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Preliminary communication

INFRARED MATRIX ISOLATION EVIDENCE FOR THE FORMATION OF (η^5-CYCLOPENTADIENYL)TRICARBONYL-MOLYBDENUM AND -TUNGSTEN RADICALS IN CARBON MONOXIDE MATRICES AT 12 K

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Summary

Infrared spectroscopic evidence including ^{13}CO labelling and energy-factored force-field fitting is presented for the first time to show that the radicals (η^5-C_5H_5)$M(CO)_3^{\cdot}$ (M = Mo, W) and HCO are produced on photolysis of (η^5-C_5H_5)$M(CO)_3H$ complexes in CO matrices at 12 K.

The reactions of transition metal hydrides are of considerable interest because of their roles in homogeneous catalytic cycles [1—5]. Recent developments have demonstrated new types of reactivity, e.g. transfer of a hydride to an electrophile [6] and the homolytic cleavage of the M—H bond [7,8]. It has been suggested that the hydrogenation of arenes and alkenes, which are catalysed by transition metal carbonyl hydrides, proceeds through free radical intermediates which are formed by H atom transfer from the metal hydride to the substrate [7,8]. A similar H atom transfer is proposed for the hydrogenation of α-methyl styrene by $HMn(CO)_5$ (eq. 1) [9].

$$C_6H_5C(CH_3)=CH_2 + 2HMn(CO)_5 \rightarrow C_6H_5CH(CH_3)_2 + Mn_2(CO)_{10} \quad (1)$$

The behaviour of $[Rh(NH_3)_5(H_2O)H]^{2+}$ on photolysis was ascribed to a chain reaction which was thought to be initiated by Rh—H bond homolysis [10]. Kinetic evidence was used by Hoffman and Brown [11] to postulate the homolysis of W—H bonds in studies of the thermal and photochemical substitution re-

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actions of $(\eta^5\text{-}C_5H_5)W(CO)_3H$. It was observed that photolysis (311 nm radiation) promoted substitution of $P(n\text{-}C_4H_9)_3$ for CO (eq. 2).

$$(\eta^5\text{-}C_5H_5)W(CO)_3H + P(n\text{-}C_4H_9)_3 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)W(CO)_2(P(n\text{-}C_4H_9)_3)H + CO \quad (2)$$

The quantum yield for the overall substitution reaction varied from 6 to 30 suggesting a radical chain mechanism (eq. 3). Support for the initial W—H bond homolysis; which was thought to have quite a low quantum yield, came from a

$$(\eta^5\text{-}C_5H_5)W(CO)_3H \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)W(CO)_3^{\bullet} + H^{\bullet} \quad (3)$$

trapping experiment with $(C_6H_5)_3CCl$ (eqn. 4) which gave complete conversion

$$(\eta^5\text{-}C_5H_5)W(CO)_3H + (C_6H_5)_3CCl \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)W(CO)_3Cl + (C_6H_5)_3CH \quad (4)$$

to $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$, i.e. photoprocesses of metal carbonyl hydrides are not necessarily dominated by CO ejection.

The matrix isolation technique [12] enables highly reactive species to be stabilised for long enough to be characterised spectroscopically. Grebenik et al. [13] have reported that photolysis of $(\eta^5\text{-}C_5H_5)_2ReH$ in CO matrices yields $(\eta^5\text{-}C_5H_5)_2Re$ and HCO radicals, which are presumably formed by Re—H bond homolysis. Similarly Co—H and Mn—H bond homolysis for $HCo(CO)_4$ and $HMn(CO)_5$ in CO matrices gave HCO radicals together with $Co(CO)_4$ [14] and $Mn(CO)_5$ [15]. In this communication we present evidence which puts the possibility of M—H bond cleavage for $(\eta^5\text{-}C_5H_5)M(CO)_3H$ complexes (M = Mo, W) on a very firm basis.

TABLE 1

INFRARED BAND POSITIONS (cm^{-1}) OBSERVED IN THE TERMINAL CO-STRETCHING REGION FOR $(\eta^5\text{-}C_5H_5)M(CO)_3H$ COMPLEXES (M = Mo, W) AND THEIR PHOTOPRODUCTS IN CO MATRICES AT 12 K

Complex	ν(CO)	
$(\eta^5\text{-}C_5H_5)Mo(CO)_3H$	2029.2	
	1946.7 1940.5	} [a]
$(\eta^5\text{-}C_5H_5)W(CO)_3H$	2024.3	
	1936.1 1931.1	} [a]
$(\eta^5\text{-}C_5H_5)Mo(CO)_3^{\bullet}$	2008.9	
	1915.5 1908.4	} [b]
$(\eta^5\text{-}C_5H_5)W(CO)_3^{\bullet}$	1999.3	
	1900.3 1896.5	} [b]
$H^{12}CO^{\bullet}$	1859.1	
$H^{13}CO^{\bullet}$	1817.0	

[a] Overlapping A' and A'' bands of C_s $M(CO)_3$ fragment. [b] Broad split band.

Infrared spectra from an experiment with $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ isolated at high dilution (ca. 1/2000—1/5000) in a pure CO matrix at 12 K are shown in Fig. 1. Before photolysis the spectrum (Fig. 1(a)) shows two strong bands at 2029.2 and (1946.7, 1940.5 cm^{-1})* (Table 1) with weak bands (marked with ★) arising from $(\eta^5\text{-}C_5H_5)Mo(^{12}CO)_2(^{13}CO)H$ in natural abundance. Irradiation of the matrix with UV light ($230 < \lambda < 390$ nm) produced new bands at 2008.9 and (1915.5, 1908.4)* cm^{-1} (Fig. 1(b)). Further irradiation with the same energy

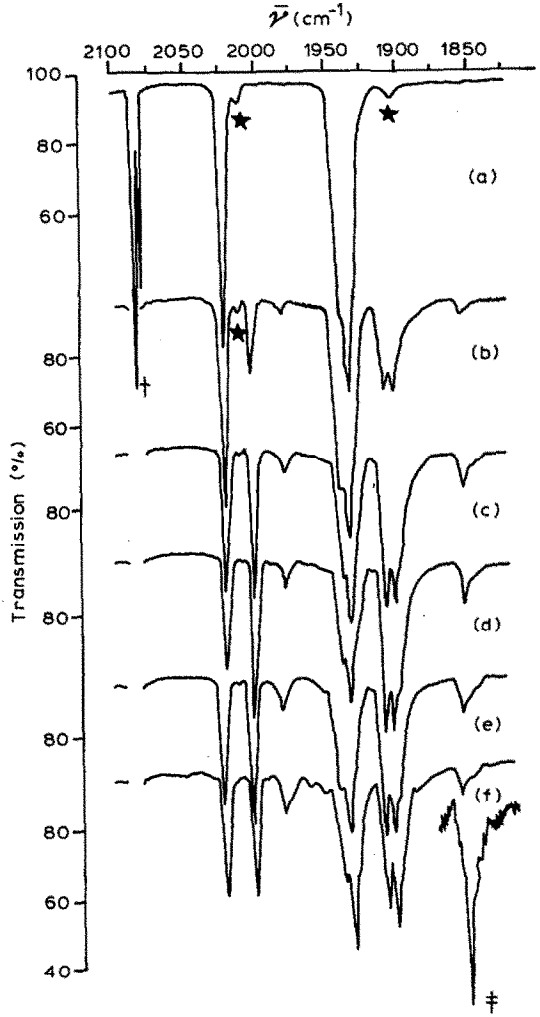

Fig. 1. Infrared spectra from an experiment with $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ isolated at high dilution in a CO matrix at 12 K: (a) after deposition, (b) after 15 min photolysis using $230 < \lambda < 390$ nm radiation, (c) after 30 min further photolysis using the same source, (d) after further 30 min photolysis using the same source, (e) after 30 min reversal using $\lambda > 430$ nm radiation, and (f) after annealing to ~30 K for 2 min. Bands marked (*) are due to $(\eta^5\text{-}C_5H_5)Mo(^{12}CO)_2(^{13}CO)H$ present in natural abundance, those marked (†) to ^{13}CO, and that marked ‡ is assigned to the $H^{12}CO$ radical and is expanded 5 times.

*Band splitting arising from matrix effects and from accidental overlapping of fundamentals (see [16] and Table 1).

light enhanced the yield of the new bands at the expense of the parent bands and a weak band started to grow at 1859 cm^{-1} (Fig. 1(c) and 1(d)). Prolonged photolysis reduced the yield of the band at 1859 cm^{-1}. Irradiation with low energy light ($\lambda > 430$ nm) caused the pairs of bands at 2008.9 and (1915.5, 1908.4) cm^{-1} to decrease slightly with regeneration of the bands due to the starting material (Fig. 1(e)). Annealing the matrix for 2 min and then recooling to 12 K, showed that the new product bands were observed to decrease with the regeneration of bands due to $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ (Fig. 1(f)). The relative intensities of the new terminal CO-stretching bands remained constant under a variety of photolysis conditions (time and wavelength of radiation), indicating that the bands arose from a single product species. In Fig. 1(f) the new photoproduct has three infrared bands. Annealing the matrix caused a change in the shape of the lower band and so this doublet is probably due to matrix splitting [12].

In order to establish the nature of the metal-containing product experiments were carried out using ^{13}CO-enriched $(\eta^5\text{-}C_5H_5)W(CO)_3H$ in a mixed $^{13}CO/^{12}CO$ (25/75) matrix which employed the same photolysis sources used previously for $(\eta^5\text{-}C_5H_5)W(CO)_3H$ in pure ^{12}CO. Irradiation of the matrix with UV light ($230 < \lambda < 390$ nm) produced a number of bands which were seen in the terminal CO stretching region for $(\eta^5\text{-}C_5H_5)W(CO)_3H$ in ^{12}CO together with a new band at very much lower wavenumbers (1817 cm^{-1}) [16].

The band at 1859 cm^{-1} in ^{12}CO matrices may be assigned to the HCO radical by analogy with previous Re [13], Co [14] and Mn [15] studies and from the capture of H atoms by CO [19]. The shift of this band to 1817 cm^{-1} is exactly what is predicted for the replacement of a ^{12}C by a ^{13}C atom, i.e. $H^{13}CO$. The remaining new bands were subjected to an energy-factored force-field fitting procedure for metal carbonyl fragments, which has been described elsewhere [17,18]. Comparison of the observed and calculated band positions shows that there is excellent agreement for a C_{3v} $M(CO)_3$ fragment [16]. Since the other photoproduct is the formyl radical, the metal-containing species must be the $(\eta^5\text{-}C_5H_5)M(CO)_3$ radicals (M = Mo, W) characterised now for the first time.

Comparing the photochemical reactivity of the Mo and W complexes in CO matrices reveals that the generation of the $(\eta^5\text{-}C_5H_5)M(CO)_3$ radical is faster for Mo than for W using the same light source and the same period of irradiation. This suggests that the W—H bond is the stronger and is consistent with the supposition [20,21] that the W—H bond energy is larger than the Mo—H bond energy.

Matrix isolation studies have, therefore, with the characterisation of $(\eta^5\text{-}C_5H_5)M(CO)_3$ radicals (M = Mo, W) for the first time, established the reality of a radical pathway in the reactions of $(\eta^5\text{-}C_5H_5)M(CO)_3H$ complexes (M = Mo, W). Further work will seek to compare the reactivity of the Cr complexes $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ and $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ with their Mo and W analogues.

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