Journal of Organometallic Chemistry, 246 (1983) C37—C41
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

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

KHALIL A. MAHMOUD, ANTONY J. REST*,
Department of Chemistry, The University, Southampton SO9 5NH (Great Britain)
and HELMUT G. ALT
Laboratorium für Anorganische Chemie, Universität Bayreuth, D-8580, Bayreuth (West Germany)

(Received January 4th, 1983)

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 $(\eta^5\text{-}C_5H_5)M(CO)_3^{\bullet}$ (M = Mo, W) and HCO are produced on photolysis of $(\eta^5\text{-}C_5H_5)M(CO)_3H$ 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].

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

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-

---

*Author to whom correspondence should be addressed.

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).

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

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

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

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

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

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 (η^5-C_5H_5)Mo(CO)$_3$H 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 (η^5-C_5H_5)Mo(^{12}CO)$_2$(^{13}CO)H in natural abundance. Irradiation of the matrix with UV light (230 < λ < 390 nm) produced new bands at 2008.9 and (1915.5, 1908.4)* cm^{-1} (Fig. 1(b)). Further irradiation with the same energy

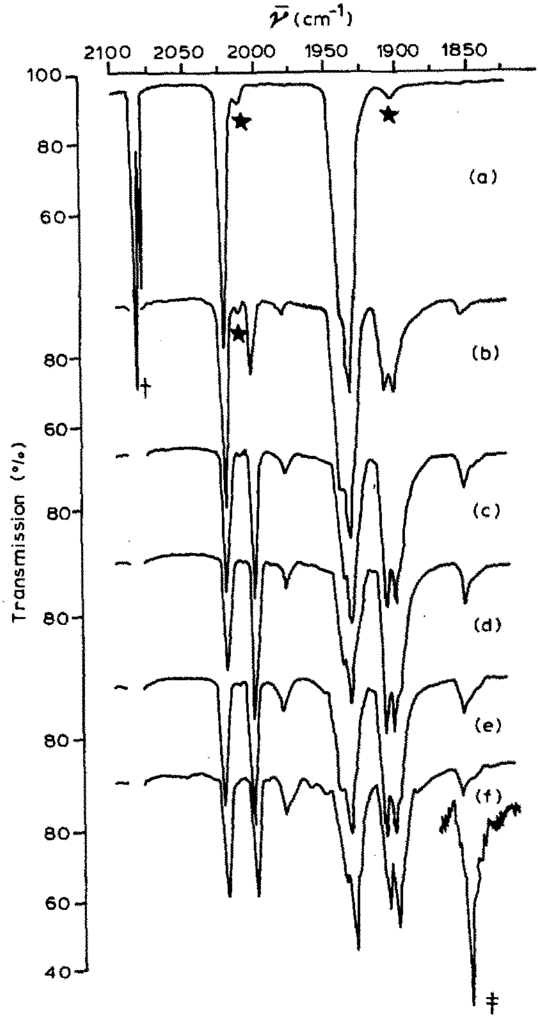

Fig. 1. Infrared spectra from an experiment with (η^5-C_5H_5)Mo(CO)$_3$H isolated at high dilution in a CO matrix at 12 K: (a) after deposition, (b) after 15 min photolysis using 230 < λ < 390 nm radiation, (c) after 30 min further photolysis using the same source, (d) after further 30 min photolysis using the same source, (e) after 30 min reversal using λ > 430 nm radiation, and (f) after annealing to ~30 K for 2 min. Bands marked (★) are due to (η^5-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.

Acknowledgements. We thank the University of Lebanon Faculty of Science for a Studentship (to KAM), the SERC for a grant (to AJR) and the Deutsche Forschungsgemeinschaft for support (to HGA).

References

1 H.D. Kaesz, J. Organometal. Chem., 200 (1980) 145.
2 H.D. Kaesz and R.B. Saillant, Chem. Rev., 72 (1972) 231.
3 J. Halpern, J. Organomet. Chem., 200 (1980) 133.
4 G.L. Geoffroy and J.R. Lehman, Adv. Inorg. Chem. Radio. Chem., 20 (1977) 189.
5 A. Humphries and H.D. Kaesz, Prog. Inorg. Chem., 25 (1979) 145.
6 T. Bodnor, S.J. Lacroce and A.R. Cutler, J. Am. Chem. Soc., 102 (1980) 3294.
7 M.F. Lappert and P.W. Lednor, Adv. Organomet. Chem., 14 (1976) 345; P.J. Krusic, P.J. Fagan and J. San Fillipo, J. Am. Chem. Soc., 99 (1977) 250.
8 H.M. Feder and J. Halpern, J. Am. Chem. Soc., 97 (1975) 7186.
9 R.L. Sweany and J. Halpern, J. Am. Chem. Soc., 99 (1977) 8335.
10 J.F. Endicott, C.L. Inove Wong and P.T. Natarajan, Inorg. Chem., 18 (1979) 450.
11 N.W. Hoffman and T.L. Brown, Inorg. Chem., 17 (1978) 613.
12 A.J. Rest in A.J. Barnes, W.J. Orville-Thomas, A. Muller and R. Gaufres (Eds.), NATO Advanced Study Institute Series, D. Reidel Publishing Company, Dordrecht, 1981, Chapter 9.
13 P. Grebenik, A.J. Downs, M.L.H. Green and R.N. Perutz, J. Chem. Soc. Chem. Commun., (1979) 742; J. Chetwynd-Talbot, P. Grebenik, R.N. Perutz and M.H.A. Powell, Inorg. Chem., submitted for publication.
14 R.L. Sweany, Inorg. Chem., 19 (1980) 3512.
15 S.P. Church, M. Poliakoff, J.A. Timney and J.J. Turner, J. Am. Chem. Soc., 103 (1981) 7515.
16 K.A. Mahmoud, A.J. Rest and H.G. Alt, J. Chem. Soc. Dalton Trans., in press.
17 J.K. Burdett, H. Dubost, M. Poliakoff and J.J. Turner in R.J.H. Clark and R.E. Hester (Eds.), Advances in Infrared and Raman Spectroscopy, Vol. 2, Heyden, London, 1976, p. 1.
18 R.N. Perutz and J.J. Turner, Inorg. Chem., 14 (1975) 262.
19 D.E. Milligan and M.E. Jacox, J. Chem. Phys., 51 (1969) 278.
20 J.A. Connor, Top. Curr. Chem., 71 (1977) 71.
21 The tungsten hydride, $(\eta^5\text{-}C_5H_5)W(CO)_3H$ is much more stable and less thermally sensitive than its molybdenum analogue, E.O. Fisher, W. Hafner and H.O. Stahl, Z. Anorg. Allg. Chem., 282 (1955) 47.