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Preliminary communication

MATRIX ISOLATION STUDIES OF HYDROFORMYLATION INTERMEDIATES. INFRARED SPECTROSCOPIC EVIDENCE FOR STEPWISE SUBSTITUTION OF ETHYLENE INTO (η^5-CYCLOPENTADIENYL)TRICARBONYL(HYDRIDO)-MOLYBDENUM AND -TUNGSTEN COMPLEXES FOLLOWED BY INSERTION INTO THE METAL—HYDROGEN BOND

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Summary

Infared spectroscopic evidence is presented to show that photolysis of (η^5-C_5H_5)M(CO)$_3$(H) complexes (M = Mo, W) isolated at high dilution in C_2H_4 doped (5%) CH_4 matrices at 12 K leads to the formation of the 16 electron species (η^5-C_5H_5)M(CO)$_2$(H) and the 18 electron species *cis*- and *trans*-(η^5-C_5H_5)-M(CO)$_2$(C_2H_4)(H) and that further photolysis produces the 16 electron insertion species (η^5-C_5H_5)M(CO)$_2$(C_2H_5). The results are related to the intermediates proposed in mechanisms for catalytic hydroformylation processes.

The hydroformylation of olefins in the presence of transition metal carbonyl catalysts is proposed to proceed as shown in Scheme 1 [1]. The catalytic cycle involves a number of coordinatively saturated 18 electron species (I, III, V), for which stable model compounds have been isolated, and some unstable coordinatively unsaturated 16 electron species (II, IV, VI). In order to fully understand the catalytic cycle it is essential that evidence for the existence of species II, IV and VI and any other potential intermediates should be sought.

The matrix isolation technique [2] enables highly reactive species to be stabilised for long enough to be characterized spectroscopically. Matrix isolation studies have already contributed to the understanding or hydroformylation.

(a) An early study [3] showed that photolysis of HMn(CO)$_5$ in Ar at 20 K

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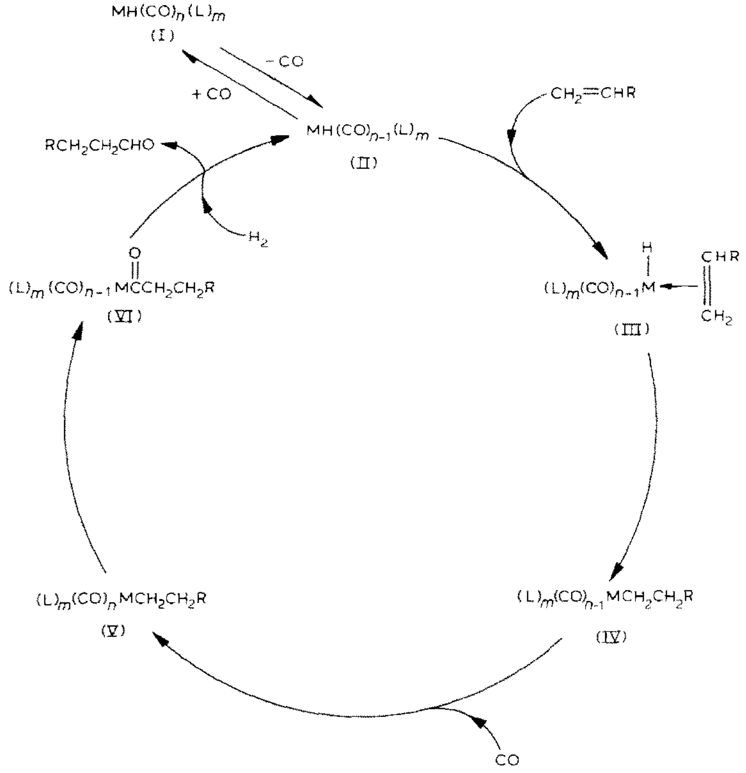


SCHEME 1

gave CO and $HMn(CO)_4$ and that this process was reversible; i.e. analogous to I ⇌ II. Later experiments have shown that photolysis of $HCo(CO)_4$ does indeed generate CO and $HCo(CO)_3$ [4,5] but it was also discovered that cleavage of the Co—H bond could occur to give $Co(CO)_4^{\cdot}$ and $H^{\cdot}$ [5]. Photolysis of $HMn(CO)_5$ has also been shown to produce $Mn(CO)_5^{\cdot}$ and $H^{\cdot}$ [6].

(b) Photolysis of $(CH_3CO)Mn(CO)_5$ [7] and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(COCH_3)$ [8] has been shown to generate the alkyl complexes $(CH_3)Mn(CO)_5$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_3)$ via the coordinatively unsaturated acetyl species $(CH_3CO)Mn(CO)_4$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(COCH_3)$; i.e. VI → V.

(c) Photolysis of $(CH_3)Mn(CO)_5$ [7] and $(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_3)$ [9] generates the coordinatively unsaturated species $(CH_3)Mn(CO)_4$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CH_3)$ in a process which is reversible, i.e. V ⇌ IV.

(d) Finally, photolysis of alkylmetal complexes with β-hydrogens results in the formation of olefin metal hydride species, i.e. V → III, e.g. $(\eta^5\text{-}C_5H_5)W(CO)_3(C_2H_5) \rightarrow (\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_4)H$ [10,11]. This process has been shown to be reversible [11].

In this communication we report on the photolysis of $(\eta^5\text{-}C_5H_5)M(CO)_3(H)$ complexes (M = Mo, W) in C_2H_4 doped (5%) CH_4 matrices at 12 K and we relate the formation of $(\eta^5\text{-}C_5H_5)M(CO)_2(H)$, $(\eta^5\text{-}C_5H_5)M(CO)_2(C_2H_4)(H)$ and $(\eta^5\text{-}C_5H_5)M(CO)_2(C_2H_5)$ species to the catalytic hydroformylation process.

Infrared spectra from an experiment with $(\eta^5\text{-}C_5H_5)W(CO)_3(H)$ isolated at high dilution (ca. 1/2000—1/5000) in a 5% C_2H_4 doped CH_4 matrix at 12 K [12] are shown in Fig. 1. Before photolysis the spectrum (Fig. 1a) shows strong two bands at 2024.0 and 1932.5 cm^{-1} (Table 1) with weak bands (marked with ○) arising from $(\eta^5\text{-}C_5H_5)W(^{12}CO)_2(^{13}CO)(H)$ in natural abundance. Irradiation of the matrix with long wavelength light ($\lambda > 430$ nm) produced no change in the spectrum even after several hours irradiation. Irradiation with higher energy light ($290 < \lambda < 370$ nm) produced new bands at 1956.0 and 1874.5 cm^{-1} (Fig. 1(b)). Further irradiation with the same energy light caused the appearance of new bands at 1986.2, 1974.0, 1945.3, 1927.8, 1897.5 and 1859.5 cm^{-1}

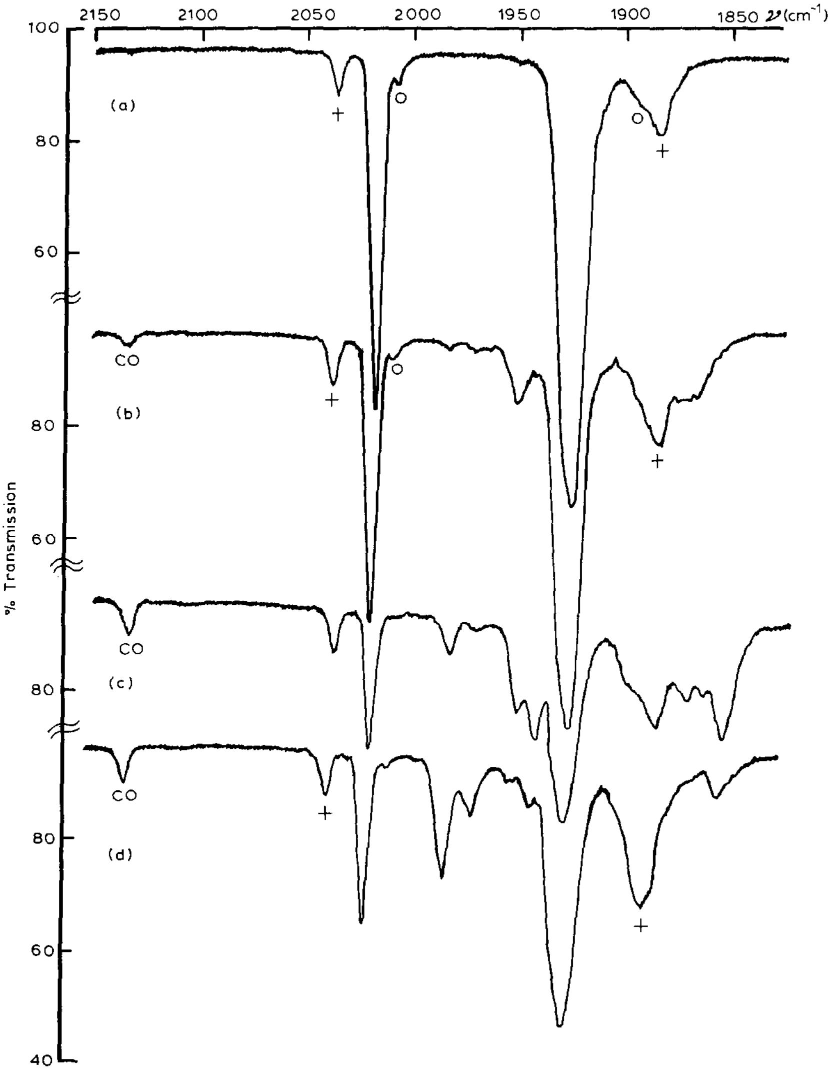


Fig. 1. Infrared spectra from an experiment with $(\eta^5\text{-}C_5H_5)W(CO)_3(H)$ isolated at high dilution in a C_2H_4 doped (5%) CH_4 matrix at 12 K: (a) after deposition, (b) after 3 min photolysis with $290 < \lambda < 370$ nm radiation, (c) after 15 min further photolysis using the same radiation, (d) after 90 min photolysis with $\lambda > 430$ nm light. Bands marked ○ are due to $(\eta^5\text{-}C_5H_5)W(^{12}CO)(^{13}CO)(H)$ occurring in natural abundance and bands marked + are due to C_2H_4.

TABLE 1

INFRARED TERMINAL CO STRETCHING BAND POSITIONS (cm^{-1}) FOR $(\eta^5\text{-}C_5H_5)M(CO)_3(H)$ COMPLEXES (M = Mo, W) AND THEIR PHOTO-PRODUCTS IN C_2H_4 DOPED (5%) CH_4 MATRICES AT 12 K

Species	Mo	W
$(\eta^5\text{-}C_5H_5)M(CO)_3(H)$	2028.2	2024.0
	1944.0 1939.3 [a]	1932.5
$(\eta^5\text{-}C_5H_5)M(CO)_2(H)$	1962.2	1956.0
	1882.7	1874.5
cis-$(\eta^5\text{-}C_5H_5)M(CO)_2(C_2H_4)(H)$	[b]	1986.2
		1927.8
trans-$(\eta^5\text{-}C_5H_5)M(CO)_2(C_2H_4)(H)$	1974.8	1974.0
	1901.3	1897.5
$(\eta^5\text{-}C_5H_5)M(CO)_2(C_2H_5)$	1955.0	1945.3
	1872.5	1859.5

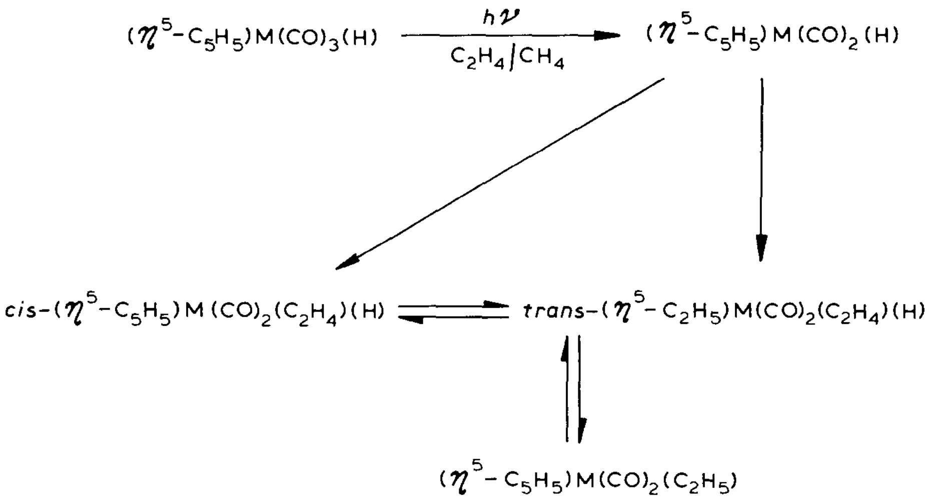
[a] Matrix splitting. [b] Only the *trans* isomer has been detected for $(\eta^5\text{-}C_5H_5)Mo(CO)_2(C_2H_4)(H)$.

(Fig. 1(c)). Prolonged photolysis showed that the pairs of bands at 1956.0 and 1874.5 cm^{-1} and 1945.3 and 1859.5 cm^{-1} increase more rapidly than the other bands with bands of $(\eta^5\text{-}C_5H_5)W(CO)_3(H)$ steadily decreasing in intensity. Irradiating now with low energy light ($\lambda > 430$ nm) caused the pairs of bands at 1986.2 and 1927.8 cm^{-1} and 1974.0 and 1897.5 cm^{-1} to increase markedly while other bands decreased (Fig. 1(d)). The relative intensities of the two parent $(\eta^5\text{-}C_5H_5)W(CO)_3(H)$ bands also changed with the lower band decreasing more slowly than the upper band. This was due to the growth of a band at 1927.8 cm^{-1} on the side of the parent band at 1932.5 cm^{-1}.

Comparison of the above band positions with those for $(\eta^5\text{-}C_5H_5)W(CO)_2(H)$, *cis*- and *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_4)(H)$ and $(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_5)$ [11] species generated in separate experiments [11,13] enabled all the new bands in C_2H_4 doped CH_4 matrices to be assigned. For example: (i) the bands at 1956.0 and 1874.5 cm^{-1} are due to $(\eta^5\text{-}C_5H_5)W(CO)_2(H)$, (ii) the bands at 1945.3 and 1859.5 cm^{-1} are due to $(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_5)$, (iii) the bands at 1986.4 and 1927.8 cm^{-1} can be assigned to *cis*-$(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_4)(H)$, and (iv) the bands at 1974.0 and 1897.5 cm^{-1} correspond to those of *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_4)(H)$ (Table 1). Analogous species were formed when $(\eta^5\text{-}C_5H_5)Mo(CO)_3(H)$ was photolysed in C_2H_4 doped (5%) CH_4 matrices at 12 K (Table 1).

The photoreactions of $(\eta^5\text{-}C_5H_5)M(CO)_3(H)$ complexes (M = Mo, W) in C_2H_4 doped CH_4 are summarised in Scheme 2. It is important to note that the rate of formation of the *cis* and *trans* isomers of $(\eta^5\text{-}C_5H_5)M(CO)_2(C_2H_4)(H)$ depends on the rate of formation of the 16 electron species $(\eta^5\text{-}C_5H_5)W(CO)_2(H)$ and that the various forward and reverse reactions depend on the type of irradiating energy being used. The detailed evidence for the *cis* $\rightleftharpoons$ *trans* isomerisation and for reversible β-elimination $\rightleftharpoons$ olefin insertion will be presented elsewhere [11,13].

The species observed in this matrix isolation study correspond to steps I $\rightleftharpoons$ II, II → III and III → IV in Scheme 1. This is the first time that such steps have been delineated. Further work will seek to isolate and characterise analogous intermediates starting from $HCo(CO)_4$, a known hydroformylation catalyst, and to apply matrix isolation studies to other homogeneous catalysis processes.



SCHEME 2

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References

1 Adapted from C. Masters, Homogeneous Transition-metal Catalysis, Chapman and Hall, London, 1981; page 105.
2 A.J. Rest in A.J. Barnes, W.J. Orville-Thomas, A. Müller and R. Gaufres (Eds.), Matrix Isolation Spectroscopy, NATO Advanced Study Institute Series, D. Reidel Publishing Company, Dordrecht, 1981, Chapter 9.
3 A.J. Rest and J.J. Turner, Chem. Comm., (1969) 375.
4 P. Wermer, B.S. Ault and M. Orchin, J. Organometallic Chem., 162 (1978) 189.
5 R.L. Sweany, Inorg. Chem., 19 (1980) 3512; ibid., 21 (1982) 752.
6 S.P. Church, M. Poliakoff, J.A. Timney and J.J. Turner, J. Amer. Chem. Soc., 103 (1981) 7515.
7 A.J. Rest, J. Organometallic Chem., 25 (1970) C30; T.M. McHugh and A.J. Rest, J. Chem. Soc. Dalton Trans., (1980) 2332.
8 D.J. Fettes, R. Narayanaswamy and A.J. Rest, J. Chem. Soc. Dalton Trans., (1981) 2311; R.B. Hitam, R. Narayanaswamy and A.J. Rest, J. Chem. Soc. Dalton Trans., (1982) in press.
9 K.A. Mahmoud, R. Narayanaswamy and A.J. Rest, J. Chem. Soc. Dalton Trans., (1981) 2199.
10 R.J. Kazlauskas and M.S. Wrighton, J. Amer. Chem. Soc., 102 (1980) 1727; idem, J. Amer. Chem. Soc., in press.
11 K.A. Mahmoud, A.J. Rest, H.G. Alt, M.E. Eichner and B.M. Jansen, J. Chem. Soc. Dalton Trans., submitted for publication.
12 For a detailed description of the cryostat, spectrometers, matrix gases, filters to achieve wavelength-selective photolysis and techniques for making gas matrices at 12 K in our laboratory see refs [7]—[9] together with ref. [2].
13 K.A. Mahmoud, A.J. Rest and H.G. Alt, J. Chem. Soc. Dalton Trans., submitted for publication.