Comparative Photochemistry of Tricarbonyl(η^5-cyclopentadienyl)methyl- and -ethyl-molybdenum and -tungsten in Poly(vinyl chloride) Film Matrices at 12—298 K

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The photoreactions of [M(η^5-C_5H_5)(CO)$_3$(CH_3)] and [M(η^5-C_5H_5)(CO)$_3$(C_2H_5)] complexes (M = Mo or W) in poly(vinyl chloride) (pvc) film matrices over a wide temperature range have been monitored using i.r. spectroscopy. At 298 K the methyl complexes dealkylate on irradiation ($\lambda > 300$ nm) to form [M(η^5-C_5H_5)(CO)$_3$Cl], [M(η^5-C_5H_5)(CO)$_3$H], and [M$_2$(η^5-C_5H_5)$_2$(CO)$_6$]. Photolysis at 12 K leads primarily to the formation of [M(η^5-C_5H_5)(CO)$_2$(CH_3)]. In the case of molybdenum, M–CH_3 bond cleavage also occurs at 12 K and the complexes [Mo(η^5-C_5H_5)(CO)$_3$Cl] and [Mo(η^5-C_5H_5)(CO)$_3$H] are generated on warming the matrices. Photolysis of [M(η^5-C_5H_5)(CO)$_3$(C_2H_5)] at 12 K proceeds with the formation of [M(η^5-C_5H_5)(CO)$_2$(C_2H_5)] which rearranges photochemically or thermally to form *trans*-[M(η^5-C_5H_5)(CO)$_2$(C_2H_4)H]. The *cis*-ethylene–hydride complex is also observed for tungsten at temperatures below *ca.* 50 K. At 298 K, photolysis of [W(η^5-C_5H_5)(CO)$_3$(C_2H_5)] leads directly to *trans*-[W(η^5-C_5H_5)(CO)$_2$(C_2H_4)H] which reacts further to form [W(η^5-C_5H_5)(CO)$_3$H], [W(η^5-C_5H_5)(CO)$_2$(C_2H_4)Cl], [W(η^5-C_5H_5)(CO)$_3$Cl], and [W$_2$(η^5-C_5H_5)$_2$(CO)$_6$]. However, on photolysis of [Mo(η^5-C_5H_5)(CO)$_3$(C_2H_5)] at 298 K the main product observed is [Mo(CO)$_6$] with trace amounts of [Mo(η^5-C_5H_5)(CO)$_3$H], [Mo(η^5-C_5H_5)(CO)$_3$Cl], and [Mo$_2$(η^5-C_5H_5)$_2$(CO)$_6$].

The complexes [M(η^5-C_5H_5)(CO)$_3$(R)] (M = Mo or W, R = CH_3 or C_2H_5) undergo facile photosubstitution of CO by other ligands in solution.[1–4] These reactions are thought to proceed dissociatively *via* the 16-electron species [M(η^5-C_5H_5)(CO)$_2$(R)].

The methyl complexes dealkylate on irradiation in hydrocarbon solvents, in the absence of external ligands, to form CH_4 and the dimers [M$_2$(η^5-C_5H_5)$_2$(CO)$_n$] (n = 4 or 6).[5] In pure chlorocarbon solvents the derivatives [M(η^5-C_5H_5)(CO)$_3$Cl] are also formed. Cleavage of the M–CH_3 bond was originally suggested to be the primary photoprocess in these reactions.[5] However, in a later study of the photoreactivity of [W(η^5-C_5H_5)(CO)$_3$(CH_3)], Severson and Wojcicki[6] found that the rate of formation of the dimer [W$_2$(η^5-C_5H_5)$_2$(CO)$_6$] when the irradiation was carried out under a CO atmosphere was much slower than that under Ar. It was also noted that whilst the complex [W(η^5-C_5H_5)(CO)$_3$Cl] was generated in cyclohexane containing PhCH_2Cl, only the substitution product [W(η^5-C_5H_5)(CO)$_2$(PPh$_3$)(CH_3)] was formed when PPh$_3$ ligands were also present. These results implied dissociative loss of CO as the primary photochemical step and it was proposed that, in the absence of ligands, radicals are formed in a secondary process: equations (i)—(iii).

$$[\mathrm{W}(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)] \xrightarrow{h\nu} [\mathrm{W}(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)] + CO \quad \text{(i)}$$

$$[\mathrm{W}(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)] \longrightarrow [\mathrm{W}(\eta^5\text{-}C_5H_5)(CO)_2]^{\cdot} + CH_3^{\cdot} \quad \text{(ii)}$$

$$[\mathrm{W}(\eta^5\text{-}C_5H_5)(CO)_2]^{\cdot} + CO \longrightarrow [\mathrm{W}(\eta^5\text{-}C_5H_5)(CO)_3]^{\cdot} \quad \text{(iii)}$$

The paramagnetic species [M(η^5-C_5H_5)(CO)$_2$(CH_3)]$^{\cdot -}$, observed in e.s.r. studies on irradiation of [M(η^5-C_5H_5)(CO)$_3$(CH_3)] complexes (M = Cr or Mo) in toluene,[7] is thought to form *via* a pathway involving the radicals [M(η^5-C_5H_5)(CO)$_2$]$^{\cdot}$ and [M(η^5-C_5H_5)(CO)$_3$]$^{\cdot}$ and methyl radical transfer. However, the proposal[6] that the tungsten dimer is formed by coupling of radicals, generated according to steps (i)—(iii), has recently been rejected by Tyler.[8]

In pure alkane solvents the ethyl complexes [M(η^5-C_5H_5)(CO)$_3$(C_2H_5)] undergo photoinduced β-elimination to form the hydrides [M(η^5-C_5H_5)(CO)$_3$H] and subsequently the dimers [M$_2$(η^5-C_5H_5)$_2$(CO)$_6$].[4] The intermediate complexes, *trans*-[M(η^5-C_5H_5)(CO)$_2$(C_2H_4)H], have been observed in solution.[9]

The unstable species [M(η^5-C_5H_5)(CO)$_2$(CH_3)] and [M(η^5-C_5H_5)(CO)$_2$(C_2H_5)] have recently been generated on photolysis of the methyl and ethyl complexes, respectively, in frozen gas matrices at 12 K[10,11] and in solid paraffin matrices at 77 K.[12] The [M(η^5-C_5H_5)(CO)$_2$(C_2H_5)] fragments rearrange to form *trans*-[M(η^5-C_5H_5)(CO)$_2$(C_2H_4)H] on warming the paraffin matrices and the same reaction occurs photochemically in frozen gas matrices where the *cis*-ethylene–hydrido-complex is also formed in the case of tungsten.

In our earlier communication[13] we reported some photoreactions of [Mo(η^5-C_5H_5)(CO)$_3$(CH_3)] observed in solvent-cast poly(vinyl chloride) (pvc) films.[14] It was demonstrated that these films provide photochemists with a matrix which can be used not only over a wide temperature range but also for investigating radical pathways in the reactions of organometallic complexes. We report here a full study of the photochemistry of [M(η^5-C_5H_5)(CO)$_3$(CH_3)] (M = Mo or W) and the corresponding ethyl complexes in pvc films at 12—298 K and we relate the reactions observed with those seen for these compounds in solution and in other low-temperature matrices.

Experimental

Polymer Films.—The compounds [Mo(η^5-C_5H_5)(CO)$_3$(CH_3)], [W(η^5-C_5H_5)(CO)$_3$(CH_3)], [Mo(η^5-C_5H_5)(CO)$_3$(C_2H_5)], and [W(η^5-C_5H_5)(CO)$_3$(C_2H_5)] were synthesised according to literature procedures.[15,16] The polymer films were cast from two different solvents. Powdered pvc (Corvic D60/11,† obtained from I.C.I.) was dissolved in either sodium-dried tetrahydrofuran (thf) (500 mg in 20 cm^3) at 20 °C or 1,2-dichloroethane (300 mg in 50 cm^3) at 35 °C, with rapid stirring. A sample (4 mg) of metal carbonyl was then added in the dark at 20 °C and the resulting solution poured into a Petri dish (diameter 10 cm) which was supported on a mer-

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† This form of pvc is of a high purity and contains no photostabilisers or other additives. Only trace quantities (<0.01%) of residual peroxide catalyst are present in the polymer.[17]

cury bath. The bath was kept in the dark whilst the solvent was allowed to evaporate, to give a film of uniform thickness. The film was extracted from the Petri dish by filling the latter with cold distilled water and cutting round the edge of the film which then floated to the surface.

Apparatus.—Cryogenic temperatures (*ca.* 12 K) were obtained using a Displex CSA-202 closed-cycle helium refrigerator system (Air Products and Chemical Inc.). A piece of polymer film was evenly clamped between two CaF_2 windows (diameter 25 mm) at the cryotip. It was important that the diameter of the film was the same as that of the windows so that the former could be clamped as flat* and as tightly as possible to ensure a good thermal contact. The cryotip was cooled within a vacuum shroud (1.33×10^{-5} N m^{-2}) containing outer spectroscopic (CaF_2) windows. The polymer matrix could then be irradiated at 12 K and subsequently warmed up slowly to room temperature by switching off the refrigerator. Temperatures were monitored using an Air Products Displex control gauge. In experiments at 77 K the polymer films were held between CaF_2 windows in a liquid-nitrogen cooled glass cryostat. In room temperature studies (298 K) the films were mounted between windows in a Nujol mull plate holder.

Photolysis and Spectroscopy.—A water-cooled medium-pressure mercury lamp (Philips HPK, 125 W) was used as the photolysis source at a distance of *ca.* 20 cm from the polymer matrix. Irradiation into specific wavelength bands was achieved using glass light filters (filter A, $330 < \lambda < 390$ nm; filter B, $\lambda > 350$ nm; and filter C, $\lambda > 400$ nm) in conjunction with a quartz heat filter.

I.r. spectra were recorded using a Nicolet 7199 Fourier-transform infrared (F.t.i.r.) spectrometer (resolution 1.0 cm^{-1}). An advantage in using this instrument was that spectra could be accumulated rapidly whilst the polymer matrices were warming up. Further, the computer availability enabled spectral subtractions † to be obtained interactively so that reactions occurring in the matrices could be monitored more easily. The spectra showed no absorptions for the polymer matrix in the frequency range 2 200—1 800 cm^{-1}. Absorptions were seen for ketone groups (1 730—1 710 cm^{-1}) in the pvc, present probably as a result of some thermal or photochemical degradation of the polymer in solution.[18] I.r. bands for residual thf in spectra of films cast from this solvent were revealed in the range 1 500—900 cm^{-1} when polymer absorptions were subtracted out, whilst other bands were seen for oxidised thf residues [19] (ν_{CO} = 1 775 and 1 740 cm^{-1}). Very little change in intensity of the above absorptions occurred either under the photolysis conditions used in this study or on leaving the polymer films in the dark for several months No significant thermal decomposition of the complexes under study was seen in the films over this period.

U.v.-visible spectra of the title compounds in films cast from dichloroethane were recorded on a Pye-Unicam SP 1 800 u.v. spectrophotometer with a blank film in the reference beam. In experiments at 298 K the compounds were irradiated at wavelengths corresponding to the lowest energy electronic absorption. Only very weak absorptions for the pvc were present in spectra ($\lambda > 240$ nm) of freshly cast films. These increased after several minutes of irradiation of films (filter A) in air at 298 K and are probably due to polyenes in the pvc.[18]

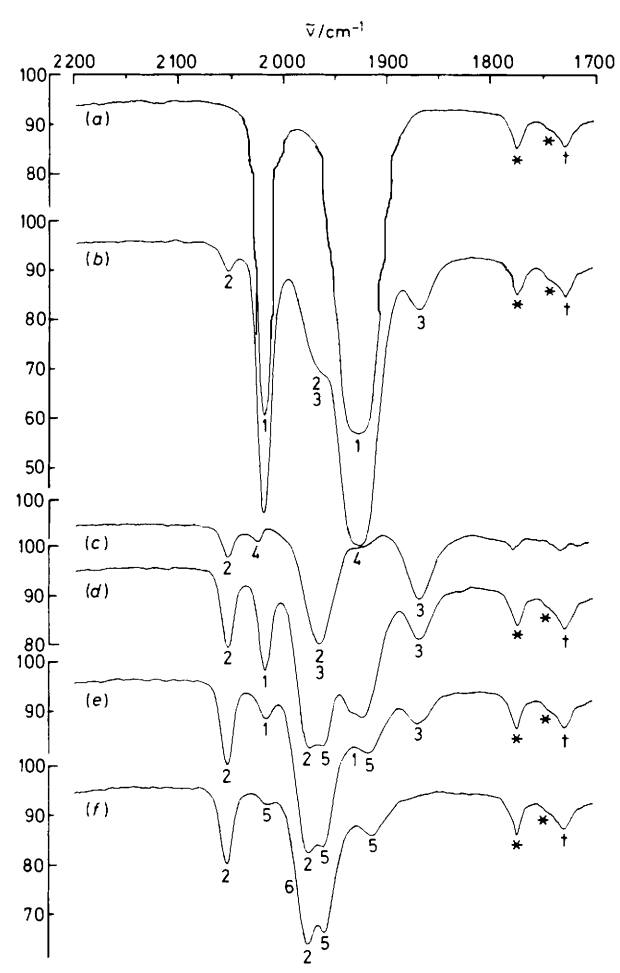

Figure 1. I.r. spectra from an experiment with [Mo(η^5-C_5H_5)(CO)$_3$(CH$_3$)] at 298 K in a pvc film cast from thf: (*a*) before irradiation; (*b*) after 5 min irradiation using filter A; (*c*) difference spectrum, (*b*) − *N* (*a*), where *N* is a scaling factor; (*d*) after a further 35 min; (*e*) 65 min; and (*f*) 85 min irradiation using filter A. The numbering refers to those species, as given in the text, which give rise to these bands. The bands marked (*) and (†) are due to oxidised thf residues

E.s.r. measurements were obtained at 293 K using a Bruker spectrometer. The polymer films (cast from dichloroethane) were rolled up and placed inside e.s.r. tubes which were flushed with N_2 and sealed.

Results

Photochemistry of [M(η^5-C_5H_5)(CO)$_3$(CH$_3$)] (M = Mo *or* W).—(*a*) *Photolysis at room temperature.* The i.r. spectrum of [Mo(η^5-C_5H_5)(CO)$_3$(CH$_3$)] (1) ‡ in a pvc film cast from thf solution is shown in Figure 1(*a*). Three terminal carbonyl stretching bands are expected for this complex which has local C_s symmetry but only two bands are actually observed [ν_{CO} = 2 016 (A') and 1 924 cm^{-1} ($A' + A''$)], in agreement with the solution spectra. A short period of photolysis using filter A [irradiating into the absorption at 360 nm observed for (1) in pvc films] gave rise to new carbonyl bands at 2 052, *ca.* 1 960, and 1 864 cm^{-1} and a reduction in the parent bands. Two

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* Interference fringes were observed in spectra of films which were not held completely flat.

† All spectra subtractions were performed on spectra recorded in absorbance units. Spectra were then converted into the more usual percentage transmission form for display in the Figures.

‡ The numbering of the species in the text, the Table, and in Schemes 1 and 2 corresponds to that used in Figures 1—6 in assigning the i.r. absorptions.

Table. Infrared band positions observed in the terminal CO stretching region for $[M(\eta^5-C_5H_5)(CO)_3(CH_3)]$ and $[M(\eta^5-C_5H_5)(CO)_3(C_2H_5)]$ complexes and their photoproducts [a] in pvc films

Complex	ν_{CO}/cm^{-1}
(1) $[Mo(\eta^5-C_5H_5)(CO)_3(CH_3)]$ [b]	[c] 2 016, 1924
	[d] 2 015, 1 928, 1 918
(7) $[Mo(\eta^5-C_5H_5)(CO)_2(CH_3)]$ [e]	1 949, 1 857
(3) $[Mo(\eta^5-C_5H_5)(CO)_2$(' pvc ')$(CH_3)]$ [f]	*ca.* 1 960, 1 864
$[Mo(\eta^5-C_5H_5)(CO)_2(thf)(CH_3)]$ [e]	1 920, 1 820
(2) $[Mo(\eta^5-C_5H_5)(CO)_3Cl]$	2 052, 1 973 [g]
(5) $[Mo_2(\eta^5-C_5H_5)_2(CO)_6]$	2 010, 1 955, 1 909 [g]
(4) $[Mo(\eta^5-C_5H_5)(CO)_3H]$ [h]	2 022, 1 935
(6) $[Mo(CO)_6]$	1 980 [g]
(11) $[Mo(\eta^5-C_5H_5)(CO)_3(C_2H_5)]$ [i]	2 011, 1 917
(18) $[Mo(\eta^5-C_5H_5)(CO)_2(C_2H_5)]$ [e]	1 940, 1 852
(23) $[Mo(\eta^5-C_5H_5)(CO)_2(thf)(C_2H_5)]$ [e]	— 1 818 [j]
(12) *trans*-$[Mo(\eta^5-C_5H_5)(CO)_2(C_2H_4)H]$	1 964, 1 885
(15) $[Mo(\eta^5-C_5H_5)(CO)_2(thf)H]$ [e]	— 1 825 [j]
(24) $[Mo(\eta^5-C_5H_5)(CO)_2$(' pvc ')$H]$ [f]	*ca.* 1 960, 1 867
(8) $[W(\eta^5-C_5H_5)(CO)_3(CH_3)]$ [k]	[c] 2 012, 1 914
	[d] 2 012, 1 919, 1 907
(9) $[W(\eta^5-C_5H_5)(CO)_2(CH_3)]$ [e]	1 939, 1 840
$[W(\eta^5-C_5H_5)(CO)_2$(' pvc ')$(CH_3)]$ [f]	*ca.* 1 940, 1 843
(10) $[W(\eta^5-C_5H_5)(CO)_2(thf)(CH_3)]$ [e]	1 912, 1 803
(13) $[W(\eta^5-C_5H_5)(CO)_3Cl]$	2 045, 1 956 [g]
(17) $[W_2(\eta^5-C_5H_5)_2(CO)_6]$	2 007, 1 952, 1 900 [g]
(14) $[W(\eta^5-C_5H_5)(CO)_3H]$	2 018, 1 926 [g]
$[W(CO)_6]$	1 974 [g]
(20) $[W(\eta^5-C_5H_5)(CO)_3(C_2H_5)]$ [l]	2 007, 1 910
(21) $[W(\eta^5-C_5H_5)(CO)_2(C_2H_5)]$ [e]	1 935, 1 839
$[W(\eta^5-C_5H_5)(CO)_2(thf)(C_2H_5)]$ [e]	— 1 800 [j]
(22) *trans*-$[W(\eta^5-C_5H_5)(CO)_2(C_2H_4)H]$	1 964, 1 882
(19) *cis*-$[W(\eta^5-C_5H_5)(CO)_2(C_2H_4)H]$ [e]	1 980, 1 910
(16) *cis*-$[W(\eta^5-C_5H_5)(CO)_2(C_2H_4)Cl]$	2 008, 1 942
(25) $[W(\eta^5-C_5H_5)(CO)_2(thf)H]$ [e]	— 1 823 [j]

[a] Observed at 298 K unless otherwise stated. [b] $\lambda_{max} = 315, 360$ (sh) nm. [c] At 298 K. [d] At 12 K. [e] Photoproduct at 12 K. [f] Species discussed in text (Results section). [g] I.r. data for authentic sample of this complex in pvc film at 298 K. [h] Thermally unstable at 298 K. [i] $\lambda_{max} = 318, 365$ (sh) nm. [j] Higher energy carbonyl band hidden by other bands. [k] $\lambda_{max} = 316, 354$ (sh) nm. [l] $\lambda_{max} = 316, 355$ (sh) nm.

other new bands at 2 022 and 1 935 cm^{-1} were revealed in the difference spectrum in which the bands for (1) were subtracted out completely [Figure 1(*b*) and (*c*)]. With further irradiation the product bands at 2 022, 1 960, 1 935, and 1 864 cm^{-1} gained little intensity and subsequently disappeared after complete reaction of the parent complex.These bands were also seen to decrease on leaving the irradiated pvc film in the dark. However, the other band at 2 052 cm^{-1} continued to increase together with further new carbonyl bands at 2 010, 1 973, 1 955, and 1 909 cm^{-1} [Figure 1(*d*)—(*f*)]. The final product bands at 2 052 and 1 973 cm^{-1} and those at 2 010, 1 955, and 1 909 cm^{-1} are assigned to the complexes $[Mo(\eta^5-C_5H_5)(CO)_3Cl]$ (2) and $[Mo_2(\eta^5-C_5H_5)_2(CO)_6]$ (5), respectively, since the spectra of these complexes in similar pvc films exhibited the same bands [20] (Table). The new absorptions at 2 022 and 1 935 cm^{-1} can be assigned to $[Mo(\eta^5-C_5H_5)(CO)_3H]$ (4) by comparison with the i.r. band positions for this complex, relative to those for (1), in solution.[12] The same metal hydride is formed on irradiation of $[Mo(\eta^5-C_5H_5)(CO)_3(C_2H_5)]$ (11) in pvc films at 12—298 K (see below).

Subtraction of the bands for (2) from the difference spectrum [Figure 1(*c*)] revealed that the other 'intermediate' bands at 1 960 and 1 864 cm^{-1} are of similar intensity. The relative positions of these bands suggest that they arise from a dicarbonyl species $[Mo(\eta^5-C_5H_5)(CO)_2$(' pvc ')$(CH_3)]$ (3). The bands are at higher wavenumbers than those of the unstable fragment $[Mo(\eta^5-C_5H_5)(CO)_2(CH_3)]$ (7) observed in pvc matrices at 12 K (see below) but are at significantly lower wavenumbers than those expected for the radical $[Mo(\eta^5-C_5H_5)(CO)_3]^\cdot$ which has been generated in frozen CO matrices [21] [$\nu_{co} = 2\,009$ (A_1) and 1 911 cm^{-1} (E)]. It is possible that the photoproduct (3) results from bonding of Cl or H from the pvc to the fragment (7) at the vacant co-ordination site. Another product band at 1 980 cm^{-1}, which is characteristic of the complex $[Mo(CO)_6]$ (6) in pvc films,[22] was seen after subtraction of the bands for (2) from the final spectrum [Figure 1(*f*)]. The hexacarbonyl is the main photoproduct generated from (11) in the polymer matrix at 298 K (see below). No reactions of (1) with residual thf in pvc films occurred at room temperature and the same photoproducts were observed to be formed in films cast from dichloroethane solution.

Photolysis of (1) (filter A) in pvc films containing no thf residues within an e.s.r. cavity gave rise to a signal for a paramagnetic species having axial symmetry and which has a lifetime of at least 2 h at 293 K. The e.s.r. signal consisted of two broad features ($g_\perp = 1.976$ and $g_\parallel = 1.942$) which indicates that the species does not rotate rapidly in the polymer matrices at room temperature. A second much weaker signal (a single line with a g value of 2.004), which disappeared after a few minutes of terminating the photolysis, was also seen. On irradiation of similar pvc films containing no metal carbonyl only the latter signal was observed and this can be attributed to radicals in the pvc matrix.

By analogy with the above reactions, irradiation of $[W(\eta^5-C_5H_5)(CO)_3(CH_3)]$ (8) in pvc films under the same conditions resulted in a similar rate of formation of $[W(\eta^5-C_5H_5)(CO)_3Cl]$ (13), $[W(\eta^5-C_5H_5)(CO)_3H]$ (14), $[W_2(\eta^5-C_5H_5)_2(CO)_6]$ (17), and traces of $[W(CO)_6]$. These photoproducts were identified on the basis of their i.r. absorptions (Table) which have been measured for authentic samples of these complexes * in similar pvc film matrices.[20,22] A thermally unstable photoproduct ($\nu_{co} = ca.$ 1 940 and 1 843 cm^{-1}) analogous to the species (3) observed on photolysis of (1) was also seen to form. In contrast, however, no e.s.r. signal attributable to a species generated from (8) could be detected at 293 K.

(*b*) *Photolysis at* 12 K *and thermal reactions on warming*. The i.r. spectra of metal carbonyls in pvc films at 12 K are much broader than those seen for frozen gas matrices at the same temperature. The bands are relatively broader even when only 0.2% of carbonyl (1 : 500 mg) is present in the pvc matrix suggesting possibly that significant polymer–solute interactions exist. Figure 2(*a*) shows the i.r. spectrum of (1) at 12 K in a film cast from dichloroethane solution. The lower energy carbonyl band for this complex splits into two components on cooling probably because of trapping-site effects in the polymer matrix. Irradiation (filter A) produced new bands at 1 949 and 1 857 cm^{-1}, together with a band for free CO at 2 135 cm^{-1}, whilst the bands for (1) decreased [Figure 2(*b*) and (*c*)]. On further irradiation with visible light (filter C) the parent complex is regenerated in the matrix. The reversibility of the reaction and the appearance of new carbonyl bands at lower wavenumbers than the parent bands are consistent with the formation of the 16-electron fragment (7) by dissociative loss of CO from (1). The asymmetry of the bands for this fragment suggests that they overlap other new bands at lower wavenumbers. Further evidence for the latter bands was seen on warming the irradiated matrix in the dark to 40 K which led to a reduction and apparent shift (*ca.* 17 cm^{-1}) to lower

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* A pvc film of the hydride $[W(\eta^5-C_5H_5)(CO)_3H]$ can be cast directly at 20 °C although considerable conversion of this complex to $[W(\eta^5-C_5H_5)(CO)_3Cl]$ and $[W_2(\eta^5-C_5H_5)_2(CO)_6]$ occurs in the solvent.[20]

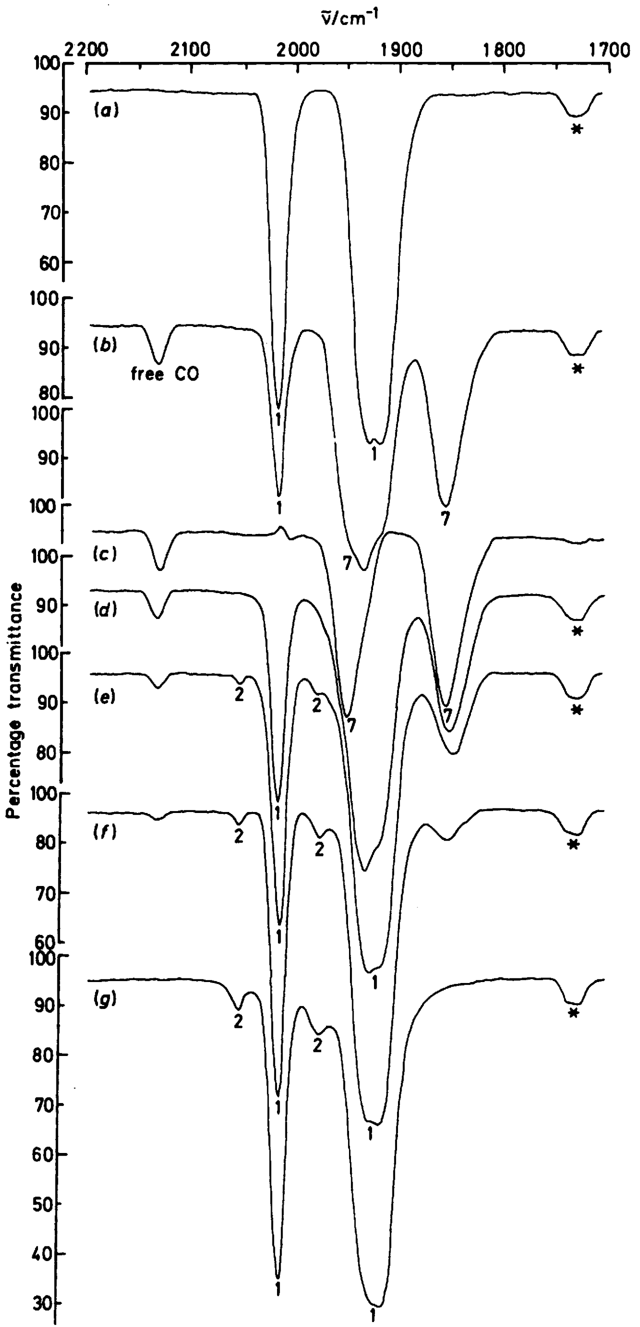


Figure 2. I.r. spectra from an experiment with [Mo(η^5-C_5H_5)(CO)$_3$-(CH_3)] at 12 K in a pvc film cast from dichloroethane: (*a*) before irradiation; (*b*) after 40 min irradiation using filter A; (*c*) difference spectrum, (*b*) − *N* (*a*); (*d*) after warming to 40 K; (*e*) 90 K; (*f*) 150 K; and (*g*) 298 K and leaving film in the dark for 12 h. The numbering refers to those species, as given in the text, which give rise to these bands. The band marked (*) is due to ketones on the pvc

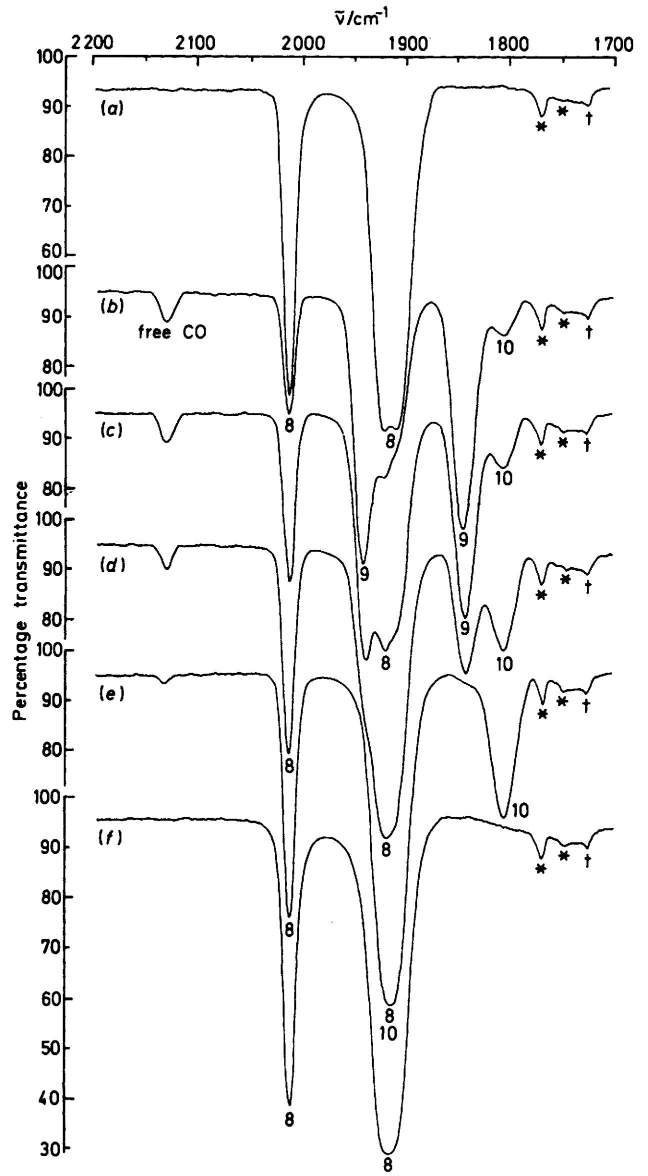


Figure 3. I.r. spectra from an experiment with [W(η^5-C_5H_5)(CO)$_3$-(CH_3)] at 12 K in a pvc film cast from thf: (*a*) before irradiation; (*b*) after 16 min irradiation using filter A; (*c*) after further 7 min irradiation using filter B; (*d*) after warming to 50 K; (*e*) 100 K; and (*f*) 298 K. The numbering refers to those species, as given in the text, which give rise to these bands. The bands marked (*) and (†) are due to oxidised thf residues and ketones respectively

wavenumbers of the bands for (7) and a reduction in the band for free CO, whilst the bands for (1) increased again [Figure 2(*d*)]. On further warming, bands for (2) grew steadily in the spectrum and further regeneration of the parent complex occurred [Figure 2(*e*)—(*g*)]. A subtraction of the spectrum of (1) at 298 K from the spectrum obtained on initially warming the polymer matrix to this temperature revealed that the hydride (4) another room temperature photoproduct had also been generated, although there was no evidence for the formation of the dimer [Mo_2(η^5-C_5H_5)$_2$(CO)$_6$] (5). On leaving the warmed-up matrix in the dark for a few hours some thermal conversion of (4) to (2) occurred. Irradiation of (1) at 12 K in pvc films cast from thf solutions also led primarily to the formation of (7). On warming these films to 200 K some regeneration of the parent complex was observed whilst a new product with i.r. absorptions at 1 920 and 1 820 cm^{-1} was formed. The product, which is converted thermally to (1), at temperatures above 200 K, is most probably the complex [Mo(η^5-C_5H_5)(CO)$_2$(thf)(CH_3)] formed by reaction of (7) with residual thf in the matrix. This reaction also occurs at 12 K or at 77 K on prolonged irradiation with near-u.v. light (filter A) and is completely reversed on subsequent irradiation with visible light. No significant formation of (2) was seen on warming irradiated films containing thf ligands until the temperature reached *ca.* 200 K.

Analogous reactions were observed on photolysis of (8) under the same conditions (Figure 3) except that no generation of (13) or (14) occurred on warming the irradiated pvc films. The positions of the i.r. bands for [W(η^5-C_5H_5)(CO)$_2$(thf)(CH$_3$)] (10) (ν_{co} = 1 912 and 1 803 cm^{-1}), formed by reaction of [W(η^5-C_5H_5)(CO)$_2$(CH$_3$)] (9) with thf in pvc films at 12—200 K, agree closely with those observed[8] for this complex in thf at −78 °C.

Photochemistry of [M(η^5-C_5H_5)(CO)$_3$(C_2H_5)] (M = Mo *or* W).—(*a*) *Photolysis at room temperature.* The i.r. spectrum of [W(η^5-C_5H_5)(CO)$_3$(C_2H_5)] (20) in a pvc film cast from thf solution is shown in Figure 4(*a*). Initial irradiation (filter A) gave rise to several new carbonyl bands [Figure 4(*b*)—(*d*)] at 2 045, 2 018, 1 964, 1 926s, 1 882, and 1 823 cm^{-1}, at the expense of the parent bands. The bands at 1964 and 1882 cm^{-1}, which increased very rapidly at the same rate in an intensity ratio of 1 : 2, can be assigned to the complex *trans*-[W(η^5-C_5H_5)(CO)$_2$(C_2H_4)H] (22) by analogy with the photoreactions observed for (20) in solution.[9] The product bands at 2 018 and 1 926 cm^{-1} revealed in the difference spectrum [Figure 4(*c*)] and that at 2 045 cm^{-1} are characteristic of the complexes (14) and (13) isolated in pvc films[20] (Table). The other product band at 1 823 cm^{-1} was only observed after photolysis of [W(η^5-C_5H_5)(CO)$_3$(C_2H_5)] (20) in pvc films containing residual thf and is probably associated with the species [W(η^5-C_5H_5)(CO)$_2$(thf)H] (25) which has been generated photochemically from *trans*-[W(η^5-C_5H_5)(CO)$_2$(C_2H_4)H] (22) in thf solution.[23] On further irradiation [Figure 4(*e*) and (*f*)], with the disappearance of the parent complex, the bands for (13) continued to increase whilst those for (14), (22), and [W(η^5-C_5H_5)(CO)$_2$(thf)H] (25) decreased. Subtraction of the bands for (13) from the spectra revealed that another species (16) with two carbonyl absorptions of almost equal intensity (ν_{CO} = 2 008 and 1 942 cm^{-1}) was being formed. The identity of this species is most likely to be the complex *cis*-[W(η^5-C_5H_5)(CO)$_2$(C_2H_4)Cl] (16) in view of the fact that the positions and relative intensities of the i.r. absorptions are very similar to those observed for this complex (ν_{CO} = 2 012 and 1 945 cm^{-1}) generated on photolysis of (13) at 12 K in a CH_4 matrix doped with C_2H_4.[24] With still further irradiation [Figure 4(*g*)] the bands assigned to (16) also disappeared whilst those for (13) increased in intensity. The dimer [W_2(η^5-C_5H_5)$_2$(CO)$_6$] (17) was also observed to be formed on prolonged irradiation of the matrix.

An experiment at 77 K provided some firmer evidence for the photoproduct (16) as being the complex [W(η^5-C_5H_5)(CO)$_2$(C_2H_4)Cl]. Irradiation of an authentic sample of (13) in a pvc film at 77 K gave a new species (ν_{CO} = 1 958 and 1 859 cm^{-1}) together with free CO. The same reaction was seen on photolysis of (13) in a CH_4 matrix at 12 K and the product has been identified, on the basis of ^{13}CO labelling, as being the species [W(η^5-C_5H_5)(CO)$_2$Cl]. Photolysis of the product (16) in pvc films cooled to 77 K also led to the formation of [W(η^5-C_5H_5)(CO)$_2$Cl] and the reaction was completely reversed on warming the matrix to room temperature.

In contrast to the above reactions, photolysis of (11) in pvc films at 298 K with either near-u.v. or visible light (filter A or C) led principally to the formation of a product having one terminal CO i.r. absorption (ν_{CO} = 1 980 cm^{-1}). This product can be identified as the complex (6) which exhibits the same absorption in pvc films.[22] The hydride (4) (ν_{CO} = 2 022 and 1 935 cm^{-1}) was also formed from the ethyl complex, *cf.* solution reactions,[4] and was subsequently converted thermally or photochemically to the species (2) and (5).

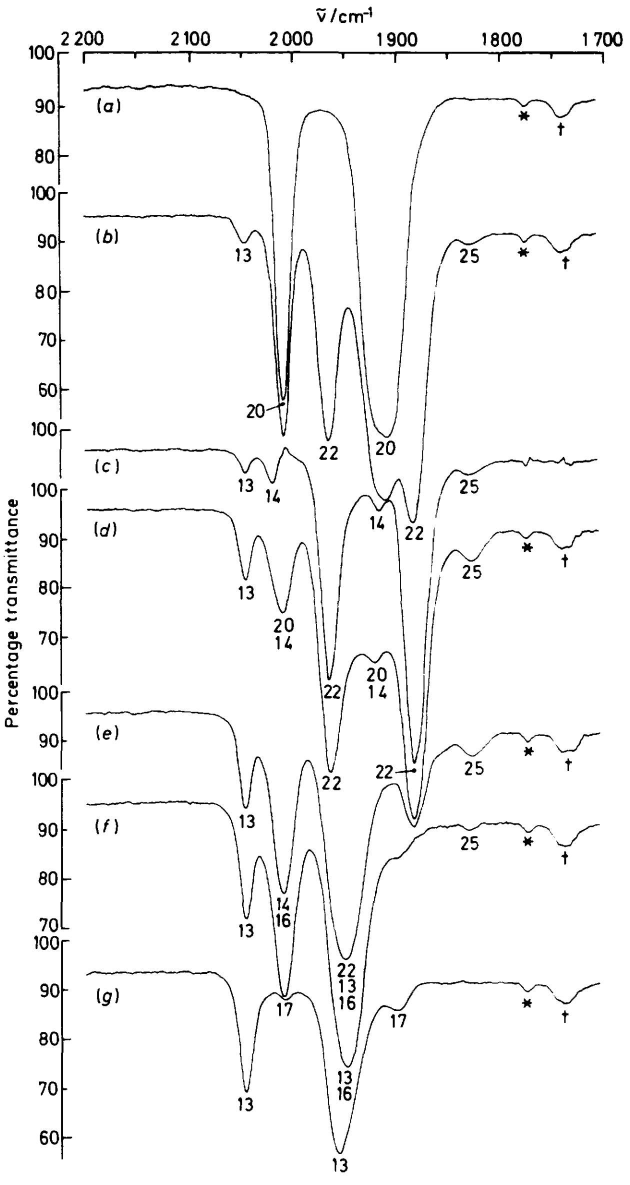


Figure 4. I.r. spectra from an experiment with [W(η^5-C_5H_5)(CO)$_3$(C_2H_5)] at 298 K in a pvc film cast from thf: (*a*) before irradiation, (*b*) after 3 min irradiation using filter A; (*c*) difference spectrum, (*b*) − *N* (*a*); (*d*) after further 6 min; (*e*) 25 min; (*f*) 50 min; and (*g*) 80 min irradiation using filter A. The numbering refers to those species, as given in the text, which give rise to these bands. The bands marked (*) and (†) are due to oxidised thf residues and ketones, respectively

(*b*) *Photolysis at* 12 K *and thermal reactions on warming.* I.r. measurements showed that irradiation of (20) at 12 K in a pvc film, cast from dichloroethane solution, with near-u.v. light resulted primarily in dissociative loss of CO and the formation of a metal dicarbonyl species [W(η^5-C_5H_5)(CO)$_2$(C_2H_5)] (21) [Figure 5(*a*) and (*b*)]. On subsequent irradiation with visible light (filter C) conversion of the dicarbonyl to (22) and another new species (19) [ν_{CO} = 1 980 (sh) and *ca.* 1 910 cm^{-1}] was observed; the lower energy carbonyl band for the latter was revealed after subtraction of the bands for (20). Further photolysis with higher energy light (filter B) led to a more rapid production of (22) and to the formation of the hydride (14), whilst further depletion of (20) occurred [Figure 5(*c*)]. On prolonged irradiation, after the disappearance of the parent

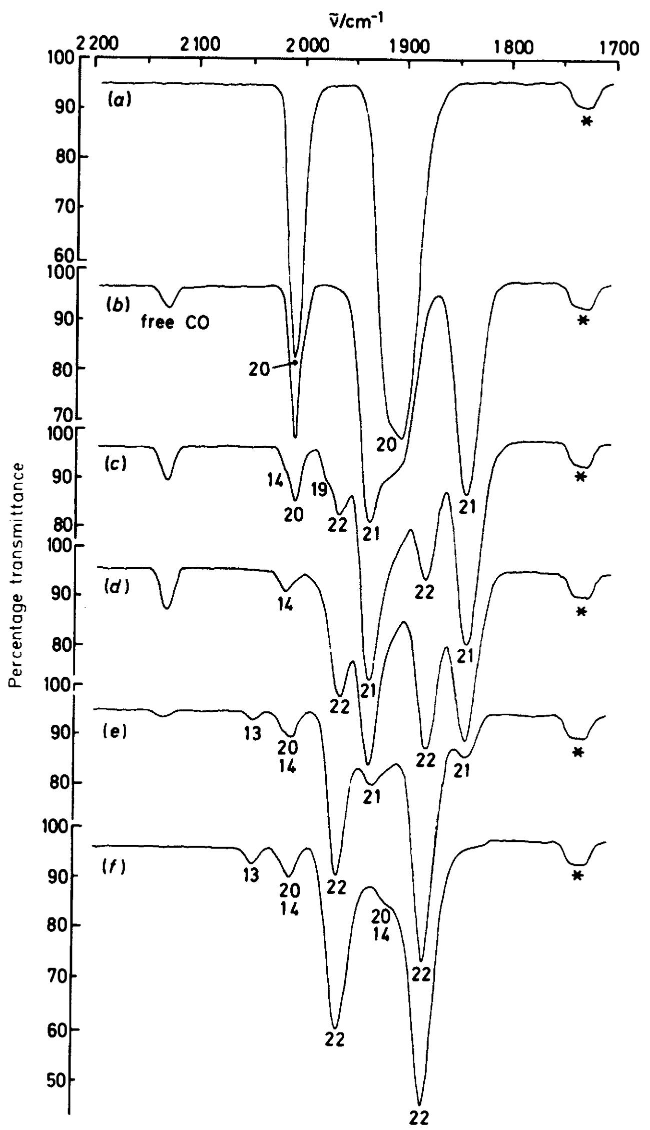


Figure 5. I.r. spectra from an experiment with [W(η^5-C_5H_5)(CO)$_3$-(C_2H_5)] at 12 K in a pvc film cast from dichloroethane: (*a*) before irradiation, (*b*) after 10 min irradiation using filter A; (*c*) after further 60 min irradiation (30 min with filter C plus 30 min with filter B); (*d*) after a further 70 min irradiation using filter B; (*e*) after warming to 150 K; and (*f*) to 298 K. The numbering refers to those species, as given in the text, which give rise to these bands. The band marked (*) is due to ketones in the pvc

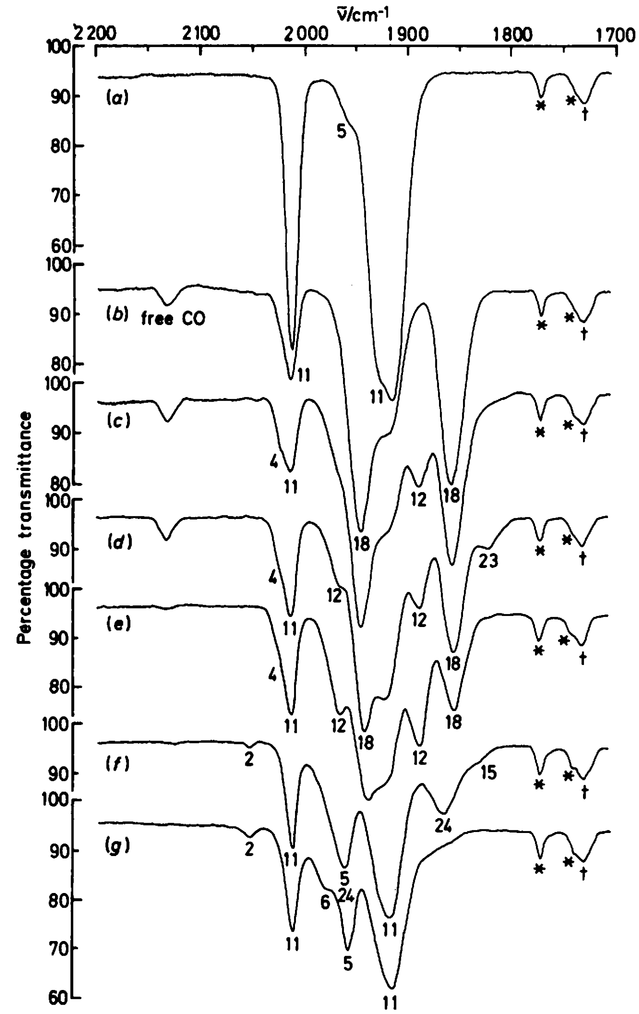
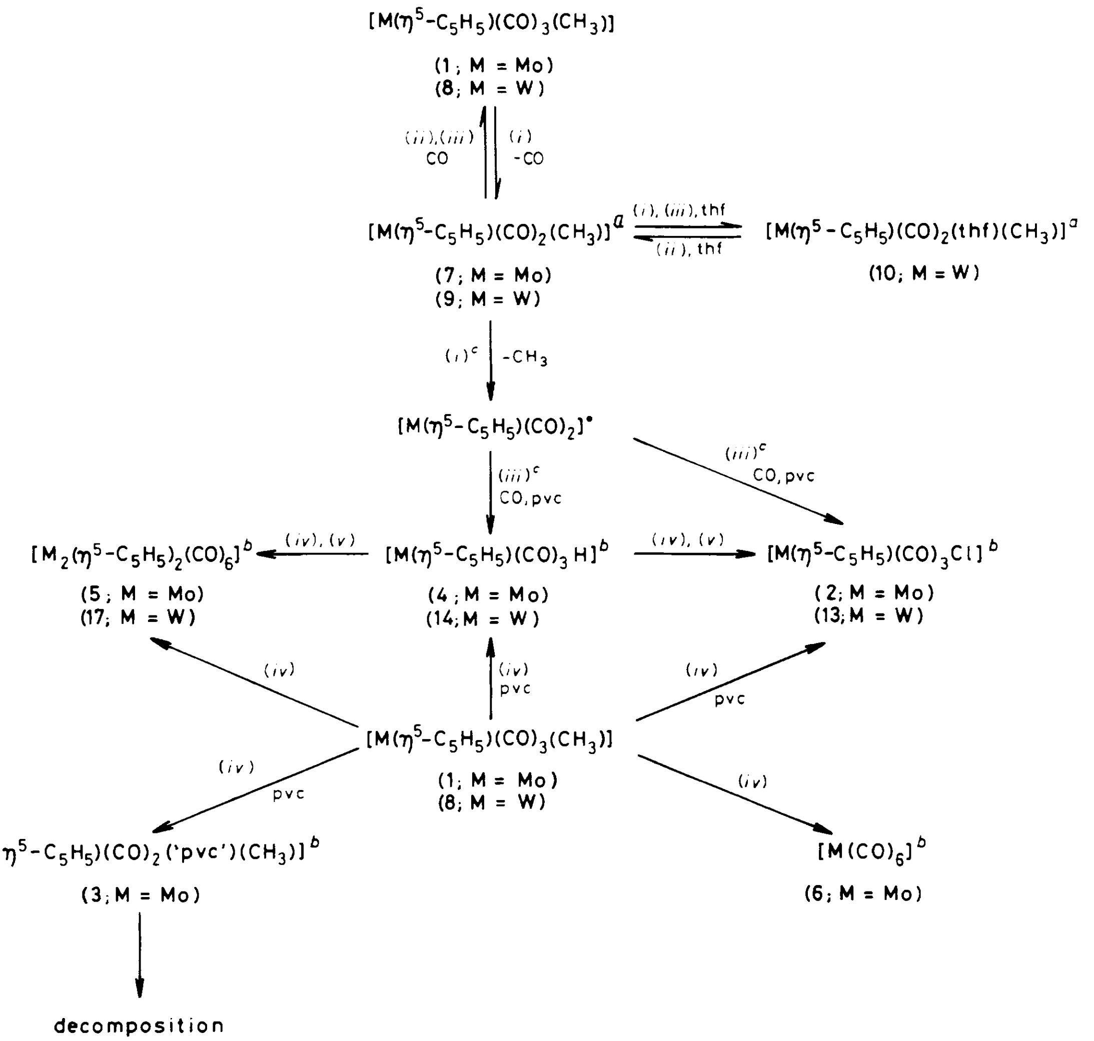


Figure 6. I.r. spectra from an experiment with [Mo(η^5-C_5H_5)(CO)$_3$-(C_2H_5)] at 12 K in a pvc film cast from thf: (*a*) before irradiation; (*b*) after 20 min irradiation using filter A; (*c*) after further 100 min irradiation using filter B; (*d*) after warming to 90 K; (*e*) 250 K; (*f*) 298 K; and (*g*) after leaving the warmed up matrix in the dark for 24 h. The numbering refers to those species, as given in the text, which give rise to these bands. The bands marked (*) and (†) are due to oxidised thf residues and ketones, respectively

complex, further generation of (22) from the primary photoproduct (21) was seen [Figure 5(*d*)]. It is possible to generate (21) from the *trans*-ethylene–hydrido-complex (22) in the matrix by irradiating with near-u.v. light (filter A). These reactions in the polymer film are similar to those seen for (20) in frozen gas matrices [11] and the primary photoproduct (21) and the new species (19) can be identified as [W(η^5-C_5H_5)-(CO)$_2$(C_2H_5)] and *cis*-[W(η^5-C_5H_5)(CO)$_2$(C_2H_4)H], respectively, by comparison of their i.r. absorptions, relative to those for (20), in the different matrix environments. Warming the matrix in the dark [Figure 5(*e*) and (*f*)] led to the formation of (13) and some regeneration of (20) whilst rapid conversion of (21) to (22) occurred. An additional species was observed to be formed on u.v. irradiation of (20) at 12 K in pvc films cast from thf. The identity of this species, which has an i.r. absorption at 1 800 cm^{-1}, is most likely to be [W(η^5-C_5H_5)(CO)$_2$-(thf)(C_2H_5)], *cf.* [W(η^5-C_5H_5)(CO)$_2$(thf)(CH_3)] (ν_{CO} = 1 912 and 1 802 cm^{-1}) in solution.[8] On warming these films to *ca.* 200 K the complex (25) was also formed. These products evidently result from reaction of thf with (21) and [W(η^5-C_5H_5)(CO)$_2$H], respectively, where the latter 16-electron fragment is the intermediate in the conversion of the *trans*-ethylene hydride to the hydride (14). It is thought [12] that the conversion of (21) to (22), seen on warming solid paraffin matrices irradiated at 77 K, involves a β-hydrogen transfer which proceeds *via* (19). The *cis* isomer thermally rearranges to the *trans* isomer on warming pvc matrices from 12 to 50 K.

I.r. spectra from an experiment with (11) in a pvc film cast from thf solution are shown in Figure 6. Some thermal conversion of this complex to (5) occurred in solution while preparing the film. The photoreactions of (11) observed at 12 K were similar to those of the tungsten analogue although a contrasting reactivity of species was seen on warming the polymer matrix. The primary photoproduct [Mo(η^5-C_5H_5)-(CO)$_2$(C_2H_5)] (18) was converted to *trans*-[Mo(η^5-C_5H_5)(CO)$_2$-(C_2H_4)H] (12), identified by comparison with i.r. data [11,12] for



Scheme 1. (*i*) *h*ν (filter A) at 12 K; (*ii*) *h*ν (filter C) at 12 K; (*iii*) warming up matrix from 12 K; (*iv*) *h*ν (filter A) at 298 K; (*v*) thermal reaction at 298 K ([a] Photoproduct at 12 K. [b] Photoproduct at 298 K. [c] Reaction for M = Mo)

this complex in other matrices, on irradiation with visible light, although no i.r. evidence for the *cis* isomer was seen [Figure 6(*a*)—(*c*)]. Photoconversion of (12) to the hydride (4) occurred more rapidly than that of the tungsten analogue under the same conditions. On warming the polymer film to 90 K the 16-electron fragment (18) was seen to react slowly with photoejected CO, or with thf ligands, regenerating the parent complex or forming [Mo(η^5-C_5H_5)(CO)$_2$(thf)(C_2H_5)] (23), respectively, whilst very little conversion to the ethylene–hydrido-complex occurred [Figure 6(*d*)]. Surprisingly, a significant amount of (18) remained in the matrix even on warming to 250 K, *i.e.* after the disappearance of (23) [Figure 6(*e*)]. Further warming led to the decomposition of both the dicarbonyl–ethyl and the ethylene–hydrido-complexes and the formation of a new species [Mo(η^5-C_5H_5)(CO)$_2$(' pvc ')H] (24) having i.r. absorptions (ν_{CO} = *ca.* 1 960 and 1 867 cm^{-1}) at similar wavenumbers to those of the unstable photoproduct (3) generated from (1) at 298 K. This species, which was observed as a minor product on photolysis (filter B) of (11) at 298 K, may arise from bonding of the pvc to the fragment [Mo(η^5-C_5H_5)(CO)$_2$H], formed in the thermal decomposition of (12). Another absorption [ν_{CO} = 1 825 (sh) cm^{-1}], which was only seen on warming films in which thf was present, probably indicates formation of [Mo(η^5-C_5H_5)(CO)$_2$(thf)H] (15). On warming to room temperature [Figure 6(*f*)] the hydrides (4) and (15) rapidly decomposed and absorptions for the room temperature photoproducts (2) and (5) appeared in the spectrum. The other species (24) decomposed with the formation of (6) on leaving the warmed-up matrix in the dark [Figure 6(*g*)].

Discussion

The final products formed in the photoinduced dealkylation reactions of the title compounds in pvc matrices at 298 K are the same as those formed in chlorocarbon solvents. Evidence that the species generated on irradiation of films at 12 K are intermediates in these reactions is provided by the fact that room temperature photoproducts are seen to form on warming the matrices.

The variety of reactions observed for (1) and (8) in pvc films at 12—298 K are summarised in Scheme 1. The photochemical conversion of these complexes to the hydrido- and chloro-derivatives, seen at 298 K, evidently involves a reaction with H and Cl radicals, respectively, from the matrix.

Radicals are probably released during dehydrochlorination of the pvc which is known to occur on irradiation with u.v.–visible light ($\lambda > 300$ nm) when polyenes or other chromophoric impurities (*e.g.* ketones), which can absorb this light, are present in the polymer chains.[18] During this process cleavage of allylic C–Cl bonds, possibly due to energy transfer from polyene excited states,[25] leads to the formation of Cl and polyene chain radicals, where the former can abstract H atoms from the chains to generate HCl. The weak e.s.r. signal observed for the polymer matrix on irradiation can be attributed to a relatively long-lived polyenyl chain radical.[18] The reactions seen for (1) at 12 K and on warming the polymer matrix are consistent with the mechanism proposed by Severson and Wojcicki[6] for the photoconversion of (8) to (13) in solution. The primary photoproduct (7) generated at 12 K has also been seen to form reversibly in frozen gas matrices. The observation that (2) and (4) are formed on warming an irradiated polymer matrix of (1) indicates that another unstable photoproduct is generated at 12 K which is capable of a thermal reaction involving the pvc. It is probable that the radical $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]^\cdot$ is formed by cleavage of the $\mathrm{Mo{-}CH_3}$ bond in the fragment (7). Whilst photoejected CO, which remains trapped in the matrix, combines with this fragment on warming to regenerate (1), reaction of Cl or H and CO with the 15-electron radical would lead to the formation of (2) and (4), respectively. This reaction may proceed either *via* the species $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{Cl}]$ and $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{H}]$ or the 17-electron radical $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3]^\cdot$. Support for this mechanism is provided by the fact that, when thf ligands are present, the complex (2) is not generated significantly until the polymer matrix has warmed up to *ca.* 200 K. Since thf readily combines with (7) on warming to form $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{thf})(\mathrm{CH_3})]$, thus preventing an immediate back reaction of the 16-electron fragment with CO, it is likely that reaction of thf with $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]^\cdot$, forming $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{thf})]^\cdot$, also occurs. The latter complex may then react with the pvc to form $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{thf})\mathrm{Cl}]$ and $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{thf})\mathrm{H}]$ which are subsequently converted to (2) and (4), respectively, at temperatures above *ca.* 200 K.

It is interesting that no reactions suggesting radical formation were seen on warming polymer films of (8). Presumably, photolytic cleavage of the $\mathrm{W{-}CH_3}$ bond in (8) does not occur in the matrix at 12 K. Since $\mathrm{Mo{-}CH_3}$ bond cleavage only occurs as a minor process at low temperatures the i.r. absorptions associated with the species involved in the dealkylation reaction are hidden by those of the primary photoproduct (7), and $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{thf})(\mathrm{CH_3})]$. In our earlier report[13] we assigned some i.r. bands to the radical $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3]^\cdot$ although it is now evident that these bands are associated with $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{thf})(\mathrm{CH_3})]$. The absorptions at lower wavenumbers than those of (7), revealed on initially warming matrices containing no thf (Figure 2), may be attributed to the species $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{ketone})(\mathrm{CH_3})]$, formed by interaction of the dicarbonyl–methyl complex with ketone groups in the pvc, since similar bands were seen on warming matrices containing (9).

Deuterium-labelling studies[5] have shown that the formation of $\mathrm{CH_4}$ in the photoinduced dealkylation of (1) in pure solvents involves abstraction by the $\mathrm{CH_3}$ group of a hydrogen atom from the cyclopentadienyl ring. In another study[8] of the dealkylation of the tungsten analogue (8) it was found that the $\mathrm{CH_3}$ radicals abstract hydrogen atoms from solvent molecules. Any $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]^\cdot$ radicals generated from $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{CH_3})]$ in the polymer films may be stabilised as a result of trapping of the released $\mathrm{CH_3}$ group by radicals in the matrix itself. As mentioned earlier, the unstable photoproduct (3) and its tungsten analogue generated from (1) and (8) at 298 K in the polymer films may arise from bonding of Cl or H from the pvc to (7) and (9) respectively. Elimination of $\mathrm{CH_4}$ or $\mathrm{CH_3Cl}$ from such a species could provide a pathway for the generation of the radicals $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]^\cdot$ in the polymer matrices. The e.s.r. signal observed on photolysis of (1) at 293 K provides direct evidence for the formation of a metal-centred radical which is probably stabilised by the polymer matrix. The fact that no signal was seen on similar photolysis of (8) is interesting in view of other observations in a solution study. Irradiation of (1) in toluene at 293 K gives rise to an e.s.r. signal[7] attributable to the radical $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{CH_3})]^{\cdot-}$ whilst no signal is observed on photolysis of (8) under the same conditions.

Tyler[8] has reported that photolysis ($\lambda \sim 366$ nm) of (8) in pure chlorocarbon solvents leads initially to the formation of (17) and $\mathrm{CH_4}$ where the dimer reacts to form (13), probably *via* cleavage of the W–W bond,[26] in a secondary process. The reaction steps (iv)—(vii) were proposed.

$$[\mathrm{W}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3(\mathrm{CH_3})] \xrightarrow{h\nu} [\mathrm{W}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{CH_3})] + \mathrm{CO} \quad \text{(iv)}$$

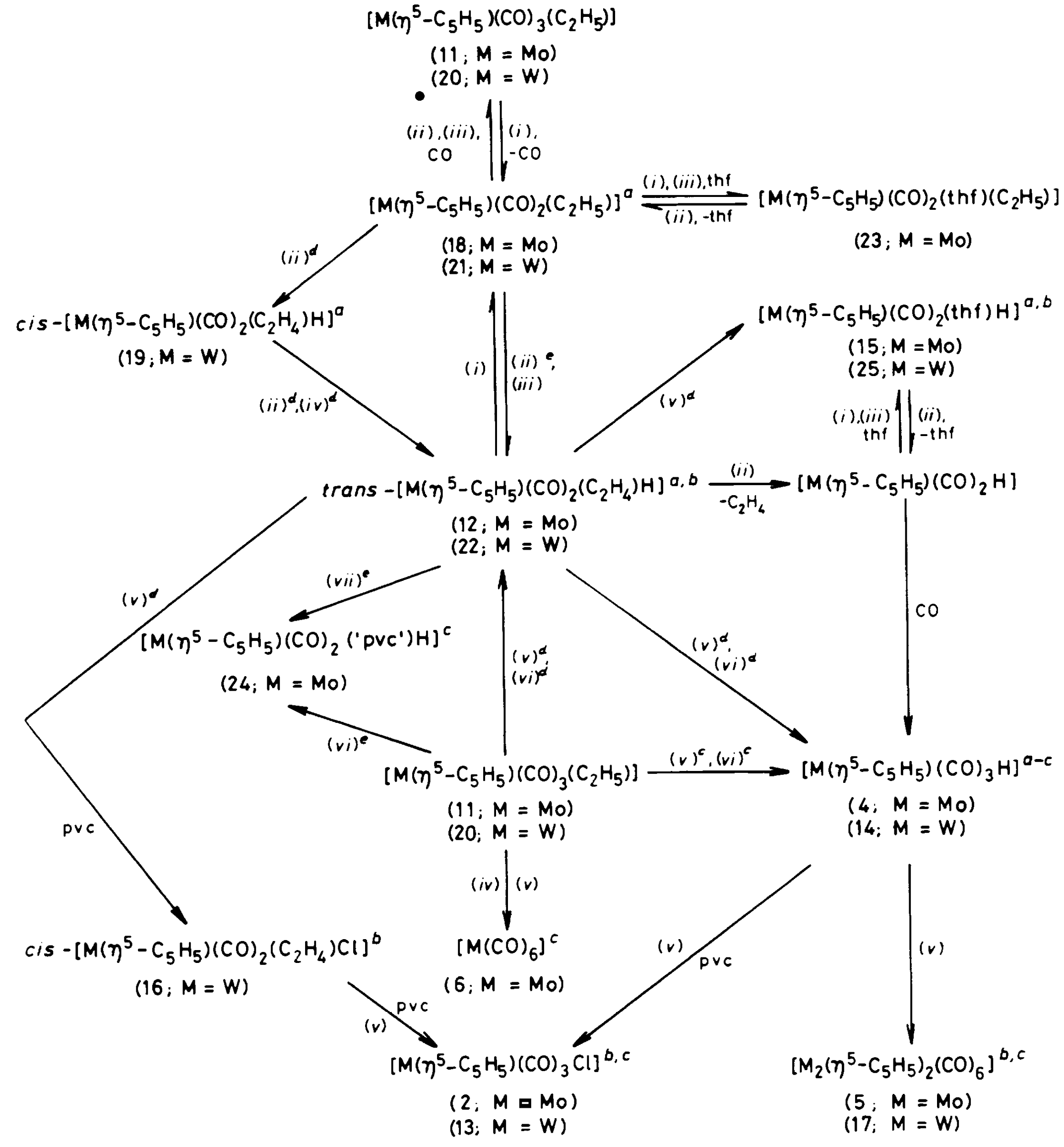
$$[\mathrm{W}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{CH_3})] + [\mathrm{W}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3(\mathrm{CH_3})] \longrightarrow [\mathrm{W_2}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{CO})_5] + 2\mathrm{CH_3}^\cdot \quad \text{(v)}$$

$$[\mathrm{W_2}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{CO})_5] + \mathrm{CO} \longrightarrow [\mathrm{W_2}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{CO})_6] \quad \text{(vi)}$$

$$[\mathrm{W_2}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{CO})_6] \xrightarrow[\text{chlorocarbon solvent}]{h\nu} 2[\mathrm{W}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\mathrm{Cl}] \quad \text{(vii)}$$

Formation of $[\mathrm{W_2}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{CO})_6]$ *via* coupling of photogenerated $[\mathrm{W}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3]^\cdot$ radicals, as previously proposed,[6] was not suggested since the quantum yield of the dimer was found to be independent of the light intensity.[27] Evidence for the thermal reactions in steps (v)—(vi) was provided by the fact that (17) was found to form on warming up a thf solution of (10), CO, and (8) in a sealed cell at −78 °C. Since no dimer was generated in this work on warming the polymer matrices of the same species it is likely that the parent molecules are isolated in our solvent-cast films at low temperatures. At 298 K, however, the molecules have sufficient mobility for bimolecular processes to take place. Photoejected CO evidently diffuses through the matrix at this temperature as is seen by the formation of the hexacarbonyls. The dimers may be generated in the pvc films at room temperature by the non-radical pathway above. However, the complexes (2) and (13), and similarly the hydrides (4) and (14), are formed directly from (1) and (8) respectively in the polymer matrices (Scheme 1), and not *via* the dimers. This is evident from the fact that the rate of formation of the chloro-complexes on direct photolysis (filter A) of the molybdenum and tungsten dimers in pvc films[20] is negligible compared to that seen in this study on photolysis of the methyl complexes, under the same conditions. The difference in rates is probably due to the rigidity of the polymer matrix where the $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3]^\cdot$ fragments generated from the dimers on irradiation cannot easily separate and a thermal back-reaction occurs. The fact that photoinduced $\mathrm{M{-}CH_3}$ bond cleavage has not been observed in frozen gas matrices[10] is probably because the matrix molecules pack very tightly around the carbonyl molecules[28] thus preventing even the relatively small $\mathrm{CH_3}$ group from diffusing away from the photolysis site.

The photoreactions of (11) and (20) in pvc film matrices at 12—298 K are summarised in Scheme 2. The photogeneration of the hydride $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\mathrm{H}]$ *via* the *trans*-ethylene-hydrido-complex has been seen in frozen gas matrices.[11] The observation that the complex (19) thermally rearranges to the *trans* isomer on warming polymer matrices from 12 to 50 K is consistent with the fact that whilst the former isomer has been generated from (21) in frozen gas matrices it has not been seen at higher temperatures in solid paraffin matrices.[12] Since the molybdenum analogue of the *cis* isomer is not observed in



Scheme 2. (*i*) *h*ν (filter A) at 12 K; (*ii*) *h*ν (filter B or C) at 12 K; (*iii*) warming from 12 K; (*iv*) warming from 12 to 50 K; (*v*) *h*ν (filter A) at 298 K; (*vi*) *h*ν (filter B) at 298 K; (*vii*) warming above 25 K ([a] Photoproduct at 12 K. [b] Photoproduct at 298 K, M = W. [c] Photoproduct at 298 K, M = Mo. [d] Reaction for M = W. [e] Reaction for M = Mo)

the polymer films at 12 K it is, if formed, evidently photochemically labile. Similarly, this species has not been observed in frozen gas matrices.

The difference in thermal reactivity of the molybdenum and tungsten dicarbonyl–ethyl fragments on warming the films to 250 K is similar to that seen by Kazlauskas and Wrighton [12] on warming solid paraffin matrices. These workers noted that whilst (21) rapidly rearranges on warming, in the absence of ligands, to form (22), the molybdenum fragment exists in an equilibrium with the ethylene hydride which is almost temperature insensitive up to 250 K. It was also noted that the dicarbonyl ethyls do not recombine with photoejected CO or PPh_3 ligands at 195 K nearly so readily as the corresponding $[M(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ species. It was proposed that, on warming from 77 to 195 K, the dicarbonyl ethyls can adopt a structure which has a weak M–β-H bond which blocks the vacant co-ordination site. A similar structure may be adopted in the polymer matrices in view of the slower regeneration of the parent molecules from the $[M(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_5)]$ species on warming than from the dicarbonyl-methyl analogues.

It is interesting that the same reaction of thf with (18) and (21) occurs in the pvc films containing this ligand. The photoconversion of (20) to (22) in alkane solutions at −78 °C is known [12] to be retarded when thf is present, probably because the species $[W(\eta^5\text{-}C_5H_5)(CO)_2(thf)(C_2H_5)]$ is formed inhibiting the β-hydrogen transfer.

The complex (12) is more photochemically labile, with respect to loss of C_2H_4, than the tungsten analogue as is seen by the faster conversion of the former to the tricarbonyl hydride at 12 K. The molybdenum ethylene hydride is known to be thermally unstable [9,12] and is not observed in solution at temperatures above *ca.* 250 K. It is likely that the formation of (6) from (11) in the polymer matrix at 298 K results from decomposition of this hydride in view of the reactions seen on warming the matrix from 250 K. The formation of (16) in the pvc films at 298 K evidently results from a reaction of (22) which could proceed either *via* the radical $[W(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)]^{\cdot}$, or $[W(\eta^5\text{-}C_5H_5)(CO)_2H]$ and $[W(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ followed by a back reaction with photoejected C_2H_4. Evidence for W–H bond cleavage in (22) has been seen in the reaction of this complex with CCl_4 to form $CHCl_3$.[12]

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