Metal Carbonyl Photochemistry. Part 2.[1] Photochemistry of Hexacarbonyls in Glasses containing Oxygen Donors; the Species $[M(CO)_5(mthf)]$ † ($M = Cr, Mo, W, or V^{-1}$), *cis*-$[M(CO)_4(mthf)_2]$, and *fac*-$[M(CO)_3(mthf)_3]$ ($M = Cr, Mo, or W$)

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The title species have been prepared by photolysis of $[M(CO)_6]$ in mthf glass at 77 K, and (for M = Mo or W) in doped hydrocarbon glasses {in which there is evidence for photoconversion of $Mo(CO)_5$ into $[Mo(CO)_5(mthf)]$}. The compounds $[Mo(CO)_5(CH_3COCH_3)]$, $[Mo(CO)_5(OCHCH_3)]$, and $[Mo(CO)_5(HOR)]$ have also been characterised at low temperature.

SOME of the earliest photochemical studies of the metal hexacarbonyls were carried out in the presence of oxygen-donating ligands,[2,3] while oxygen-containing solvents such as tetrahydrofuran (thf) have long been used in indirect photosubstitution reactions.[4] Interest in the low (*ca.* 80 K) temperature reactions of metal carbonyl fragments led us to extend our studies [1] of photolysis from hydrocarbons to more strongly co-ordinating glasses; an incidental benefit is the ability to extend the range of species that can easily be studied. Solvent–solute interactions proved to be of great importance both before and after photolysis, and this led us to examine the effects of hydrocarbon glasses doped with donors. A preliminary account of parts of this work has already appeared.[5]

EXPERIMENTAL

General procedures, cells, lamps, and some materials and solvents are described in Part 1.[1] The salt $[Na(diglyme)_2]$-$[V(CO)_6]$ was freshly purchased from Strem Chemicals and was generally used without further purification [diglyme = bis(2-methoxyethyl) ether]; $[NMe_4][V(CO)_6]$ (precipitated from boiled-out water) gave identical results. For use as solvents, 2-methyltetrahydrofuran (mthf) (which cools to a glass) and tetrahydrofuran (thf) were distilled from CaH_2 under dry nitrogen and stored under nitrogen in sealed ampoules in the dark until use. Ethers required only as minor components of glasses were in some cases stored over and distilled from sodium diphenyl ketyl.

RESULTS AND DISCUSSION

(*i*) *Photochemistry of the* $[V(CO)_6]^-$ *Anion in mthf.*—A 10^{-2} mol dm^{-3} solution of $[Na(diglyme)_2][V(CO)_6]$ in mthf showed a broad T_{1u} ν(CO) band [full width at half-maximum (f.w.h.m.) 17 cm^{-1}] at 1 859 cm^{-1}, with a partly resolved band (E_g) at around 1 895 cm^{-1}. On cooling to 80 K, the spectrum became much sharper, giving a band at 1 859vs (f.w.h.m. 11 cm^{-1}, T_{1u}), 1 894w (f.w.h.m. 12 cm^{-1}, E_g), and 1 975 cm^{-1} (A_{1g}?, faint) [lit. (Raman + i.r.),[6] 1 858, 1 894, and 2 020 cm^{-1} (in acetonitrile)].

The solution was irradiated in a cell with NaCl windows (because of interest in bands below 1 750 cm^{-1}) at 80 K for 1 h, using a soda-glass filter. Near-quantitative conversion took place to a species to which we assign a C_{4v} structure from its i.r. spectrum (Figure 1, Table). This species, formulated as $[V(CO)_5(mthf)]^-$, persisted for a short time above the softening point of the solvent, the spectrum becoming somewhat broader and the lower A_1 band less pronounced. This fact, together with a close scrutiny of frequency shifts between $[Cr(CO)_6]$, $Cr(CO)_5$, and $[Cr(CO)_5(mthf)]$ (see below), led us to reject the alternative formulation as $[V(CO)_5]^-$.

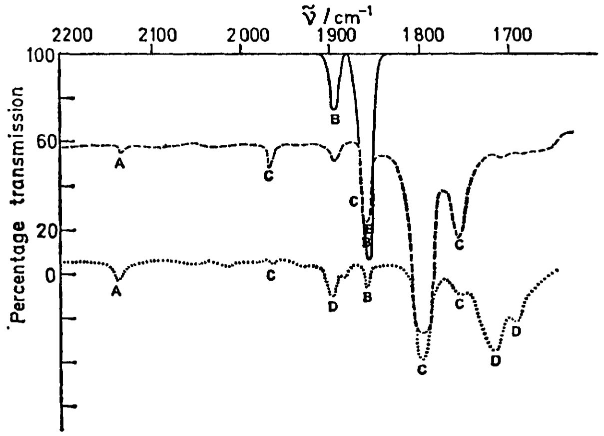

FIGURE 1 Photolysis of $[V(CO)_6]^-$ in mthf at 77 K: (——), before photolysis; (– – –), after irradiation for 1 h using soda-glass filter; (· · ·), after irradiation for another 5 min (unfiltered). Species: A = CO, B = $[V(CO)_6]^-$, C = $[V(CO)_5(mthf)]^-$, and D = *cis*-$[V(CO)_4(mthf)_2]^-$ (?). Curves (– – –) and (. . .) have been staggered with respect to the 0—100% transmission to avoid overlap.

Secondary photolysis took place rapidly (5 min, unfiltered light) to give extensive formation of a lower carbonyl {probably *cis*-$[V(CO)_4(mthf)_2]^-$, see Table}. This is reconverted into $[V(CO)_5(mthf)]^-$ on glass softening, and $[V(CO)_5(mthf)]^-$ under our closed-cell conditions quantitatively is itself converted back into $[V(CO)_6]^-$ as the cell returns to room temperature.

The anion $[V(CO)_6(mthf)]^-$ is stable at 80 K in the dark. Irradiation with visible light however (filter GG 420) causes photoreversal, which we ascribe to photochemical loss of mthf and possible reorientation of the resulting fragment.‡ The visible band of $[V(CO)_5(mthf)]^-$ (see

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† mthf = 2-Methyltetrahydrofuran.

‡ For a discussion of this process, see our remarks [1] on the photochemistry of $[Cr(CO)_5(OH_2)]$.

Table), which is no doubt responsible for this behaviour, has been independently observed by Wrighton *et al.*[7] in a mthf glass.

Photochemical substitution into the anions $[M(CO)_6]^-$ (M = V, Nb, or Ta) is important in synthesis because of the thermal inertness of these anions. If the mthf–M bond is real, this would explain the otherwise surprising[8] result that[9] photosubstitution into $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ in thf required mild thermal as well as photochemical activation. The low threshold for efficient photolysis in $[V(CO)_6]^-$ compared with $[Cr(CO)_6]$ is of course a direct consequence of the differences in their absorption spectra,[10] and illustrates the point that photochemical thresholds depend on detailed electronic pathways rather than on bond strengths as such.

Spectroscopic data for photochemically generated species $[M(CO)_{6-n}L_n]$, at 77 K unless otherwise stated

Species	Solvent	ν(CO) bands [a]	Visible–u.v. bands [a,b]
$[V(CO)_5(mthf)]^-$	mthf	1 966vw (A_1), 1 868w (B_2), 1 795vs (E), 1 757s (A_1)	18 200 [c] (3 400) *d*
cis-$[V(CO)_4(mthf)_2]^-$ (?)	mthf	1 895 (A_1), 1 715s,br (A_1,B_1), 1 690 (B_2)	
$[Cr(CO)_5(mthf)]$	mthf	2 078w (A_1), 1 983w (B_2), 1 933vs (E), 1 881s (A_1)	39 900 [e] (23 000), 22 900 [c] (4 000)
$[Mo(CO)_5(mthf)]$	mthf	2 078w (A_1), 1 985w (B_2), 1 936vs (E), 1 882s (A_1)	24 850 [c] (*ca.* 6 000) *d*
	Methylcyclohexane–isopentane (4 : 1)	2 078w (A_1), 1 931vs (E), 1 887s (A_1)	
$[W(CO)_5(mthf)]$	mthf	2 074w (A_1), 1 980w (B_2), 1 924vs (E), 1 878s (A_1)	40 100 [e] (30 000), 24 000 [c] (3 600)
	Methylcyclohexane–isopentane (4 : 1)	2 072w (A_1), 1 928vs (E), 1 901s (A_1)	
$[Cr(CO)_4(mthf)_2]$ [f]	mthf	2 016m (A_1), 1 880 [g] (B_1), 1 870 (sh) (A_1), 1 825s (B_2)	
$[Mo(CO)_4(mthf)_2]$ [f]	mthf	2 018m (A_1), 1 884vs (B_1), 1 868s (A_1), 1 823s (B_2)	
	Methylcyclohexane–isopentane (4 : 1)	2 018m (A_1), *ca.* 1 885 [h] (A_1,B_1), 1 828 (B_2)	
$[W(CO)_4(mthf)_2]$ [f]	mthf	2 015m (A_1), 1 871vs (B_1), 1 861 (sh) (A_1), 1 820s (B_2)	
$[Cr(CO)_3(mthf)_3]$ [i]	mthf	1 917m (A_1), 1 764vs (E)	
$[Mo(CO)_3(mthf)_3]$ [i]	mthf	1 913m (A_1), 1 767vs (E)	
	Methylcyclohexane–isopentane (4 : 1)	1 915m (A_1), 1 773vs (E)	
$[W(CO)_3(mthf)_3]$ [i]	mthf	1 905m (A_1), 1 758vs (E)	
trans-$[Mo(CO)_4(mthf)_2]$ (?)	Methylcyclohexane–isopentane (4 : 1)	1 873	
$[Mo(CO)_5(OCHCH_3)]$	CH_3CHO [j]	2 075vw (A_1), 1 944vs (E), 1 903s (A_1)	
$[Mo(CO)_5(HOR)]$	EtOH–MeOH (4 : 1)	2 078vw (A_1), 1 937s (E), 1 883ms (A_1)	
$[Mo(CO)_5\{HO(CH_2)_4CH_3\}]$	Isopentane [k]	2 075vw (A_1), 1 930m (E), 1 903w (A_1)	
$[Mo(CO)_5(CH_3COCH_3)]$	Methylcyclohexane–isopentane (4 : 1)	2 075w (A_1), 1 940s (E), 1 901m (A_1)	

[a] w = Weak, m = medium, s = strong, v = very, sh = shoulder, and br = broad. [b] Molar absorption coefficients ($dm^3\,mol^{-1}\,cm^{-1}$) are given in parentheses. [c] $A_1 \rightarrow E$ ($xz,yz \rightarrow z^2$). [d] Charge-transfer region not measured. [e] Metal-to-ligand charge transfer. [f] *cis* Isomer; assignments by band position and intensity. [g] Masked by band of $[Cr(CO)_5(mthf)]$ at 1 881 cm^{-1} until secondary photolysis almost complete. [h] Overlaps band of $[Mo(CO)_5(mthf)]$ at 1 887 cm^{-1}. For relative shift of A_1,B_1 compare R. Poilblanc and M. Bigorgne, *J. Organometallic Chem.*, 1966, **5**, 93. [i] *fac* Isomer. [j] At 195 K. [k] At 300 K.

(*ii*) *Photochemistry of the Group* 6 *Hexacarbonyls in Neat mthf*.—The ν(CO) T_{1u} bands of the parent hexacarbonyls were much broader in mthf than in hydrocarbons, with a shoulder [ν(CO) E_g] around 2 020 cm^{-1}. On cooling to 77 K, the band at 2 020 cm^{-1} became clearly resolved, and ν(CO) A_{1g} became weakly visible around 2110 cm^{-1}. The frequency of the centre of the T_{1u} band shifted slightly to lower frequencies, and the half-width increased to about 1.5 times its original value, although band width close to the baseline did not increase (see Figure 2). The expected low-frequency shoulder due to $[M(CO)_5(^{13}CO)]$ is not resolved either at room temperature or at 77 K, while the high-frequency shoulder, corresponding to the band of $[Mo(CO)_5(^{13}CO)]$ at 2 011 cm^{-1},[11] is resolved at room temperature only. These facts are consistent with incipient splitting of the T_{1u} band, and lowering of effective symmetry, in a range of poorly defined sites. Photolysis of glasses with WG 305-filtered light led to production of the expected $[M(CO)_5(mthf)]$ (see Table).* This showed the predicted i.r. ν(CO) pattern, in which however the higher A_1 band is very weak, even weaker than the formally forbidden B_2 band. The electronic spectra are similar to those of $M(CO)_5$ (glass) but with the first resolved band at lower frequency, and showing a further slight red shift on warming. It seems strange that a band of considerable *d–d* character should move to lower frequency when hydrocarbon glass is replaced by mthf, but the unusual behaviour of this band has been satisfactorily explained by other workers.[12,13]

Further photolysis with WG 305-filtered or (far more

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* For M = Cr, there was always some secondary photolysis.

rapidly) with unfiltered light led to formation of *cis*-$[M(CO)_4(mthf)_2]$ and *fac*-$[M(CO)_3(mthf)_3]$, identified by their i.r. spectra, and appearance sequence (Figure 3). Other isomers are either absent or present as very minor components, their spectra being completely masked by those of the dominant species. No photoreversal or photoisomerisation could be detected, in contrast to $M(CO)_5$ [1,12-14] and to $[V(CO)_5(mthf)]^-$.

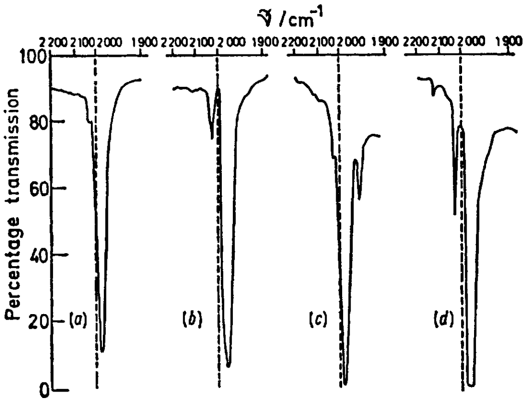

FIGURE 2 Spectrum of $[Mo(CO)_6]$ in mthf-containing solvents: (*a*) neat mthf, room temperature; (*b*) as (*a*) but at 77 K; (*c*) in methylcyclohexane–isopentane (4 : 1) + 1 mol dm^{-3} mthf at room temperature; and (*d*) as (*c*) but at 77 K

(*iii*) *Photochemistry of the Group* 6 *Hexacarbonyls in Methycyclohexane–Isopentane* (4 : 1) *doped with mthf*.—The spectrum of 5 × 10^{-3} mol dm^{-3} $[W(CO)_6]$ in methylcyclohexane–isopentane (4 : 1) in the presence of as little as 5 × 10^{-2} mol dm^{-3} mthf at 77 K clearly shows the ν(CO) E_g band. Photolysis (Pyrex filter) gives a mixture of $W(CO)_5$ and $[W(CO)_5(mthf)]$. On warming, $[W(CO)_5(mthf)]$ is formed in solution, and is converted at room temperature into $[W(CO)_6]$.

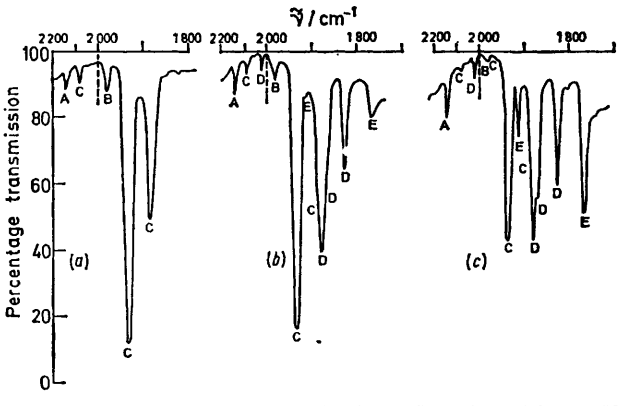

FIGURE 3 Stages in the photolysis of $[Mo(CO)_6]$ in mthf at 77 K: (*a*) after irradiation with WG 305-filtered light; (*b*) as (*a*), after irradiation with unfiltered light; and (*c*) as (*b*), after further irradiation with unfiltered light. Species: A = CO, B = $[Mo(CO)_6]$, C = $[Mo(CO)_5(mthf)]$, D = *cis*-$[Mo(CO)_4(mthf)_2]$, and E = *fac*-$[Mo(CO)_3(mthf)_3]$

In the presence of 1 mol dm^{-3} mthf, 5 × 10^{-2} mol dm^{-3} $[Mo(CO)_6]$ can be cooled to 77 K in the same solvent without precipitation, although in the absence of mthf such precipitation begins at around 10^{-2} mol dm^{-3}. The spectrum shows clearly the ν(CO) A_{1g} and ν(CO) E_g bands, with incipient splitting of ν(CO) T_{1g} (Figure 2). These facts, and the results of the secondary photolysis experiments described below, strongly suggest a degree of solute–cosolute interaction, especially at low temperature.

Irradiation with unfiltered or Co^{2+}, Ni^{2+}-filtered [15] light gave initially both $Mo(CO)_5$ and $[Mo(CO)_5(mthf)]$.

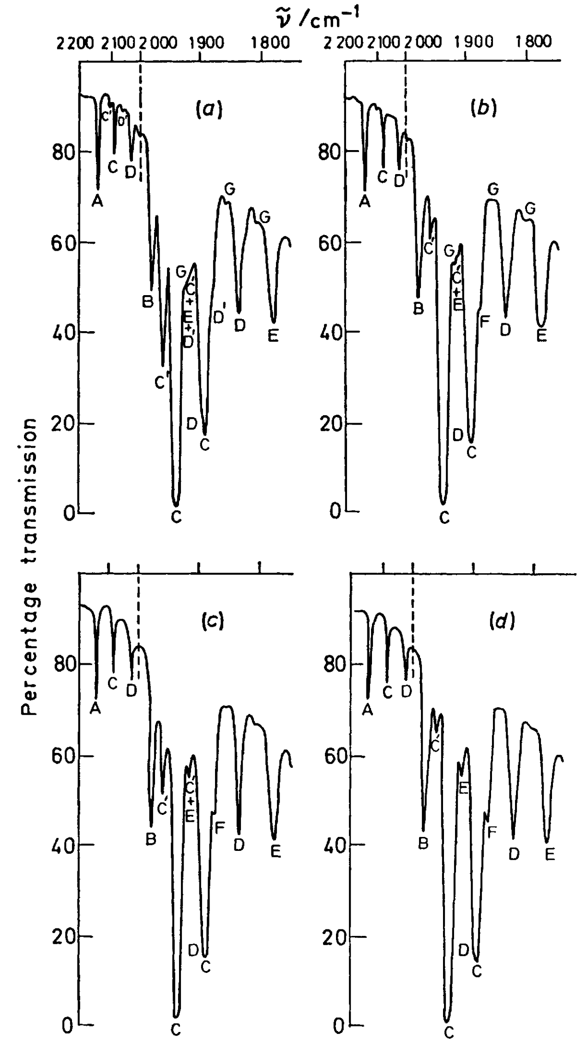

FIGURE 4 Irradiation of $[Mo(CO)_6]$ in methylcyclohexane–isopentane (4 : 1) + 1 mol dm^{-3} mthf: (*a*) after irradiation for 1 h with u.v. light (Co^{2+}, Ni^{2+} filter); (*b*) as (*a*), after 30 min in i.r. beam; (*c*) as (*b*), after visible irradiation for 30 min (WG 335 filter); and (*d*) as (*c*), after 30 min in i.r. beam. Species: A = CO, B = $[Mo(CO)_6]$, C = $[Mo(CO)_5(mthf)]$, C′ = $Mo(CO)_5$, D = *cis*-$[Mo(CO)_4(mthf)_2]$, D′ = *cis*-$Mo(CO)_4$, E = *fac*-$[Mo(CO)_3(mthf)_3]$, F = *trans*-$[Mo(CO)_4(mthf)_2]$ (?), and G = other minor species

Further irradiation led to formation of *cis*-$[Mo(CO)_4(mthf)]$ and *fac*-$[Mo(CO)_3(mthf)_3]$, with frequencies only slightly displaced from those in neat mthf glass, and to traces of $Mo(CO)_4$ and weak bands possibly due to such species as $[Mo(CO)_4(mthf)]$ [Figure 4(*a*)].

Further irradiation with visible light gave rise to several interesting processes. The light of the i.r. beam (PE 227) caused disappearance of $Mo(CO)_4$, $Mo(CO)_5$, and the weak minor bands, with formation of a small amount of [Mo(CO)$_6$] {and, presumably, [Mo(CO)$_5$(mthf)] and/or *cis*-[Mo(CO)$_4$(mthf)] [Figure 4(*a*) to (*b*); (*c*) to (*d*)]}. Visible-near-u.v. light, however (Hg lamp, $\lambda > 335$ nm), led to formation of Mo(CO)$_5$ and [Mo(CO)$_6$], presumably by photolysis of [Mo(CO)$_5$(mthf)] with, in some molecules, CO capture by the reorientating[12,13] Mo(CO)$_5$ fragment [Figure 4(*b*) to (*c*)]. Throughout all these changes there was growth in a peak at 1 873 cm^{-1} which we attribute tentatively to *trans*-[Mo(CO)$_4$(mthf)$_2$].

It seems that the interconversion of [Mo(CO)$_5$(mthf)] and Mo(CO)$_5$ (hydrocarbon) is a reaction that can occur photochemically in either direction, although the degree of mthf loss is always small despite the large excess of [Mo(CO)$_5$(mthf)] present. These facts seem consistent with a reorientation process which can itself be largely frustrated, for bulky ligands, by a cage effect. If, as has been suggested,[16] large ligands can recombine *thermally* with Mo(CO)$_5$ at 77 K, it is not clear how any Mo(CO)$_5$ survives long enough to undergo such recombination *photochemically*.

(*iv*) *Miscellaneous Reactions*.—On irradiation, [Mo(CO)$_6$] in EtOH–MeOH (4 : 1) gave what is presumably a mixture of [Mo(CO)$_5$(HOEt)] and [Mo(CO)$_5$(HOMe)]. The compound [Mo(CO)$_5$(CH$_3$COCH$_3$)] was formed in acetone-doped methylcyclohexane–isopentane (4 : 1) [together with Mo(CO)$_5$] and in acetone at 195 K, as was [Mo(CO)$_5$(OCHCH$_3$)] in the mixed solvent only. Irradiation in the mixed solvent at 77 K in the presence of glyme (1,2-dimethoxyethane) gave a species of type [M(CO)$_5$L], but L is probably adventitious H$_2$O. In all these cases [Mo(CO)$_6$] was regenerated on warming. The compound [Mo(CO)$_5${HO(CH$_2$)$_4$CH$_3$}] was prepared by irradiation in isopentane (2-methylbutane) at room temperature. Its spectrum resembles that of [Mo(CO)$_5$(HOR)] at 77 K, apart from a 20 cm^{-1} displacement to lower frequency of the $A_1{}^1$ band in the latter. This band generally seemed the most sensitive to minor environmental influences, as expected, since it corresponds to the only oscillation with a large component parallel to the permanent dipole of the molecule.

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