Photochemistry of Some Dinuclear Molybdenum and Tungsten Cyclopentadienyl Carbonyl Complexes in Frozen Gas Matrices at *ca.* 12 K: Infrared Spectroscopic Evidence for Carbon Monoxide Ejection as a Primary Photoprocess

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Infrared spectroscopic evidence, including the use of ^{13}CO-labelling, is presented to show that CO ejection is a primary process when the non-methylene-bridged and methylene-bridged dimers, $[\{M(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ and $[M_2(\mu\text{-}\eta^5{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ (M = Mo or W), respectively, are photolysed in frozen argon, methane, carbon monoxide, and nitrogen matrices at *ca.* 12 K. The $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ (M = Mo or W) photoproduct fragments for the non-methylene bridged species are proposed to have two terminal, two bridging (2-electron) and one bridging (4-electron) CO ligands whereas in the case of the photolysis of the parent methylene bridged species, which are constrained in a *cis* geometry and which undergo slower photolysis, the $[M_2(\mu\text{-}\eta^5{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)(CO)_5]$ photoproduct fragments are proposed to contain three terminal and two bridging (2-electron) CO ligands. Surprisingly, no secondary reactions were observed in carbon monoxide and nitrogen matrices and no ^{13}CO-exchange was observed for ^{13}CO-doped methane matrices. The low-temperature results are discussed in relation to solution and flash photolysis studies at ambient temperatures.

The photochemistry of a number of carbonyl containing transition metal, metal–metal bonded dimers has been extensively investigated. The classic models for such studies have been $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$, $[M_2(CO)_{10}]$ (M = Mn or Re) and $[\{M(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ (M = Mo or W).[1] In the case of the latter group 6A metal dimers which have been known for a considerable period of time, a wide range of photochemical reactions have been observed in solution.[2–4] These reactions can be divided broadly into five categories: (*i*) halogen abstraction reactions in the presence of halogenocarbon solvents such as CCl_4, CPh_3Cl, and CH_2PhCl, to yield $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ (M = Mo or W) [equation (1)];[5,6] (*ii*) outer-sphere electron-transfer reactions [equation (2)];[7] (*iii*) photosubstitution reactions involving the loss of CO and its replacement by an incoming ligand [equation (3)];[8,9] (*iv*) disproportionation reactions with either good σ-bonding ligands such as Cl^-, Br^-, and NCS^- or donor solvents that are not too sterically bulky [equation (4)];[10–16] and (*v*) photochemical ejection of two CO ligands to give a triply metal–metal bonded species [equation (5)].[17,18]

$$[\{M(\eta^5\text{-}C_5H_5)(CO)_3\}_2] \xrightarrow[CCl_4]{h\nu} 2[M(\eta^5\text{-}C_5H_5)(CO)_3Cl] \qquad (1)$$

M = Mo or W

$$[\{W(\eta^5\text{-}C_5H_5)(CO)_3\}_2] + 2[Fe(\eta^5\text{-}C_5H_5)_2]^+ + 2CH_3CN \xrightarrow{h\nu} 2[W(\eta^5\text{-}C_5H_5)(CO)_3(CH_3CN)]^+ + 2[Fe(\eta^5\text{-}C_5H_5)_2] \qquad (2)$$

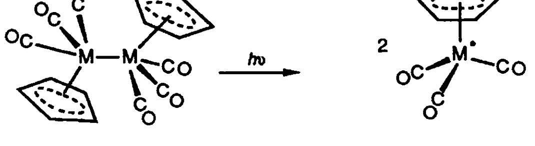
$$[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2] + PPh_3 \xrightarrow[C_6H_6]{h\nu} [Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5(PPh_3)] + CO \qquad (3)$$

$$[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2] + 2L \xrightarrow{h\nu} [\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]^- + [Mo(\eta^5\text{-}C_5H_5)(CO)_2L_2]^+ + CO \qquad (4)$$

$$[\{M(\eta^5\text{-}C_5H_5)(CO)_3\}_2] \xrightarrow[N_2\ \text{purge}]{h\nu} [(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}M(CO)_2(\eta^5\text{-}C_5H_5)] + 2CO \qquad (5)$$

Interest has also been stimulated in closely related analogues of these dimers including asymmetric mixed-metal dimers[19] and dimers containing the cycloheptatrienyl ligand.[20]

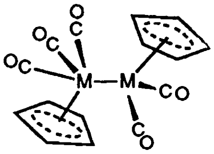
The photochemistry of metal–metal bonded dimers of type (**1**) has been rationalised in terms of a primary step which involves homolytic cleavage of the metal–metal single bond to give two 17-electron radical species (**2**) which then undergo further reaction [equation (6)].[21] Such radical species have been proposed as reaction intermediates in a number of organometallic reactions.[22] For molybdenum the $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^{\bullet}$ radical has recently been generated by $H^{\bullet}$ ejection from $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$.[23] Most authors suggest that any photochemical CO-loss process which occurs for the metal dimers is either unimportant,[7] or results in photochemical decomposition.[6] Whilst this may be true for processes (*i*) and



(6)

(**1**) M = Mo or W (**2**)

(*iv*) above, which can only be reasonably rationalised in terms of such a radical process, it is not so for processes (*iii*) and (*v*) where a CO-loss mechanism may well be implicated. In fact, in the case of process (*v*) the proposed radical mechanism[18] for reversible formation of the triply metal–metal bonded species [equation (5)] seems somewhat unlikely. The proposed 'back reaction', involves initial cleavage of the metal–metal triple bond to give $[M(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet}$ (M = Mo or W), which then goes on to capture CO and reform the singly metal–metal bonded species $[\{M(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$. Given that the half lives of the triply metal–metal bonded species $[\{M(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ are in the time range of just under one minute at CO pressures of one atmosphere or below,[18] such a mechanism seems somewhat unlikely, as it is probable that cleavage of the metal–metal triple bond is not sufficiently facile at room temperature to allow such a process. An alternative mechanism involving initial CO loss to give the pentacarbonyl species (**3**)

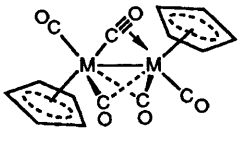

(**3**) M = Mo or W

and then subsequent secondary photolysis resulting in further CO loss to give the triply metal–metal bonded species, [equation (5)] seems far more plausible in terms of its reversibility.

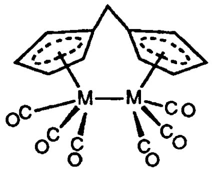
Luminescence studies on the $[\{M(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ dimers (M = Mo or W),[24] in cyclohexane solution at room temperature revealed two emission peaks. Of these the high-energy emission at *ca.* 440 nm for M = Mo was assigned to fluorescence from a weak metal-to-cyclopentadienyl π^* transition, while the origin of the lower energy *ca.* 570 nm emission was unclear.

A flash photolysis study of the $[\{M(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ dimers (M = Mo or W), provided evidence for two distinctly different intermediates immediately following the flash.[25] Both intermediates were found to reform the starting dimer by relatively rapid second-order processes, but the processes were sufficiently different in timescale to allow them to be resolved. The intermediate which disappeared on a fast timescale (*ca.* 0.05—2 ms) showed a spectrum in which the intense band due to the σ–σ^* absorption of the metal–metal bond of the parent had disappeared, indicating that this bond had cleaved to produce the radical species shown in equation (6). The other intermediate, which disappeared on a slower timescale (*ca.* 2—50 ms) showed a spectrum similar to that of the parent species and was assigned to the CO-loss product (**3**) on the basis of the second-order kinetics observed for the recombination reaction with CO. The same photochemistry was demonstrated to occur as a result of both u.v. ($340 < \lambda < 405$ nm) and visible ($\lambda > 460$ nm) photolysis.

A low-temperature study (12—298 K) using poly(vinyl chloride) (pvc) films[26] showed no evidence of radical formation upon photolysis at low temperatures, the main photochemical pathway instead being CO ejection. The CO-loss product was identified as $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ (**4**) which was proposed to have two terminal, two semi-bridging and one bridging four-electron donor CO ligand. Again, the same photochemistry was observed under conditions of either u.v. ($320 < \lambda < 390$ nm) or visible photolysis ($\lambda > 400$ nm).


(**4**) M = Mo or W

This paper describes the photochemistry of $[\{M(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ complexes [M = Mo (**1a**) and W (**1b**)] and the closely related methylene-bridged dimers $[M_2(\mu\text{-}\eta^5\text{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ [M = Mo (**5a**) and W (**5b**)] in frozen gas matrices† at *ca.* 12 K. The latter species must exist exclusively in the *cis* configuration due to the methylene bridge between the two cyclopentadienyl ligands. Given this, different photochemistry could be expected for (**5a**) and (**5b**) when compared to the non-methylene-linked dimers. Such a situation has already been seen for the iron and ruthenium species for which the non-methylene-linked dimers $[\{M(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ (M = Fe or Ru), showed completely different matrix photochemistry to the more recently investigated methylene-bridged species, $[M_2(\mu\text{-}\eta^5\text{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)(CO)_4]$ (M = Fe or Ru).[28,29]


(**5**) M = Mo or W

Experimental

The low-temperature cryostat, the vacuum system, the spectrometers, the photolysis lamp, and the matrix gases have been described elsewhere.[29,30] Infrared spectra (Nicolet 7199 Fourier-transform i.r. spectrometer) were recorded at 1 cm^{-1} resolution (no. of data points = 16 384; no. of transform points = 32 768; mirror velocity = 34, *i.e.* 0.586 cm s^{-1}; aperture setting = full, amplifier gain = 4; no. of scans = 1 000; apodization function = Happ–Genzel), subtracted in absorbance mode before plotting out in conventional percentage transmission mode and were smoothed using instrument functions.

Samples of $[\{M(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ (M = Mo or W) were generously donated by Dr. N. Fitzpatrick. Samples of $[M_2(\mu\text{-}\eta^5\text{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ (M = Mo or W) were prepared by Professor T. E. Bitterwolf.[28] All four samples were used without further purification.

Matrices containing these dimers were obtained by subliming them [(**1a**) at 110 °C; (**1b**) at 120 °C; (**5a**) at 130 °C; and (**5b**) at 140 °C] from a glass finger very close to the central cold window of the cryostat and co-condensing the vapours with a large excess of matrix gas, controlled by a needle valve. Spray-on times were typically 45–60 min.

Wavelength selective photolyses were achieved using a number of broad band cut-off filters: filter A, $\lambda > 460$ nm, Corning glass filter no. 3385 (thickness 2 mm); filter B, $320 < \lambda < 390$ nm, Corning glass filter no. 5874 (thickness 2 mm); and filter C, $310 < \lambda < 360, \lambda > 550$ nm, a quartz gas cell (pathlength 27 mm) containing Br_2 (200 Torr) + Pyrex disc (thickness 2 mm).

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† Initial attempts to sublime (**1a**) and (**1b**) resulted in decomposition and hence the low-temperature study using pvc films.[26] An improvement in the sublimation technique in this work, by shortening the path of molecules to the central window such that lower heating temperatures were required and decomposition by heating was minimised, afforded minimal decomposition.[27]

Table 1. Infrared band positions (cm^{-1}) for [{M(η^5-C_5H_5)(CO)$_3$}$_2$] [M = Mo (**1a**) and W (**1b**)] and their photoproducts in the terminal- and bridging-CO stretching regions in argon, methane, and carbon monoxide matrices

Complex	ν(CO)	Ar	CH_4	CO
(**1a**) [{Mo(η^5-C_5H_5)(CO)$_3$}$_2$] $C_2{}^b$	*A*	2 035.5w	2 030.0w	2 031.0w
	B	1 970.0vs	1 963.0s	1 965.5vs
	A	1 955.5vw	1 947.5w	1 946.0w
	A	1 925.5s	1 918.5s	1 920.0s
	B	1 918.5m	1 912.5m	1 910.0m
	B	1 903.0w	1 897.0w	1 898.5w
(**4a**) [Mo_2(η^5-C_5H_5)$_2$(CO)$_5$] C_s	*A′*	1 987.5vw	1 981.5w	1 980.5vw
	A′	1 947.5s	1 939.5m	1 939.5m
	A′	1 893.4w	1 885.5w	1 886.5vw
	A″	1 874.5m	1 865.5m	1 865.5m
	A′	1 672.5w	1 667.0w	1 666.5w
(**1b**) [{W(η^5-C_5H_5)(CO)$_3$}$_2$] $C_2{}^b$	*A*	2 029.5w	2 024.0w	2 026.0w
	B	1 967.5s	1 962.5s	1 962.0vs
	A	1 953.0w	1 950.0w	1 950.5w
	A	1 923.0s	1 914.5s	1 916.5s
	B	1 910.5m	1 906.0m	1 908.0m
	B	1 896.0w	1 891.0w	1 894.0w
(**4b**) [W_2(η^5-C_5H_5)$_2$(CO)$_5$] C_s	*A′*	1 979.5vw	1 973.0w	1 973.0w
	A′	1 940.0s	1 936.0s	1 937.5s
	A′	1 886.5w	1 881.0w	1 882.5vw
	A″	1 868.5m	1 861.5m	1 863.0m
	A′	1 659.5w	1 651.0w	1 654.0w

[a] Relative intensities: w = weak, m = medium, s = strong, and v = very. [b] Symmetry lowered from C_{2h} to C_2 in a matrix environment (see text).

Results

(*a*) *Photolysis of* [{M(η^5-C_5H_5)(CO)$_3$}$_2$] *Complexes* [M = Mo (**1a**) *or* W (**1b**)] *isolated at High Dilution in Argon, Methane, and Carbon Monoxide Matrices at* ca. 12 K.—Analogous results were obtained for species (**1a**) and (**1b**) in all three matrix gases with the appropriate differences due to matrix shifts in each case. A comparison of the respective band positions of the starting species and of the photoproducts is given in Table 1. The i.r. spectrum of (**1a**) isolated at high dilution in a methane matrix is shown in Figure 1(*a*). The spectrum corresponds to a matrix laid by slow deposition at 110 °C and shows some signs of decomposition occurring in the deposition head. However, no signs of decomposition products were observed in the actual matrix i.r. spectrum at this temperature except for the trace of 'free CO'. On raising the deposition temperature by *ca.* 20 °C a large number of new i.r. bands were seen to appear, possibly including the *cis*-isomer of (**1a**) by analogy with the band positions for (**5a**) and the photoproduct (**4a**) which was observed in pvc films. There were, however, additional bands due to other 'decomposition products' and the band for 'free CO' in the starting spectrum exceeded 1.5 absorbance units indicating considerable decomposition in the deposition head. Experiments at the higher deposition temperature were irreproducible and hence only those at the lower more controlled temperature will be presented.

Under the controlled conditions the i.r. spectrum of (**1a**) showed six bands, three relatively strong and three very weak [Figure 1(*a*)]. For a strict C_{2h} geometry only three i.r. active bands would be expected ($A_u + 2B_u$) which from the spectrum observed in cyclohexane solution[31] correspond to the three strongest bands observed in the methane matrix at 1 963.0, 1 918.5, and 1 912.5 cm^{-1}. Previous i.r. studies in various media including pvc matrices[32] and room-temperature solutions using solvents of differing polarities,[31,33–36] have also shown a variable number of extra bands which have been attributed to a significant contribution from the *gauche*, C_2 isomer of (**1a**). This species may be produced by either a 60 or 120° rotation of one half of the dimer about the metal–metal bond. The relative intensities of the bands however, and the fact that only three new weak bands were observed, rather than the six expected for the *gauche* isomers, indicated that the weak bands were most probably due to a reduction of symmetry in the matrix to C_2, due primarily to site asymmetries. The result of this reduction in symmetry was to cause the i.r. inactive modes in C_{2h} symmetry ($2A_g + B_g$) to become weakly i.r. active in the matrix, hence resulting in the three weak bands observed at 2 030.0, 1 947.5, and 1 897.0 cm^{-1} in the methane matrix.

The solution u.v.–visible spectrum of (**1a**) showed two absorptions in the visible and near-u.v. regions (n-hexane) at 385 (ε = 21 500) and 510 nm (ε = 1 900 dm^3 mol^{-1} cm^{-1}), in good agreement with the band positions and intensities reported previously.[1,25] The stronger of the two absorptions has been assigned to the σ–σ^* transition localized at the metal–metal bond,[5,25,37] chiefly by analogy with the spectrum of the [M_2(CO)$_{10}$] dimers (M = Mn or Re).[38] The weaker absorption in the visible region, has been attributed by the same authors to a $d\pi$–σ^* transition.

Photolysis using either a visible source, filter A, $\lambda > 460$ nm, or a near-u.v. source, filter B, $320 < \lambda < 390$ nm resulted in the same photochemistry, although u.v. photolysis was far more efficient leading to rapid formation of the photoproduct. A range of long-wavelength and selective band photolyses all failed to produce any photoreversal of the reaction. The photoproduct exhibited five i.r. bands which in the methane matrix appeared at 1 981.5, 1 939.5, 1 885.5, 1 865.5, and 1 667.0 cm^{-1}. These bands all appeared at the same rate and were accompanied by a concomitant decrease in the bands of the parent species (**1a**) [Figure 1(*b*)]. A comparison with the changes observed in pvc matrices,[26,32] showed that the same photochemistry was occurring in gas matrices, although under gas-matrix conditions the i.r. bands were much sharper and hence, the changes were easier to follow. A 1:1 subtraction [Figure 1(*c*)] clearly showed that the appearance of the five new bands was also accompanied by an increase in the amount of 'free CO'.

The lowest wavenumber band of the photoproduct observed in pvc films at 1 665 cm^{-1} has been postulated to be due to either an acyl group formed by the bonding of CO to a carbon

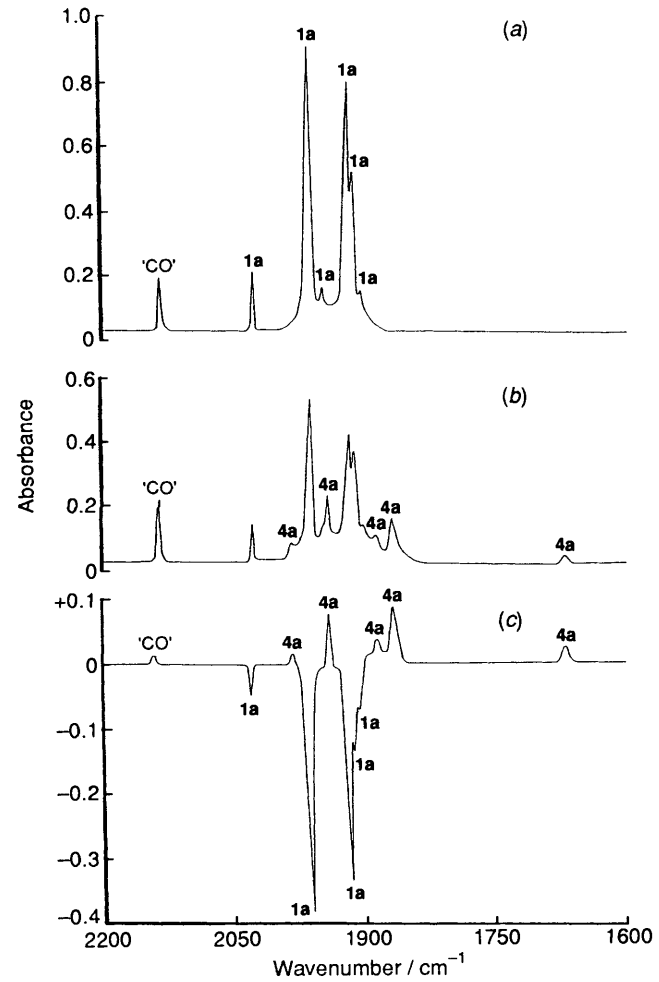
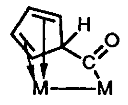
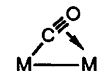


Figure 1. Infrared spectra (Nicolet 7199, CO stretching region) of [{Mo(η^5-C_5H_5)(CO)$_3$}$_2$] (**1a**) and its photoproduct isolated at high dilution in a methane matrix: (*a*) at start, (*b*) after 10 min photolysis with filter B, and (*c*) subtraction spectrum [(*b*) − (*a*)]



(**6**) acyl



(**7**) bridging

atom of the C_5H_5 ring [structure (**6**)], or a bridging four-electron donor CO ligand, providing two σ-electrons to one metal and two π-electrons to the other [structure (**7**)].[26,32] Of these two possible arrangements the bridging structure (**7**) was thought to be more likely on the grounds of the facile thermal reversibility of the photoreaction at low temperatures and the metal dependence of the i.r. band positions. Bridging CO ligands of this type are already known for a number of manganese dimers.[39,40] The bridging structure was supported by an examination of the 'ring mode' region (800—600 cm^{-1}) in gas matrices, this region being outside the working spectroscopic region of pvc films. In gas matrices this region showed no great changes between the 'ring modes' of (**1a**) and (**1b**) and those of the photoproducts (**4a**) and (**4b**). This implied that the acyl structure (**4a**) was not the correct conformation as this region would have been expected to show significant changes in the vibrations of the C_5H_5 ring involved in acyl bonding.

Identical photochemistry was seen for the tungsten analogue, (**1b**), and the band positions for this species and its photoproduct are shown in Table 1.

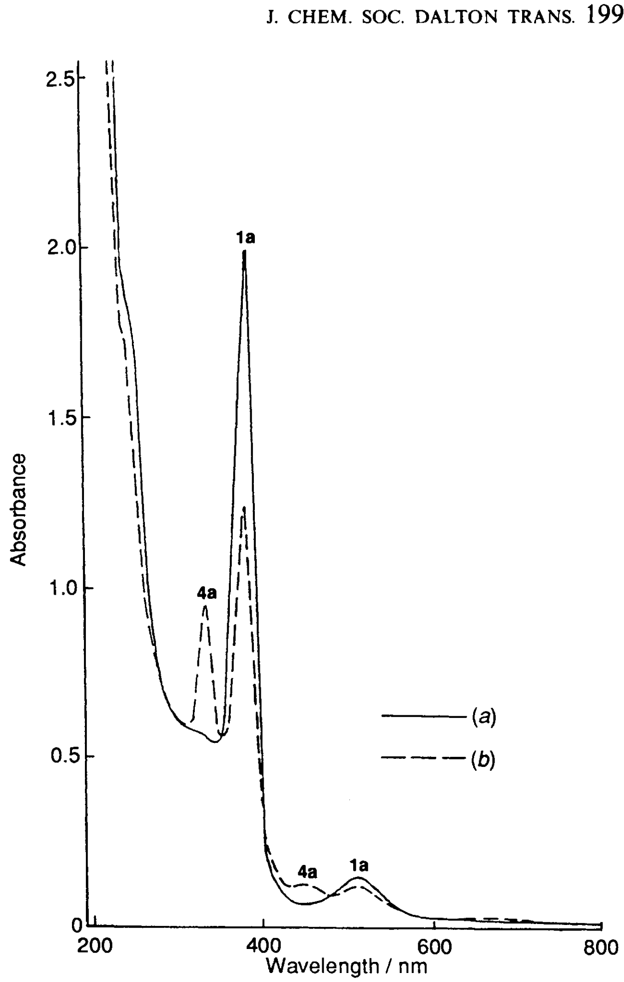


Figure 2. The u.v.–visible spectra (Perkin-Elmer Lambda 7) of [{Mo(η^5-C_5H_5)(CO)$_3$}$_2$] (**1a**) and its photoproduct isolated at high dilution in a methane matrix at *ca.* 12 K: (*a*) at start, and (*b*) after 10 min photolysis with filter B

(*b*) *Photolysis of* [{M(η^5-C_5H_5)(CO)$_3$}$_2$] *Complexes* [M = Mo (**1a**) *or* W (**1b**)] *isolated at High Dilution in Nitrogen and* ^{13}CO-*doped Methane Matrices at* ca. 12 K.—Since no back reaction could be photoinduced for either of the photoproducts (**4a**) and (**4b**) it was unlikely that either of the species could be induced to pick up a 'labelling ligand'. This indeed proved to be the case and the same photochemistry was observed as in argon, methane, or carbon monoxide matrices. Thermal reversal had been observed previously in pvc films, but this was seen to onset at *ca.* 90 K and to be complete by 180 K. No thermal reversal was observed under matrix conditions as the matrix 'pumped off' before the reversal occurred.

(*c*) *U.V.–Visible Spectra obtained Following the Photolysis of* [{M(η^5-C_5H_5)(CO$_3$)}$_2$] *Complexes* [M = Mo (**1a**) *or* W (**1b**)] *isolated at High Dilution in Argon, Methane, Carbon Monoxide, and Nitrogen Matrices at* ca. 12 K.—The u.v.–visible spectrum of (**1a**) isolated at high dilution in a methane matrix is shown in Figure 2(*a*). The spectrum agrees well with that seen in hexane solution, allowing for the expected sharpening in the low-temperature matrix.

Photolysis (filter B, total 10 min) leading to a situation equivalent to Figure 1(*b*) resulted in the appearance of two new bands [Figure 2(*b*)]. The most intense of these bands (at 334 nm) corresponds to the band reported for the metal–metal bond

Table 2. U.v.–visible band positions (nm)[a] for $[\{M(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ [M = Mo (**1a**) or W (**1b**)], $[M_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO_6)]$ [M = Mo (**5a**) or W (**5b**)], and their photoproducts in argon, methane, carbon monoxide, and dinitrogen matrices

Complex	Ar	CH_4	CO	N_2
(1a) $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ C_2[b]	382s	382s	382s	381s
	506w	508w	507w	505w
(4a) $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ C_s	332s	334s	332s	332s
	445w	448w	446w	444w
(1b) $[\{W(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ C_2[b]	355s	356s	355s	354s
	482w	484w	483w	480w
(4b) $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ C_2	304s	305s	304s	303s
	425w	426w	426w	424w
(5a) $[Mo_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ C_{2v}	374s	375s	375s	374s
	422w	426w	423w	423w
	526w	528w	526w	525w
(9a) $[Mo_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO)_5]$ C_s	327m	328m	327m	326m
	476w	478w	477w	476w
(5b) $[W_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ C_{2v}	349s	349s	348s	348s
	404 (sh) w	405w	403 (sh) w	402w
	511w	513w	512w	510w
(9b) $[W_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO)_5]$ C_s	300m	310m	301m	299m
	452w	455w	454w	452w

[a] Relative intensities: w = weak, m = medium, s = strong, and sh = shoulder. [b] Symmetry lowered from C_{2h} to C_2 in a matrix environment (see text).

Table 3. Infrared band positions (cm^{-1})* for $[M_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ [M = Mo (**5a**) or W (**5b**)] and their photoproducts in the terminal- and bridging-CO stretching regions in argon, methane, and carbon monoxide matrices

Complex	ν(CO)	Ar	CH_4	CO
(5a) $[Mo_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ C_{2v}	A_1	2 023.0s	2 022.5s	2 022.0s
	A_1	1 971.0vs	1 969.0vs	1 970.0s
	B_1	1 930.5m	1 931.0m	1 928.0m
	B_2	1 910.0m	1 908.0m	1 908.5m
	B_1	1 891.0w	1 889.5w	1 889.0w
(9a) $[Mo_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO)_5]$ C_s	A'	2 009.0vs	2 006.5s	2 008.0vs
	A'	1 956.2m	1 952.5m	1 959.0s
	A''	1 921.5s	1 918.0s	1 917.5m
	A'	1 853.5m	1 848.5m	1 854.0m
	A''	1 811.0w	1 808.0w	1 810.0w
(5b) $[W_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ C_{2v}	A_1	2 020.5s	2 018.0s	2 020.0s
	A_1	1 968.5s	1 965.5s	1 967.0s
	B_1	1 924.0m	1 919.5m	1 922.5m
	B_2	1 904.0m	1 903.0m	1 904.5m
	B_1	1 885.0w	1 881.0w	1 884.5w
(9b) $[W_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO)_5]$ C_s	A'	2 002.5s	1 998.5s	2 001.5s
	A'	1 952.2m	1 950.5m	1 952.0m
	A''	1 916.5s	1 916.0s	1 914.5s
	A'	1 849.5m	1 847.0m	1 949.0m
	A''	1 806.5w	1 802.5w	1 804.5w

* Relative intensities: w = weak, m = medium, s = strong, and v = very.

σ–σ* transition of the photoproduct in pvc films ($\lambda_{max.}$ = 330 nm).[32] The weaker of the two new bands, which was not resolved in pvc films, appeared at 448 nm at the same rate as the 334 nm band and the i.r. bands of the photoproduct and hence it was assigned to the *d*π–σ* transition of (**4a**).

As in the case of the i.r. spectra, analogous changes were observed in the u.v.–visible spectrum of the tungsten species (**1b**) and its photoproduct (**4b**). The band positions are summarized in Table 2.

(*d*) *Photolysis of* $[M_2(\mu\text{-}\eta^5\text{:}\eta^{5\prime}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ *Complexes* [M = Mo (**5a**) *or* W (**5b**)] *isolated at High Dilution in Argon, Methane, and Carbon Monoxide Matrices at* ca. 12 K.—Analogous results were obtained for both species (**5a**) and (**5b**) in all three matrix gases, with appropriate differences due to matrix shifts in each case. The band positions of the starting species and the photoproducts are given in Table 3. The i.r. spectrum of (**5a**) isolated at high dilution in a methane matrix is shown in Figure 3(*a*). As with species (**1a**) and (**1b**) a trace of 'free CO' was observed in the starting spectrum, indicating that some decomposition was occurring in the deposition head, but again no signs of decomposition products were seen in the matrix spectrum. The spectrum shows the five i.r.-active CO stretches expected for a C_{2v} *cis*-geometry, ($2A_1 + B_1 + 2B_2$). The bands appeared at 2 022.5, 1 969.0, 1 931.0, 1 908.0, and 1 889.5 cm^{-1} in a methane matrix in reasonable agreement with the band positions seen in solution.[41]

In contrast to the chemistry of (**1a**), corresponding to the visible band at 430 nm (ε = 2 400 dm^3 mol^{-1} cm^{-1}) in solution (n-hexane), photolysis of (**5a**) at λ > 450 nm (filter A) failed to produce any reaction. Photochemically induced changes were however observed upon near-u.v. photolysis with either filter C, 310 < λ < 360, λ > 550 nm, or filter B, 320 < λ < 390 nm, corresponding to the near-u.v. band at 380 nm (ε = 22 000 dm^3

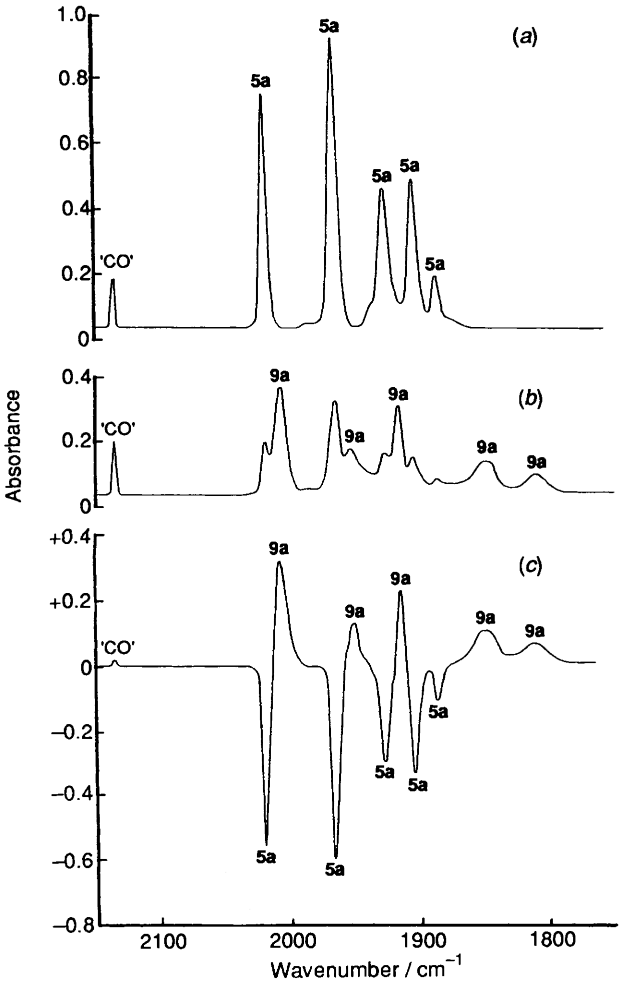
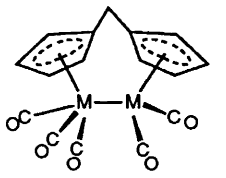


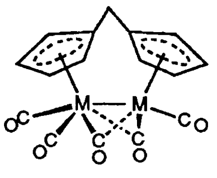
Figure 3. Infrared spectra (Nicolet 7199, CO stretching region) of $[Mo_2(\mu\text{-}\eta^5{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ (**5a**) and its photoproduct isolated at high dilution in a methane matrix: (*a*) at start, (*b*) after 60 min photolysis with filter B, and (*c*) subtraction spectrum [(*b*) − (*a*)]

mol^{-1} cm^{-1}) in solution (n-hexane). Photolysis times were much longer than for (**1a**).

The result of such near-u.v. photolysis (filter B, total 60 min) was the appearance of five new i.r. bands [Figure 3(*b*)], which in a methane matrix were at 2 006.5, 1 952.5, 1 918.0, 1 848.5, and 1 808 cm^{-1}. These new bands all grew throughout the experiment and were accompanied by a decrease in the intensities of the bands due to the parent species (**5a**). A 1:1 subtraction [Figure 3(*c*)] again showed that the appearance of the five new bands was also accompanied by an increase in the amount of 'free CO'. On this basis the photoproduct was assigned to a pentacarbonyl CO-loss species, with C_s symmetry, *i.e.* either (**8**) or (**9**).



(**8**)



(**9**)

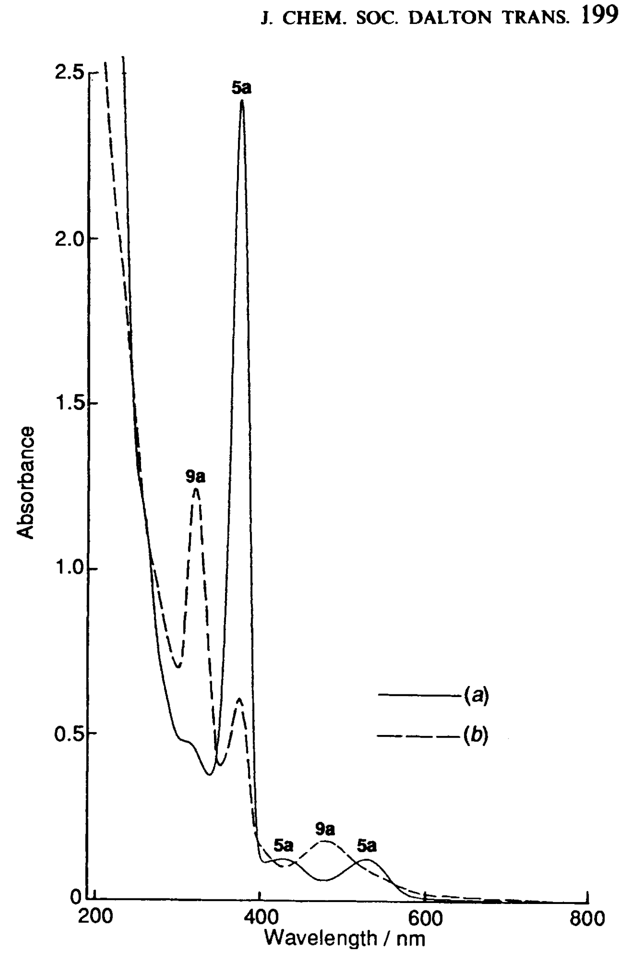


Figure 4. The u.v.–visible spectra (Perkin-Elmer Lambda 7) of $[Mo_2(\mu\text{-}\eta^5{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ (**5a**) and its photoproduct isolated at high dilution in a methane matrix at *ca.* 12 K: (*a*) at start, and (*b*) after 60 min photolysis with filter B

The lack of any CO-stretching vibrations below 1 800 cm^{-1} precluded a structure similar to that of (**4a**) which contained a four-electron bridging CO ligand. This left open two possible structures; either an all terminal CO structure (**8**), or one containing semi-bridging CO ligands (**9**). The two bands at *ca.* 1 850 and *ca.* 1 810 cm^{-1} fall in the region expected for semi-bridging CO ligands. A comparison with the band positions for the triply metal–metal bonded species $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ which is known to have semi-bridging CO groups,[17,18] and which is proposed to have two such ligands reveals that the bands for a new species such as (**9**) appear at *ca.* 40 cm^{-1} lower than expected for such a structure. This can be readily accounted for however, by the fact that in the above cases the metal centres for both species have a full 18-electron count, whereas in the case of (**9**) one metal centre has nominally only a 16-electron count. It is probable, therefore, that the new pentacarbonyl dimer has the structure (**9**), *i.e.* (**9a**) for Mo.

As in the cases of (**1a**) and (**1b**) a range of long-wavelength photolyses failed to produce any reversal of the photoreaction, and the results were the same in nitrogen and ^{13}CO-doped methane matrices as in argon, methane, and carbon monoxide. Analogous results were also observed for the tungsten species (**5b**) and the band positions and intensities for this species and its photoproduct (**9b**) are also shown in Table 3.

(*e*) *U.V.–Visible Spectra obtained Following the Photolysis of* $[M_2(\mu\text{-}\eta^5{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ [M = Mo (**5a**) *or* W (**5b**)] *isolated at High Dilution in Argon, Methane, Carbon Monoxide, and Nitrogen Matrices at* ca. 12 K.—The u.v.–visible spectrum of (**5a**) isolated at high dilution in a methane matrix is shown in Figure 4(*a*). The methane matrix spectrum shows two bands (375 and 528 nm) which correspond to those for the n-hexane solution spectrum. The spectrum also shows an additional weak band in the visible region at 426 nm which was not resolved in the solution spectrum. A comparison with the band positions for complex (**1a**) indicates that the band at 375 nm can be assigned to the metal–metal bond σ–σ* transition. The two visible bands appear above and below the position of the *d*π–σ* transition observed for (**1a**), indicating that the two filled *d*-orbitals which were degenerate in the case of (**1a**) with C_{2h} symmetry have lost their degeneracy in the case of (**5a**) which has a C_{2v} symmetry.

Photolysis, (filter B, 60 min) leading to a situation equivalent to Figure 3(*b*) resulted in the appearance of two new bands [Figure 4(*b*)] in a similar fashion to those observed for (**4a**) and (**4b**). The most intense of the two bands at 328 nm can be assigned to the metal–metal σ–σ* transition of species (**9a**) from its position and intensity, and serves to confirm the presence of a metal–metal bond in the photoproduct. The weaker band at 478 nm, can be assigned to a *d*π–σ* transition by analogy with the gas matrix spectra of (**4a**) and (**4b**).

Discussion

The photochemical reactions of the species (**1a**) and (**1b**) differed from those of the species containing the dicyclopentadienyl methane ligand, (**5a**) and (**5b**), although the only observable photoreactions in each case were those involving CO loss.

In the case of species (**1a**) and (**1b**) a comparison between gas-matrix results and those of previous studies in pvc films allowed all the information on these species to be obtained. The gas-matrix experiments gave sharper more resolved bands both in the i.r. and the u.v.–visible spectra and hence allowed the identification of a new electronic absorption in the visible region for the photoproducts (**4a**) and (**4b**). The advantage of previous studies in pvc films however, was that they allowed the photoproducts to be warmed to 298 K, in order that thermal reversal could be followed. Using a combination of these two low-temperature techniques therefore, allowed all the aspects of the spectra and reactivity of the photoproducts to be studied.

Previous photochemical studies of species (**1a**) and (**1b**) in methyltetrahydrofuran glasses at *ca.* 80 K,[42] reported the appearance of a number of new i.r. bands. These new bands were assigned to the radical species produced by metal–metal bond homolysis [equation (6)]. A comparison of the band positions quoted with those of the known radicals produced by photolysis of [M(η^5-C_5H_5)(CO)$_3$H] (M = Mo or W),[43] in gas matrices shows discrepancies and it seems likely that the new bands observed in low-temperature glasses were also due to the CO-loss products (**4a**) and (**4b**).

In contrast to the photochemistry of (**1a**) and (**1b**) which was the same under conditions of either visible or near-u.v. photolysis, photochemical reaction was only observed for the dicyclopentadienyl methane species (**5a**) and (**5b**) when a near-u.v. photolysis source was used. This contrast in photochemistry was similar to that seen for the species [M_2(μ-η^5:$\eta^{5'}$-C_5H_4-$CH_2C_5H_4$)(CO)$_4$] (M = Fe or Ru) and their non-methylene bridged-analogues.[29,44] All these species showed a simple photochemically induced CO ejection pathway in the matrix environment rather than the predominantly radical photochemistry observed in solution as a result of homolysis of the metal–metal bond.

A comparison of the band positions of the photoproducts (**9a**) and (**9b**) with those of the radical species [M(η^5-C_5H_5)(CO)$_3$]$^\cdot$ (M = Mo or W) reported in carbon monoxide matrices,[43] revealed that the highest wavenumber *A′* band of the photoproducts corresponded to the band reported for the radical species at *ca.* 2 010 (Mo) and *ca.* 2 000 cm^{-1} (W). This fitted well with the observation that it was only photolysis in the near-u.v. region which produced photochemistry. There was no band which consistently corresponded to the lower wavenumber band reported for the radicals however, and the fact that all the photoproduct bands grew at the same rate, were accompanied by an increase in the band for 'free CO', and that a band was observed for the σ–σ* transition of the photoproduct in the u.v.–visible spectrum led to the assignment of (**9a**) and (**9b**) as the pentacarbonyl CO-loss products. The low-wavenumber bands of these photoproducts indicated that these species existed in the semi-bridging conformation, (**9**).

The lack of evidence for radical chemistry in the matrix environment was not particularly surprising. In this case the two radical centres were relatively large and in gas matrices would be prevented from diffusing apart by the low temperatures involved and the matrix cage effect. Additionally, the radicals would be kept in close proximity by the methylene linkage between the two cyclopentadienyl rings. The overall effect of this would be that any radical pairs formed would readily recombine to reform the parent dimer.

Conclusion

Examination of the photochemistry of species (**1a**) and (**1b**) in gas matrices has confirmed the CO ejection pathway which had previously been observed in poly(vinyl chloride) films. A comparison of the polymer-film and gas-matrix studies also served to demonstrate the complimentary nature of these two techniques, which when used in conjunction with each other served to obtain more information than was available from either one of the techniques alone.

The confirmation of a CO ejection mechanism for complexes (**1a**) and (**1b**) which was supported by the flash photolysis results in solution, illustrated that an alternative photochemical pathway existed, in addition to homolytic metal–metal bond fission to produce radical species. The importance of this alternative pathway certainly varies, but it is clear that it may be the dominant mechanism under some circumstances, such as the possible production of triply metal–metal bonded products [equation (5)] from the species (**4a**) and (**4b**) by a second loss of CO.

The gas-matrix study of species (**5a**) and (**5b**) highlighted the difference in photochemistry between the methylene-bridged and non-methylene-bridged dimers. Although both sets of dimers underwent photochemically induced CO ejection processes, the products were different in each case, as were the rates of reaction.

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References

1 J. V. Casper and T. J. Meyer, *Chem. Rev.*, 1985, **85**, 187.
2 G. Wilkinson, *J. Am. Chem. Soc.*, 1954, **76**, 209.
3 F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1955, **1**, 175.
4 F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.
5 D. S. Ginley and M. S. Wrighton, *J. Am. Chem. Soc.*, 1975, **97**, 4246.
6 P. C. Ford and R. M. Laine, *Inorg. Chem.*, 1977, **16**, 388.
7 A. F. Hepp and M. S. Wrighton, *J. Am. Chem. Soc.*, 1981, **103**, 1258.
8 R. B. King and K. H. Pannel, *Inorg. Chem.*, 1968, **7**, 2356.
9 R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 1968, 43.
10 A. R. Burkett, T. J. Meyer, and D. G. Whitten, *J. Organomet. Chem.*, 1974, **67**, 67.

11 J. L. Hughey and T. J. Meyer, *Inorg. Chem.*, 1975, **14**, 947.
12 D. M. Allen, A. Cox, T. J. Kemp, and Q. J. Sultana, *J. Chem. Soc., Dalton Trans.*, 1976, 1189.
13 A. E. Stiegman and D. R. Tyler, *J. Am. Chem. Soc.*, 1982, **104**, 2944.
14 M. Stieglitz, A. E. Stiegman, and D. R. Tyler, *J. Am. Chem. Soc.*, 1983, **105**, 6032.
15 A. E. Stiegman and D. R. Tyler, *Coord. Chem. Rev.*, 1985, **63**, 217.
16 A. S. Goldman, C. E. Philbin, and D. R. Tyler, *Inorg. Chem.*, 1986, **25**, 4434.
17 W. Butler, M. D. Curtis, and R. J. Klingler, *J. Am. Chem. Soc.*, 1975, **97**, 3535.
18 C. R. Bock, D. S. Ginley, and M. S. Wrighton, *Inorg. Chim. Acta*, 1977, **23**, 85.
19 D. S. Ginley and M. S. Wrighton, *J. Am. Chem. Soc.*, 1975, **97**, 4908.
20 A. Ricalton and M. W. Whiteley, *J. Organomet. Chem.*, 1989, **361**, 101.
21 G. L. Geoffroy and M. S. Wrighton, in 'Organometallic Photochemistry,' Academic Press, New York, 1979, p. 61.
22 M. C. Baird, D. J. Gillis, M. J. Thomas, B. Wassink, and S. C. Wright, *J. Am. Chem. Soc.*, 1987, **109**, 1995.
23 M. C. Baird and P. R. Drake, *J. Organomet. Chem.*, 1989, **363**, 131.
24 C. G. Morgante and W. S. Struve, *Chem. Phys. Lett.*, 1980, **69**, 56.
25 C. R. Bock, J. L. Hughey, and T. J. Meyer, *J. Am. Chem. Soc.*, 1975, **97**, 4440.
26 R. H. Hooker and A. J. Rest, *J. Organomet. Chem.*, 1983, **249**, 127; 1983, **254**, C25.
27 A. K. Campen, Ph.D. Thesis, University of Southampton, 1989.
28 T. E. Bitterwolf, *J. Organomet. Chem.*, 1986, **312**, 197.
29 P. E. Bloyce, A. K. Campen, R. H. Hooker, A. J. Rest, N. R. Thomas, T. E. Bitterwolf, and J. E. Shade, following paper.
30 A. J. Rest, I. Whitwell, W. A. G. Graham, J. K. Hoyano, and A. D. McMaster, *J. Chem. Soc., Dalton Trans.*, 1987, 1181.
31 R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, 1973, **7**, 153.
32 R. H. Hooker, Ph.D. Thesis, University of Southampton, 1987.
33 D. P. Shoemaker and F. C. Wilson, *J. Chem. Phys.*, 1957, **27**, 809.
34 P. N. Brier, A. A. Chalmers, J. Lewis, and S. B. Wild, *J. Chem. Soc. A*, 1967, 1889.
35 P. S. Braterman and D. T. Thompson, *J. Chem. Soc. A*, 1968, 1454.
36 R. D. Fischer and K. Noack, *J. Organomet. Chem.*, 1969, **16**, 125.
37 H. B. Gray and R. A. Levenson, *J. Am. Chem. Soc.*, 1975, **97**, 6042.
38 G. P. Caesar, H. B. Gray, and R. A. Levenson, *J. Am. Chem. Soc.*, 1970, **92**, 3653.
39 R. Colton and C. J. Commons, *Aust. J. Chem.*, 1975, **28**, 1673.
40 A. J. Deeming and S. Donovan-Mtunzi, *Organometallics*, 1985, **4**, 693.
41 T. E. Bitterwolf, personal communication.
42 D. M. Allen, A. Cox, T. J. Kemp, and Q. Sultana, *Inorg. Chim. Acta*, 1977, **21**, 191.
43 H. G. Alt, K. A. Mahmoud, and A. J. Rest, *J. Organomet. Chem.*, 1983, **246**, C37.
44 P. E. Bloyce, Ph.D. Thesis, University of Southampton, 1988.

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