of the pentacarbonyls  $\text{M}(\text{CO})_5$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) is square pyramidal ( $\text{C}_{4v}$ ) and the species originally thought [3] to be a  $\text{D}_{3h}$  isomer of  $\text{M}(\text{CO})_5$  is considered [2, 4] to be polymeric. At low temperatures in weakly interacting matrices such as  $\text{CH}_4$  or Ar doped with nitrogen, evidence has been presented [5] suggesting that the primary photochemical product is  $\text{Cr}(\text{CO})_5\text{S}$ , where  $S = \text{CH}_4$  or  $\text{N}_2$  and it has been proposed [2, 5] on the basis of these and results of others [6] that the primary photochemical product of  $\text{Cr}(\text{CO})_6$  in solution at room temperature is  $\text{Cr}(\text{CO})_5\text{S}$ , where  $S = \text{solvent}$ . These views have been contested by Ozin [7] who prefers a trigonal bipyramidal geometry ( $\text{D}_{3h}$ ) for  $\text{M}(\text{CO})_5$ , but supported by Braterman [8]. Low temperature matrix isolation studies have also provided evidence for a variety of co-ordinatively unsaturated species including tricarbonylnickel [9], diiron octacarbonyl [10] and hydridotetracarbonyl manganese [11].

As part of our current programme aimed at elucidating the photochemistry of metal carbonyl compounds (particularly halide derivatives) in solution [12], we here present the results of irradiating some of these compounds in a transparent MTHF matrix at cryogenic temperatures, using i.r. spectroscopy as the means of monitoring the reaction and characterising products.

### Results and Discussion

The i.r. changes resulting from irradiating the iron carbonyl halides  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ , where  $X = \text{Cl}, \text{Br}, \text{I}$ , are summarized in Table I; in all cases, warming the matrix to room temperature following photolysis led to a reversal to the spectrum of starting material. We conclude that loss of CO is again the dominant process, although we cannot preclude the operation of a cage effect forcing the return of any photoproduct  $\text{Cl}^-$  (diameter 360 pm) back to the metal centre, whilst enabling the smaller CO molecule (produced possibly in smaller yield) to escape the cage, becoming trapped nearby. This behaviour is in sharp contrast to the photoreactions of those compounds in co-ordinating solvents at room temperature in which heterolysis of the Fe-X bond has been observed to give  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^+$  [3]. At 30K,  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$  underwent no perceptible change during a 28 min irradiation in contrast to its Mo and W analogues (see below).

Photolysis of some molybdenum and tungsten carbonyl halides at 77 K gives a set of results (Table II) very similar to that obtained for the iron compounds and from which we draw identical conclusions; a typical spectral profile is shown in Fig. 1. However, at much lower temperatures, photolysis of the chlorides took a different course (cf. Table III) and in particular the i.r. peak around  $2130\text{ cm}^{-1}$ , characteristic of matrix-trapped CO, was absent. This can be interpreted in several ways, (i) a homolysis or heterolysis of the metal-chlorine bond, (ii) an alteration in molecular geometry, possibly involving a change from  $\pi$ - to  $\sigma$ -bonding of the cyclopentadienyl

TABLE I. Irradiation of  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ , where X = Cl, Br, I in a MTHF matrix

Compound	Temperature /K	I.r. ( $\text{cm}^{-1}$ ) before Photolysis	Main I.r. Bands Growing in during Photolysis
$(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$	77.3	2040(vs) 1982(vs) 1910(vw), 1882(sh)	2130(vw), 1942(m)
$(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$	80	2040(vs), 1982(vs), 1913(w), 1885(sh)	2135(m), 1943(s)
$(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$	77.6	2034(vs), 1977(vs) 1917(w), 1886(sh)	2135(vw), 1945(w)

TABLE II. Irradiation of Some Molybdenum and Tungsten Carbonyl Halides in a MTHF Matrix

Compound	Temperature /K	I.r. ( $\text{cm}^{-1}$ ) before Photolysis	Main I.r. Bands Growing in during Photolysis
$(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Cl}$	77	2040(s), 1932(s)	2130(m), 1832(s), 1780(s)
$(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Cl}$	77	2040(m), 1935(s)	2130(m), 1850(s), 1815(s), 1760(s)

TABLE III. Irradiation of Some Molybdenum and Tungsten Carbonyl Halides in a MTHF Matrix at Temperatures  $\leq 40\text{K}$ .

Compound	Temperature /K	I.r. ( $\text{cm}^{-1}$ ) before Photolysis	Main I.r. Bands Growing in during Photolysis
$(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Cl}$	35	2047(s), 2010(sh), 1950(s), 1920(sh), 1890(sh), 1862(sh)	1960(s), 1860(m)
$(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{I}$	40	2032(s), 1943(s) 1920(sh)	No new bands
$(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Cl}$	27.5	2040(s), 1935(s) 1885(sh)	1945(s), 1840(s)

TABLE IV. Irradiation of  $\text{M}(\text{CO})_5\text{X}$ , where M = Mn or Re and X = Cl or Br in a MTHF Matrix

Compound	Temperature /K	I.r. ( $\text{cm}^{-1}$ ) before Photolysis	Main I.r. Bands Growing in during Photolysis
$\text{Mn}(\text{CO})_5\text{Cl}$	80	2335(w), <sup>a</sup> 2130(vw), 2040(vs), 2000(s), 1998(m), 1915(w)	2335(m), <sup>a</sup> 2130(m) 1915(m)
$\text{Mn}(\text{CO})_5\text{Br}$	77	2130(vw), 2040(vs) 2005(s)	2130(m), 1920(br)
$\text{Re}(\text{CO})_5\text{Cl}$	80	2035(vs), 1972(m) 1915(w)	2008(m), 1978(w) 1927(m)
$\text{Re}(\text{CO})_5\text{Br}$	80	2035(vs), 1980(s), 1915(w)	2008(m), 1927(m)

<sup>a</sup>Probably  $\text{CO}_2$  condensate on cell window.

ring, or from 'end-on' to 'sideways-on' bonding of one or more of the CO ligands or even an axial/equatorial ligand relocation to give a species of lower

symmetry. In all cases the starting material was regenerated during the warm-up sequence at temperatures below 77 K. Which of the several possibilities is

TABLE V. Irradiation of  $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$  where M = Mo, W in a MTHF Matrix

Compound	Temperature /K	I.r. ( $\text{cm}^{-1}$ ) before Photolysis	Main I.r. Bands Growing in during Photolysis
$[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$	81	2335(w), <sup>a</sup> 2002(m), 1948(s), 1900(s)	2335(w), <sup>a</sup> 1920(m) 1845(w)
$[(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$	80	2338(w), <sup>a</sup> 2040(m) 1945(s), 1917(sh), 1895(vs)	2338(m), <sup>a</sup> 2040(m), 1917(m), 1886(m), 1828(w), 1706(m)

<sup>a</sup>Probably  $\text{CO}_2$  condensate on cell window.

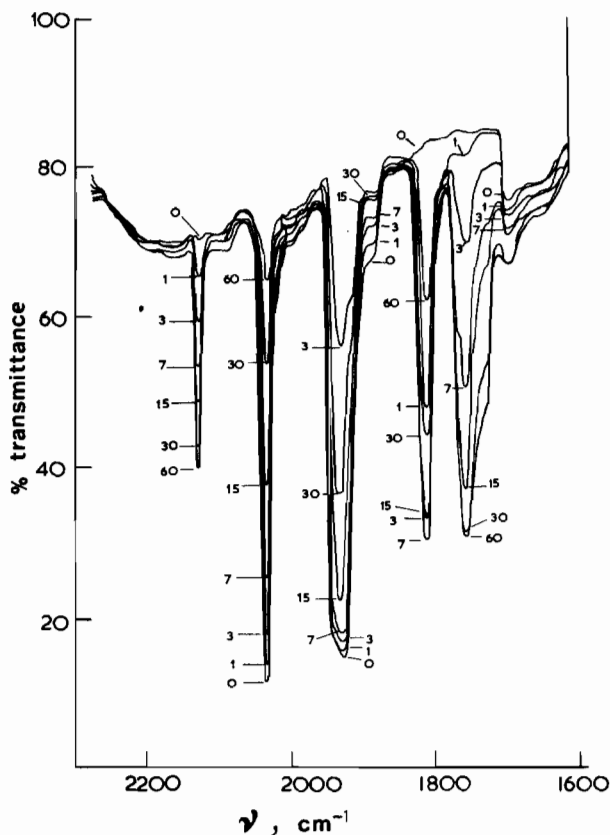


Figure 1. I.r. spectral profile for the irradiation of  $(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Cl}$  in a 2-MTHF matrix at 77 K. Irradiation times are in minutes.

correct is difficult to decide. Since at 30 K, loss of CO is clearly more difficult in the hard MTHF matrix (although not in argon [2], *etc.*) than at 77 K, it is probable that loss of Cl as the large  $\text{Cl}^-$  ion is ruled out, and temperature-reversed isomerisation is to be preferred.

The results of photolysing  $\text{M}(\text{CO})_5\text{X}$ , where M = Mn and Re and X = Cl and Br in a MTHF matrix at 77 K are summarised in Table IV. As evinced by the appearance of the peak at  $2130\text{ cm}^{-1}$  in the case of both Mn compounds, loss of CO is the main primary

photochemical step and this stands in contrast to the consequence of photolysing these materials in coordinating solvents at room temperatures [12d]. The product bands again refer to a  $\text{M}(\text{CO})_4\text{X}(\text{MTHF})$  species. At lower temperatures, photolysis of  $\text{Mn}(\text{CO})_5\text{Cl}$  was reduced to a minimal extent.  $\text{Re}(\text{CO})_5\text{X}$  photo-reacts at 77 K to produce a new band at  $2008\text{ cm}^{-1}$  without concomitant production of matrix-trapped CO, contrasting in both respects here with the Mn analogues. Apparently a different fragmentation is occurring, presumably loss of X as  $\text{X}^-$  or  $\text{X}^\cdot$  to leave  $\text{Re}(\text{CO})_5^+$  or  $\cdot\text{Re}(\text{CO})_5$  respectively; the latter probably assumes the co-ordinated form  $\text{Re}(\text{CO})_5(\text{MTHF})$  as the i.r. bands do not correspond to those found [13] for  $\text{Re}(\text{CO})_5$  prepared in an argon matrix, *i.e.* 1995(s), 1977(w).

Irradiation of  $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$  M = Mo, W in a MTHF matrix at about 80 K results in the i.r. spectral changes shown in Table V. No matrix-trapped CO is liberated and the transformations presumably involve a cleavage of the metal-metal bond to yield the  $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3^\cdot$  radical (possibly in its MTHF-solvated form): analogous homolyses have recently been characterised by e.s.r. spectroscopy following spin-trapping of the metal-centred radical [14]. At 30 K the tungsten dimer undergoes the same transformation as at 80 K, which is rather surprising in view of the size of the 'leaving' fragment.

To summarise, CO-loss together with the formation of  $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_{n-1}\text{X}(\text{MTHF})$  or  $\text{M}(\text{CO})_{n-1}\text{X}(\text{MTHF})$  is the dominant reaction of metal carbonyl halides at 77 K, although a different i.r. change takes place with  $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$  (M = Mo, W) at 30 K. Dimeric compounds tend to cleave at both 30 and 77 K, and  $\text{Re}(\text{CO})_5\text{X}$  behaves in a unique manner.

## Experimental

### Materials

2-Methyltetrahydrofuran was dried over  $\text{CaH}_2$ , doubly distilled from Na and stored under dry nitrogen.  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}]$  and  $\text{Cr}(\text{CO})_6$  were supplied by Alpha Inorganics, the former being recrystallised from (1:1) petroleum ether (60–80 °C) and benzene,

and the latter sublimed; Fe(CO)<sub>5</sub> was supplied by Strem Chemicals and used without further purification. The following compounds were prepared by literature methods, Mn(CO)<sub>5</sub>Cl [15], Mn(CO)<sub>5</sub>Br [16], Re(CO)<sub>5</sub>Cl [17], Re(CO)<sub>5</sub>Br [18], [(π-C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>]<sub>2</sub> [19], [(π-C<sub>5</sub>H<sub>5</sub>)W(CO)<sub>3</sub>]<sub>2</sub> [15], (π-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Cl [20], (π-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Br [21], (π-C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>Cl [22], (π-C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>I [23], π-C<sub>5</sub>H<sub>5</sub>W(CO)<sub>3</sub>Cl [22].

#### Apparatus

The cryostat was a model LT-3-110B Liquid Helium Refrigerator as supplied by Air Products and Chemicals Incorporated. Temperatures were recorded by means of a thermocouple comprising chromel vs. gold with 0.07 atomic %Fe, using an icebath as reference junction. A Solatron Digital Voltmeter LM 1420 was employed to record temperatures which were found to be reproducible to ± 0.1 K. Approximately 0.01 mol dm<sup>-3</sup> solutions were irradiated in a demountable cell fabricated from OFHC copper (Philip Cornes and Co. Ltd. of Redditch) and suitably machined to accept a pair of high-purity sapphire windows 0.1 cm thick and 2.5 cm diameter (supplied by Fred Lee and Co. Ltd., Coventry) separated by a 0.02 cm PTFE spacer; the cell was drilled to provide a thermocouple pocket. The entire cryostat could be evacuated to 10<sup>-4</sup> torr and the rate of cooling controlled by a flow meter. Irradiation was by means of an unfiltered Wotan 200 W point source high pressure mercury arc. I.r. spectra were recorded on a Perkin Elmer 621 spectrophotometer.

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#### References

- 1 For example, W. Strohmeier, *Angew. Chem. Internat. Edit.*, **3**, 730 (1964).
- 2 M. A. Graham, M. Poliakoff and J. J. Turner, *J. Chem. Soc. A.*, 2939 (1971).
- 3 I. W. Stolz, G. R. Dobson and R. K. Sheline, *J. Am. Chem. Soc.*, **85**, 1073 (1963).
- 4 M. J. Boylan, P. S. Braterman and A. Fullarton, *J. Organometal. Chem.*, **31**, C39 (1971).
- 5 M. A. Graham, R. N. Perutz, M. Poliakoff and J. J. Turner, *J. Organometal. Chem.*, **34**, C34 (1972).
- 6 M. A. El-Sayed, *J. Phys. Chem.*, **68**, 433 (1964); G. R. Dobson, *ibid.*, **69**, 678 (1965); J. Nasielski, P. Kirsch and L. Wilputte-Steinert, *J. Organometal. Chem.*, **29**, 269 (1971).
- 7 E. P. Kundig and G. A. Ozin, *J. Am. Chem. Soc.*, **96**, 3820 (1974).
- 8 J. D. Black and P. S. Braterman, *J. Am. Chem. Soc.*, **97**, 2908 (1975).
- 9 A. J. Rest and J. J. Turner, *Chem. Comm.*, 1026 (1969).
- 10 M. Poliakoff and J. J. Turner, *J. Chem. Soc. A.*, 2403 (1971).
- 11 A. J. Rest and J. J. Turner, *Chem. Comm.*, 375 (1969).
- 12 (a) L. H. Ali, A. Cox and T. J. Kemp, *J. Chem. Soc. Dalton*, 1475 (1973); (b) *idem*, *ibid.*, 1468 (1973); (c) D. M. Allen, A. Cox, T. J. Kemp and L. H. Ali, *ibid.*, 1899 (1973); (d) D. M. Allen, A. Cox, T. J. Kemp, Q. Sultana and R. B. Pitts, *ibid.*, 1189 (1976).
- 13 H. Huber, E. P. Kundig and G. A. Ozin, *J. Am. Chem. Soc.*, **96**, 5585 (1975).
- 14 (a) A. Hudson, M. F. Lappert, P. W. Lednor and B. K. Nicholson, *Chem. Comm.*, 966 (1974); (b) P. J. Krusic, H. Stoklosa, L. E. Manzer and P. Meakin, *J. Am. Chem. Soc.*, **97**, 667 (1975).
- 15 G. Wilkinson, *J. Am. Chem. Soc.*, **76**, 209 (1954).
- 16 E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).
- 17 J. C. Hileman, D. K. Higgins and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962).
- 18 F. R. Hartley and G. Temple-Nidd, *Educ. in Chem.*, **12**, 6 (1975).
- 19 R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).
- 20 T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. and Nucl. Chem.*, **1**, 165 (1955).
- 21 B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).
- 22 C. E. Coffey, *J. Inorg. and Nucl. Chem.*, **25**, 179 (1963).
- 23 T. S. Piper and G. Wilkinson, *J. Inorg. and Nucl. Chem.*, **3**, 104 (1956).