Infrared Spectroscopic Evidence for Photochemical Generation of the Metallocenes $[(\eta\text{-}C_5H_5)_2M]$ (M = Mo or W) in Low-temperature Matrices

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Summary U.v. photolysis of $[(\eta\text{-}C_5H_5)_2WH_2]$, $[(\eta\text{-}C_5H_5)_2WD_2]$, $[(\eta\text{-}C_5H_5)_2WCO]$, or $[(\eta\text{-}C_5H_5)_2W(CH_3)H]$ in an argon matrix at 10 K leads to a common product, identified by i.r. spectroscopy as $[(\eta\text{-}C_5H_5)_2W]$, and similarly photolysis of $[(\eta\text{-}C_5H_5)_2MoH_2]$ or $[(\eta\text{-}C_5H_5)_2MoCO]$ affords $[(\eta\text{-}C_5H_5)_2Mo]$; trapping experiments with a CO matrix show that the elimination of H_2 from $[(\eta\text{-}C_5H_5)_2MH_2]$ (M = Mo or W) is close to concerted.

PHOTOLYSIS of $[(\eta\text{-}C_5H_5)_2WH_2]$ in solution in the presence of certain hydrocarbons leads to insertion of the tungsten atom into C–H bonds. Striking examples include insertion into both sp^2 (*e.g.*, benzene) and sp^3 C–H bonds (*e.g.*, tetramethylsilane).[1] The key intermediate proposed for these reactions is tungstenocene, $[(\eta\text{-}C_5H_5)_2W]$, although alternative mechanisms have also been considered.[2] The arguments in favour of concerted elimination of H_2 to form a metallocene have been reinforced by recent experiments in which $[(\eta\text{-}C_5H_5)_2MoH_2]$ was photolysed in the presence of $[^2H_8]$toluene.[3] In this communication we report the direct detection of $[(\eta\text{-}C_5H_5)_2W]$ and $[(\eta\text{-}C_5H_5)_2Mo]$ in matrix-isolation experiments.

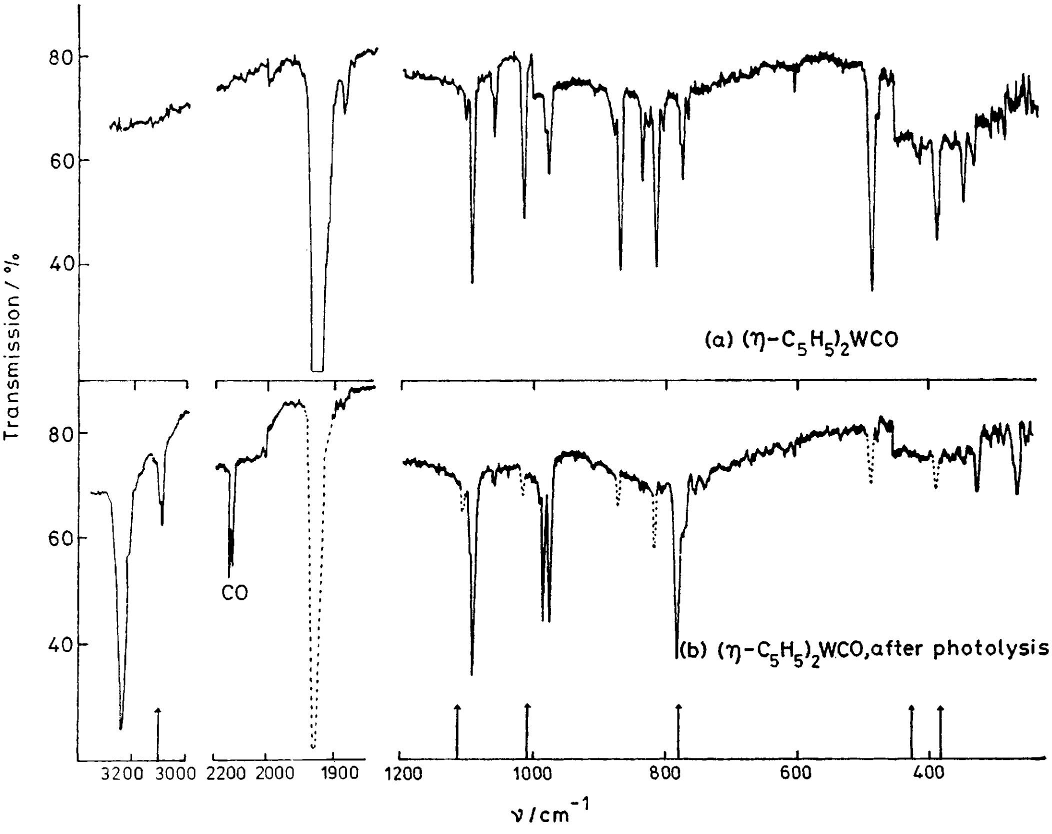

FIGURE. (a) I.r. spectrum of $[(\eta\text{-}C_5H_5)_2WCO]$ in Ar at 10 K (3·5 h evaporation at 315 K). (b) Spectrum after 40 min u.v. photolysis with a Hanovia high-pressure Hg arc. Full line shows product; broken line shows starting material. The arrows on the baseline indicate the wavenumbers of $[(\eta\text{-}C_5H_5)_2V]$ in Ar at 10 K.

The Figure shows the i.r. spectrum of $[(\eta\text{-}C_5H_5)_2WCO]$ in an argon matrix at 10 K before (a) and after (b) broad-band u.v. photolysis. An i.r. absorption characteristic of free CO (at 2137 cm^{-1}) develops with photolysis at the expense of the absorptions of the starting material. Simultaneously several new bands develop, including an intense feature at 3238 cm^{-1} (see Table), the growth patterns of which indicate a common origin. A similar spectrum is observed in experiments with the molybdenum analogue, except for the notable absence of any bands in the 3200 cm^{-1} region. Neither selective photolysis nor annealing causes reversal of the CO elimination. On the basis of the arguments outlined below, we assign the new bands to the metallocenes $[(\eta\text{-}C_5H_5)_2M]$ (M = Mo or W).

(i) Absorption bands with the same wavenumbers and relative intensities are observed on photolysis of each of $[(\eta\text{-}C_5H_5)_2WH_2]$, $[(\eta\text{-}C_5H_5)_2WD_2]$, $[(\eta\text{-}C_5H_5)_2WCO]$, and $[(\eta\text{-}C_5H_5)_2W(CH_3)H]$; with the methyl hydride methane is also detected. Similarly, a common product emerges on photolysis of $[(\eta\text{-}C_5H_5)_2MoH_2]$ and $[(\eta\text{-}C_5H_5)_2MoCO]$.

(ii) The product spectra at wavenumbers < 3200 cm^{-1} are strikingly similar to those of known metallocenes with parallel rings,[4] as is shown by the matrix spectrum of $[(\eta\text{-}C_5H_5)_2V]$ and $[(\eta\text{-}C_5H_5)_2Cr]$ [Figure (b) and Table]. The starting materials invariably have much more complex spectra.

(iii) Photolysis of $[(\eta\text{-}C_5H_5)_2WH_2]$ in a CO matrix yields the characteristic bands assigned to $[(\eta\text{-}C_5H_5)_2W]$ and a band at 1920 cm^{-1} consistent with the formation of some $[(\eta\text{-}C_5H_5)_2WCO]$.

(iv) A similar cycle of reactions has been carried out with the vanadium analogues $[(\eta\text{-}C_5H_5)_2V]$ and $[(\eta\text{-}C_5H_5)_2VCO]$ which are both stable at room temperature[5] and can be evaporated into matrices [equation (1)].

$$[(\eta\text{-}C_5H_5)_2VCO] \underset{\substack{h\nu,\ CO,\ 10\ K\\ \text{low yield}}}{\overset{h\nu,\ Ar,\ 10\ K}{\rightleftharpoons}} [(\eta\text{-}C_5H_5)_2V] + CO \qquad (1)$$

TABLE. I.r. bands of metallocenes in Ar matrices at 10 K (cm^{-1}).

$[(\eta\text{-}C_5H_5)_2W]$	$[(\eta\text{-}C_5H_5)_2Mo]$	$[(\eta\text{-}C_5D_5)_2W]$ [a]	$[(\eta\text{-}C_5H_5)_2V]$	$[(\eta\text{-}C_5H_5)_2Cr]$
3238s, br		3225s, br		
3090w	3105w	—	3100w	3110w
—	—	—	1428w	1412w
1086m	1094s	1032m	1112m	1099s
				1050w
980m	991sh	760m	1010s	994sh
971m	985m	—	—	986s
—	970w, br	—	—	—
778m	778s	—	783s	785s
				756s
323w [b]	350w	—	429w	439m
264w [b]	—	—	385w	—

s = strong; m = medium; w = weak; sh = shoulder; br = broad. [a] Only the most intense bands of $[(\eta\text{-}C_5D_5)_2W]$ were observed. [b] These bands were observed only on photolysis of $[(\eta\text{-}C_5H_5)_2WCO]$.

Most conspicuous in the i.r. spectrum of $[(\eta\text{-}C_5H_5)_2W]$ is the broad, intense band at 3238 cm^{-1} (half-width 26 cm^{-1}). Since experiments with $[(\eta\text{-}C_5D_5)_2WH_2]$ or $[(\eta\text{-}C_5D_5)_2WD_2]$† show that the band maximum shifts only 13 cm^{-1} on deuteriation, this absorption must be ascribed to an electronic transition. The absence of any vibrational progression suggests an intraconfigurational transition. The most plausible assignment involves a transition between spin-orbit sub-states of a $^3E_2$ term ($\Omega = 2 \leftarrow \Omega = 3$) of a parallel metallocene.[6] (Similar transitions have been observed for $[IrCl_6]^{2-}$ and $[OsCl_6]^{2-}$.[7]) On this basis we associate the broad band at 970 cm^{-1} with the corresponding electronic transition of $[(\eta\text{-}C_5H_5)_2Mo]$.‡

Two mechanisms can be envisaged for the elimination of H_2 from $[(\eta\text{-}C_5H_5)_2WH_2]$: stepwise loss of two hydrogen atoms or concerted elimination of H_2. If hydrogen atoms are generated, it should be possible to trap them with a CO matrix to form HCO.[8] However, no HCO is detected on photolysis of $[(\eta\text{-}C_5H_5)_2MH_2]$ (M = Mo or W) in a CO matrix. This contrasts with the ready detection of HCO in experiments performed under similar conditions with $[(\eta\text{-}C_5H_5)_2\text{-}ReH]$. Accordingly we conclude that elimination of H_2 from $[(\eta\text{-}C_5H_5)_2MH_2]$ is close to concerted.

[Bis(η-cyclopentadienyl)tungsten] and its molybdenum analogue are some of the first heavy metallocenes to be characterised outside the iron group. The generation of matrix-isolated tungstenocene represents a major step towards proving its intermediacy in the insertion reactions of $[(\eta\text{-}C_5H_5)_2WH_2]$.[1]

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† $[(\eta\text{-}C_5D_5)_2WD_2]$ was synthesised by exchange of $[(\eta\text{-}C_5H_5)_2WH_2]$ with D_2 in toluene in the presence of $Mn_2(CO)_{10}$ (H. D. Kaesz and R. Hoxmeier, personal communication). The extent of deuteriation on the rings was *ca.* 90%.

‡ The values of ζ for the neutral atoms Mo and W are 552 and 2089 cm^{-1} respectively (J. S. Griffith, 'The Theory of Transition-metal Ions,' Cambridge University Press, 1964, p. 438).

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