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Preliminary communication

MATRIX ISOLATION EVIDENCE FOR A PRIMARY CO DISSOCIATION PATHWAY IN THE PHOTOCHEMISTRY OF THE METAL–METAL BONDED DIMERS $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W)

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Summary

Photolysis of the metal–metal bonded dimers $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W) in polyvinyl chloride film (12–77 K) and frozen gas (12 K) matrices leads to the formation of the novel dimers $(\eta^5\text{-}C_5H_5)_2M_2(CO)_5$ which have a structure suggested, on the basis of IR spectroscopy, to contain a four electron donor bridging CO ligand and two semi-bridging CO ligands.

The photochemistry of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (I; M = Mo, II; M = W) in solution [1–3] has been rationalised exclusively in terms of a primary photoprocess in which homolytic cleavage of the M–M single bond occurs (eq. 1) [3,4].

$$\underset{\text{(I,II)}}{(\eta^5\text{-}C_5H_5)_2M_2(CO)_6} \xrightarrow[\text{near UV vis}]{h\nu} \underset{\text{(III)}}{2(\eta^5\text{-}C_5H_5)M(CO)_3^{\cdot}} \qquad (1)$$

The generation of M–M triple bonded dimers $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$ on photolysis of I and II in hydrocarbon solvents [5] is thought to involve CO loss from III followed by coupling of $(\eta^5\text{-}C_5H_5)M(CO)_2^{\cdot}$ radicals. Photosubstitution products, e.g. $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_2(P(OPh)_3)_2$ [2], have been proposed [3] to arise from CO substitution in III rather than from direct reaction of I or II with ligands.

A flash photolysis study [6] has, however, provided evidence for a second primary process (eq. 2) in the photochemistry of I.

$$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6 \xrightarrow[\text{near UV vis}]{h\nu} \underset{\text{(IV)}}{(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5} + CO \qquad (2)$$

We have studied the photoreactions of I and II isolated in polyvinyl chloride (PVC) films at 12–298 K and in frozen gas matrices at 12 K and report here spectroscopic evidence for reactive dimeric species formed via a CO dissociation pathway, cf. eq. 2.

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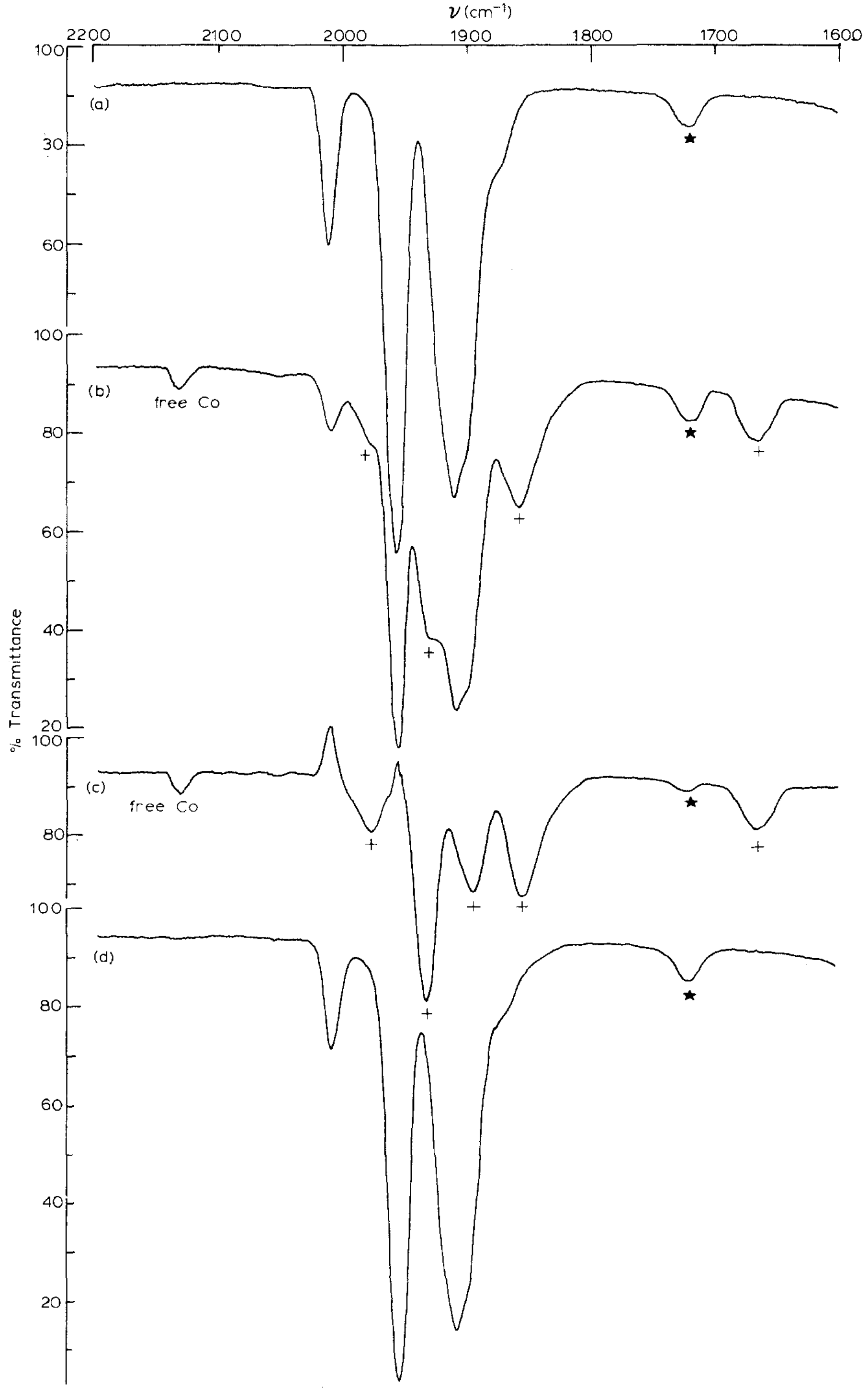
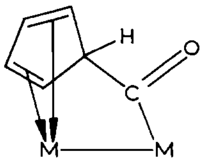


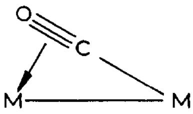
Fig. 1. Infrared spectra from an experiment with $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ (I) isolated in a PVC film matrix at 12 K (Nicolet 7199 FTIR spectrometer): (a) before irradiation. (b) after 60 min irradiation ($320 < \lambda < 390$ nm), (c) spectral subtraction, (b)–(a), with bands for I subtracted out completely, and (d) after warming the matrix to 180 K. The bands marked + are for V and that marked * is due to ketones in the PVC.

The infrared spectrum of I in a PVC film matrix * at 12 K is shown in Fig. 1a. Two terminal carbonyl stretching bands at 1955 and 1909 cm^{-1} are seen, together with a weaker band at 2010 cm^{-1}, which has been assigned [8] to non-centrosymmetric rotamers of I. On irradiation with either visible ($\lambda > 400$ nm) or near UV light ($320 < \lambda < 390$nm) (Fig. 1b) new absorptions appeared at 1978, 1933, 1855 and 1665 cm^{-1}, together with a band for free CO at 2133 cm^{-1}, whilst the bands for I decreased in intensity. A spectral subtraction revealed a fifth carbonyl band at 1898 cm^{-1} Fig. 1c). All product bands were seen to increase at the same rate indicating that they are associated with the same species (V). The reaction also occurs at 77 K and in CH_4, Ar or CO matrices at 12 K and is completely reversed on warming a PVC matrix to ca. 180 K (Fig. 1d). The product V has an intense UV absorption band (λ_{max} 330 nm; PVC matrix) which is probably associated with a $\sigma_b \rightarrow \sigma^*$(Mo–Mo) electronic transition [4]. The tungsten analogue VI (ν(CO) at 1971, 1925, 1896, 1838 and 1635 cm^{-1}; λ_{max} 300 nm; PVC matrix) of V was observed to be formed on photolysis of II in PVC films at 12–77 K.

It is evident from the observation of "free CO" that V and VI are CO loss products (cf. eq. 2). The number of infrared bands is consistent with a low symmetry dimeric species having five CO ligands and the products are clearly not III (M = Mo, ν(CO) at 2009 and 1911 cm^{-1}; M = W, ν(CO) at 1999 and 1898 cm^{-1}; CO matrix [9]) nor the known tetracarbonyl dimers $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$ (M = Mo, ν(CO) at 1889 and 1859 cm^{-1}; M = W, ν(CO) at 1885 and 1830 cm^{-1}; in isooctane [5]). The possibility that V and VI result from some reaction of III is also unlikely in view of the fact that no other reactions attributable to this radical in the irradiated PVC matrices are seen, e.g. the generation of $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ on warming a matrix [10]. The infrared spectra of V and VI have some features resembling those of the parent dimers and $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$. The most intense absorption for V (at 1933 cm^{-1}) is similar to the most intense band for I (at 1955 cm^{-1}), which has only terminal CO groups [11]. The bands at 1898 and 1855 cm^{-1} for V are at positions comparable with those of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$ [5], which has semi-bridging CO ligands [12]. The very low energy bands at 1665 and 1635 cm^{-1} for V and VI, respectively, could be attributed to either an acyl group formed by bonding of CO to a carbon of a C_5H_5 ring (as in A) or a bridging four electron donor CO ligand providing two σ-electrons to one metal and two π electrons to the other ** (as in B). The latter seems more likely in view of the facile thermal reversal of the reaction at low temperatures and the strong metal dependence of the infrared band positions. We propose, therefore, the structure shown below for V and VI, where dotted



(A)



(B)

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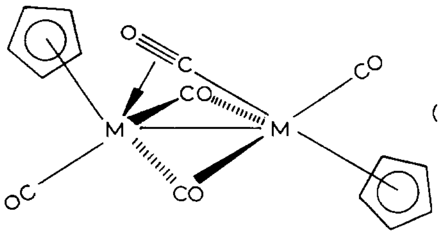
* The preparation of PVC film matrices and their use over a wide temperature range has been described previously [7].

** This type of bonding has been observed for $(OC)_2Mn(PH_2PCH_2PPh_2)_2(\mu\text{-}CO)Mn(CO)_2$ (ν(CO) at 1645 cm^{-1}) [13].

interaction represents a semibridging interaction.



(V, M = Mo ;
VI, M = W)

It is probably that V and VI are the same photoproducts as those seen by Allen et al. [14] on photolysis of I and II in methyltetrahydrofuran (mTHF) glasses at 80 K. These workers noted infrared bands which can be identified with the absorptions at 1933 and 1855 cm^{-1} for V and at 1925, 1896 and 1838 cm^{-1} for VI in the PVC films. The bands * were assigned [14] to III, possibly solvated by mTHF, but their positions and relative intensities are inconsistent with the $(\eta^5\text{-}C_5H_5)M(CO)_3^{\cdot}$ radicals characterised recently by gas matrix isolation studies [9].

The species V and VI have the same stoichiometry as that proposed for the CO loss product IV detected in the flash photolysis study [6]. The results of our matrix isolation study together with the flash photolysis study provide evidence for the previously unrecognised importance of a CO dissociation pathway in the photochemistry of the M–M bonded dimers $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$.

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* Other bands were probably obscured by parent bands or were too low in intensity to be observed as shown by Fig. 1c.