Metal Carbonyl Photochemistry. Part 3.[1] Behaviour of $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ † and Related Species at 77 K

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Photolysis of $[Mn(cp)(CO)_3]$ (cp = η-C_5H_5) in glasses at 77 K gives species $[Mn(cp)(CO)_2]$, $[Mn(cp)(CO)]$, and (in the presence of ethers) $[Mn(cp)(CO)_2(ether)]$ and $[Mn(cp)(CO)(ether)_2]$; $[Mn(mcp)(CO)_3]$ behaves similarly (mcp = methylcyclopentadienyl). Photolysis is slower than with the d^6 hexacarbonyls, and the mono-ether complexes show conformational trapping. The broadly similar behaviour of $[Cr(C_6H_6)(CO)_3]$, $[Mn(cp)(CO)_2(CS)]$, $[Fe(cp)(CO)_2I]$, and $[Mn\{C_4(CF_3)_4S(C_6F_5)\}(CO)_3]$ is briefly described.

PHOTOCHEMICAL replacement of CO in species $[M(C_nH_n)(CO)_x]$ has long been used in synthesis,[2,3] since thermal displacement of CO is often difficult in these cases, and (for n even) replacement of the organic ligand is commonly the preferred thermal process.[4] We have extended our investigations [1,5] of metal-carbonyl photochemistry to $[Mn(mcp)(CO)_3]$ and $[Mn(cp)(CO)_3]$ (mcp = η-methylcyclopentadienyl, cp = η-cyclopentadienyl), and also report brief studies on some related species. A preliminary account of part of this work has appeared,[6] and other workers have independently examined the formation of $[Mn(C_5H_5)(CO)_2]$ and $[Cr(C_6H_6)(CO)_2]$ in argon and methane matrices.[7]

EXPERIMENTAL

Apparatus and conditions were as previously described.[1,5] Lamp condition was checked regularly by the photolysis rate of $[Mo(CO)_6]$ in methylcyclohexane–isopentane (4 : 1). The compound $[Mn(cp)(CO)_3]$ was vacuum sublimed before use, but $[Mn(mcp)(CO)_3]$ (Strem Chemicals) and $[Fe(cp)(CO)_2I]$ (Alpha Inorganics) were used as purchased. The compound $[Cr(C_6H_6)(CO)_3]$ was a gift from Professor D. A. Brown, $[Mn(cp)(CO)_2(CS)]$ from Professor I. S. Butler, and $[Mn\{C_4(CF_3)_4S(C_6F_5)\}(CO)_3]$ from Professor D. W. A. Sharp and Dr. J. L. Davidson. All substances gave completely satisfactory absorption spectra in the ν(CO) region.

Solvents were in general purified as described previously.[1,5] Nujol was from freshly opened bottles and was passed down a silica gel column before use. Relative intensities of i.r. bands were estimated from the product of maximum absorbance and full width at half-maximum (f.w.h.m.), as determined on the expanded scale of a PE225 spectrometer (middle-aged but in good order) with no corrections for finite slit width or differences in band shape. Long-wavelength bandpass filters (Skan) employed are indicated by colour code and cut-out wavelength; thus filter GG420 is a green glass transmitting at $\lambda > 420$ nm.

RESULTS AND DISCUSSION

$[Mn(cp)(CO)_3]$ *and* $[Mn(mcp)(CO)_3]$.—(*a*) *In hydrocarbon glasses.* Both substrates tended to precipitate on cooling. This was suppressed in Nujol-containing glasses, but these tended to crack on cooling; otherwise they gave similar results to methylcyclohexane–isopentane (4 : 1) glasses.

Results are summarised in the Table and illustrated in Figure 1. Both substrates showed a definite shift of ν(CO) to low frequency on cooling. Photolysis was slow even with unfiltered light and complete photolysis was never achieved. Photoreversal, which occurred with WG335-filtered light,‡ could not have been responsible for the slow *initial* photolysis, and it may be that the ring–metal system is acting as an internal filter or energy trap. It may also be inhibiting reorientation, and thus favouring immediate recombination. Nonetheless, the expected species $[MnL(CO)_2]$ and, on prolonged photolysis, $[MnL(CO)]$ were observed (L = cp or mcp). Warming led to regeneration of starting material, with no evidence of intermediate water complexes (contrast the Group 6 hexacarbonyls [5]), nor of dinitrogen complexes $[MnL(CO)_2(N_2)]$, although such complexes are well known.[7,8]

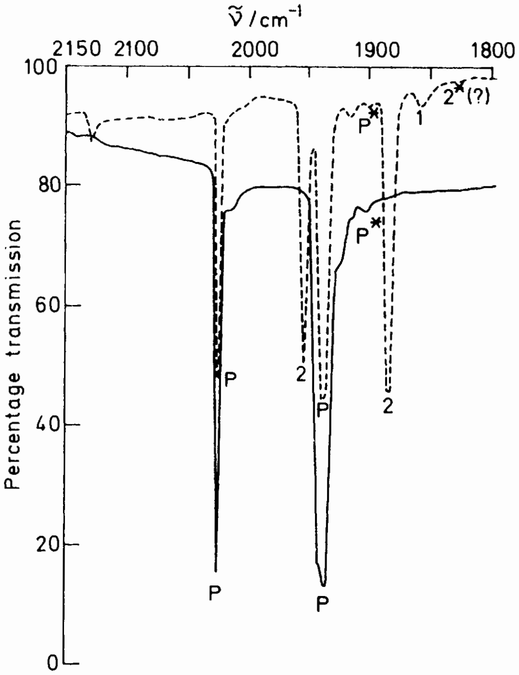

FIGURE 1 Spectra of $[Mn(cp)(CO)_3]$ in methylcyclohexane–Nujol (3 : 1) at 77 K: (——), unphotolysed; (— — —), after irradiation (unfiltered) for 125 min. Peaks: P, parent $[Mn(cp)(CO)_3]$; 1, $[Mn(cp)(CO)]$; 2, $[Mn(cp)(CO)_2]$; an asterisk signifies a ^{13}CO satellite

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† Tricarbonyl(η-cyclopentadienyl)manganese.

‡ See Experimental section for explanation of filter codes.

Data for CO stretching frequencies

Species	Solvent	T/K	$\tilde{\nu}$(CO)/cm^{-1}	k [a]	k_i [a]	δ [b]/°
[Mn(cp)(CO)$_3$]	c	293	2 032(A_1), 1 946(E)	1 575	46	
		77	2 026(A_1), 1 938(E), 1 905(^{13}CO)	1 564	47	94 [d]
	mthf	293	2 021(A_1), 1 932(E)	1 554	47	
		77	2 011(A_1), 1 915(E), 1 885(^{13}CO)	1 531	51	
	c + 5% mthf	293	2 032(A_1), 1 948(E)	1 577	45	
		77	2 021(A_1), 1 922(E)	1 544	53	
	EtOH–MeOH (4 : 1)	293	2 017(A_1), 1 931(E)	1 551	46	
		77	2 011(A_1), 1 913(E)	1 530	52	
[Mn(mcp)(CO)$_3$]	c	77	2 022(A_1), 1 936(E)	1 559	46	98
	mthf	293	2 020(A_1), 1 939(E)	1 561	43	
		77	2 015(A_1), 1 927(E)	1 546	47	
	EtOH–MeOH (4 : 1)	293	2 017(A_1), 1 932(E)	1 552	45	
		77	2 010(A_1), 1 918(E)	1 534	49	
[Mn(cp)(CO)$_2$]	c, k	77	1 955(A'), 1 886(A'')	1 490	53	100
[Mn(mcp)(CO)$_2$]	c	77	1 950(A'), 1 881(A'')	1 482	53	110
[Mn(cp)(CO)]	c	77	1 857	1 393		
[Mn(mcp)(CO)]	c	77	1 856	1 391		
[Mn(cp)(CO)$_2$(thf)]	c + 5% thf	77	1 942(A'), 1 865(A'') [e]	1 464	59	
			1 916(A'), 1 834(A'') [f]	1 420	62	
[Mn(cp)(CO)(thf)$_2$]	c + 5% thf	77	1 768	1 262		
[Mn(cp)(CO)$_2$(mthf)]	mthf	293	1 925(A'), 1 851(A'')	1 440	56	
		77	1 942(A'), 1 870(A'') [e]	1 468	55	
			1 919(A'), 1 840(A'') [f]	1 427	60	
[Mn(mcp)(CO)$_2$(mthf)]	mthf	293	*ca.* 1 932(A'),[g] 1 850(A'')	*ca.* 1 445	*ca.* 63	
		77	1 937(A'), 1 866(A'') [e]	1 461	55	
			1 915(A'), 1 836(A'') [f]	1 421	60	
[Mn(cp)(CO)$_2$(HOR)]	EtOH–MeOH (4 : 1)	293	1 920(A'), 1 847(A'')	1 433	56	
		77	1 939(A'), 1 868(A'') [e]	1 463	55	
			1 914(A'), 1 835(A'') [f]	1 420	60	
[Mn(mcp)(CO)$_2$(HOR)]	EtOH–MeOH (4 : 1)	293	1 918(A'), 1 842(A'')	1 428	58	
		77	1 938(A'), 1 867(A'')	1 462	55	
			1 912(A'), 1 833(A'')	1 417	60	
[Cr(C$_6$H$_6$)(CO)$_3$]	mthf	293	1 968(A_1), 1 889(E)	1 482	41	
		77	1 956(A_1), 1 871(E)	1 457	44	
[Cr(C$_6$H$_6$)(CO)$_2$(mthf)]	mthf	77	1 890(A'), 1 828(A'') [e]	1 396	47	
			1 867(A'), 1 801(A'') [f]	1 359	49	
[Fe(cp)(CO)$_2$I]	mthf	293	2 033(A'), 1 989(A'')	1 633	36	
		77	2 027(A'), 1 981(A'')	1 622	37	
[Fe(cp)(CO)I(mthf)]	mthf	77	1 943	1 525		
[Mn(cp)(CO)$_2$(CS)]	c	293	2 010(A'), 1 962(A'')	1 593	38	
		77	2 008(A'), 1 955(A'')	1 586	42	
[Mn(cp)(CO)(CS)]	c	77	1 940	1 520		
[Mn(cp)(CO)(CS)$_2$] [h]	c	77	1 995 [i]	1 607		
[Mn{C$_4$(CF$_3$)$_4$S(C$_6$F$_5$)}(CO)$_3$]	mthf	293	2 052(A'), 1 987(E) [j]			
		77	2 048(A_1); 1 990, 1 975(E) [j]			
[Mn{C$_4$(CF$_3$)$_4$S(C$_6$F$_5$)}(CO)$_2$(mthf)]	mthf	77	2 030w, 2 012m, 1 975s, 1 940br			

[a] N m^{-1}. [b] From relative intensities. [c] Methylcyclohexane–isopentane (4 : 1). [d] Compare crystallographic values of 91, 91, and 94° (D. J. Parker, *J. Chem. Soc., Dalton Trans.*, 1973, 155). [e] Minor rotamer. [f] Major rotamer. [g] Masked by E band of parent. [h] This work; see text. [i] Literature value (ref. 15) is 1 991 cm^{-1} (in CS$_2$ solution). [j] In idealised three-fold symmetry. [k] Literature values (ref. 7, CH$_4$, *ca.* 12 K): ν(CO) 1 961.4, 1 892.8 cm^{-1}; k = 1 501.6 N m^{-1}; k_i = 53.4 N m^{-1}.

Since in the substrate and product molecules all CO groups present are of the same type, the angle between the oscillating dipoles of these groups can be found very simply from relative intensities;[9] the results are included in the Table. Despite the crude method used, the angles found are so reasonable that we believe the increase of angle between [Mn(C$_5$H$_4$R)(CO)$_3$] and [Mn(C$_5$H$_4$R)(CO)$_2$] to be real. Presumably, as in [Cr(CO)$_5$(CH$_4$)],[10] the steric demand of weakly interacting alkane is less than that of CO. Extended-Hückel calculations [11] predict, for [Mp(cp)(CO)$_2$], non-planarity of the M–CO and M–cp(centre) directions, consistent with the smallness of the increase.

(*b*) *In alcohol glasses.* In EtOH–MeOH (4 : 1) at room temperature [Mn(cp)(CO)$_3$] shows the expected two bands; these shift markedly on cooling (Table), and the E band shows skewing suggestive of incipient splitting. Photolysis at 77 K gives two pairs of new bands, of which the higher-frequency pair is less intense and disappears on annealing (Figure 2). We find similar behaviour in several other systems of type [M(C$_n$H$_n$)(CO)$_2$(ROR')], and suggest that it is due to the creation by photolysis of two distinct families of rotamers (Figure 3), depending presumably on the arrangement of solvent molecules around the photolysed molecule. Type (A), which are the more sterically congested, are formed to a smaller extent, and the congestion also leads to poorer donation from ligand oxygen to metal. This suggested behaviour is closely related to that found by Butler and Sawai [12] in [Mn(cp)(CO)$_2$(SC$_4$H$_8$)], but in our case, since an oxygen donor is more sterically hindered than a thioether, the difference in properties is greater and only one rotamer can survive in a mobile medium. Trapping by the solid matrix no doubt depends on the leverage exerted through the bulky R and C_nH_n groups on the O–M bond. The behaviour of $[\mathrm{Mn(mcp)(CO)_3}]$ is similar.

(*c*) *In ether-containing glasses.* The CO stretching modes of both species are lower in 2-methyltetrahydrofuran (mthf) than in hydrocarbons even at room temperature and are further depressed on cooling. Photolysis at 77 K gives a four-band spectrum assignable to rotamer types (A) and (B) (Figure 3). On warming this is replaced by the two-band spectrum of the preferred rotamer (Table), which disappears on standing in a sealed cell and is replaced by that of the starting material.

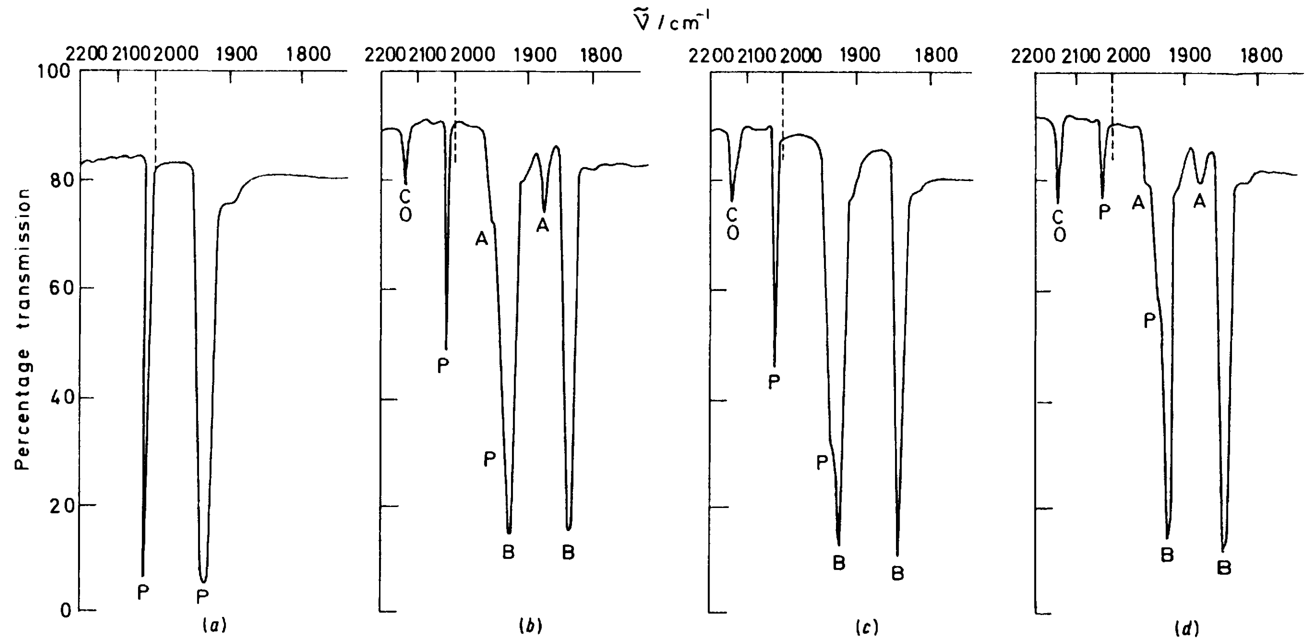

FIGURE 2 Spectra of $[\mathrm{Mn(cp)(CO)_3}]$ in EtOH–MeOH (4 : 1) at 77 K: (*a*) unphotolysed; (*b*) after irradiation (unfiltered) for 15 min; (*c*) as (*b*), but annealed at 90 K and re-cooled to 77 K; (*d*) as (*c*), after irradiation (unfiltered) for another 20 min. Peaks: P, parent $[\mathrm{Mn(cp)(CO)_3}]$; A and B, rotamer families of $[\mathrm{Mn(cp)(CO)_2(HOR)}]$ (see text)

Photolysis at 77 K of $[\mathrm{Mn(cp)(CO)_3}]$ in methylcyclohexane–isopentane (4 : 1) containing 5% v/v (*ca.* 0.5 mol dm^{-3}) thf gave closely similar products of types (A) and (B). Photolysis was faster than in pure mthf, which may indicate the greater ease of reorganisation around the metal in a less rigid matrix. Prolonged irradiation led to species $[\mathrm{Mn(cp)(CO)(thf)_2}]$ (Table). Behaviour in mthf-doped methylcyclohexane–isopentane (4 : 1) was similar but secondary substitution was not observed. The compound $[\mathrm{Mn(mcp)(CO)_3}]$ behaved, as usual, in the same way as $[\mathrm{Mn(cp)(CO)_3}]$. The effects of thf or mthf on the spectra of the unphotolysed species were considerable, indicating significant association, and will be reported elsewhere.[13]

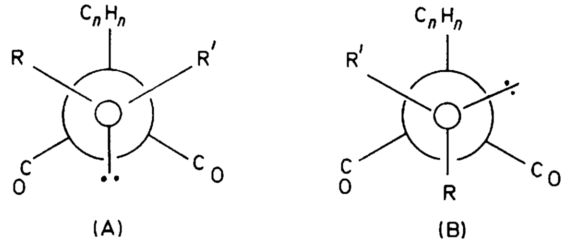

FIGURE 3 Rotamer families of alcohol or ether complexes $[\mathrm{M(C_nH_n)(CO)_2(ROR')}]$

$[\mathrm{Cr(\eta\text{-}C_6H_6)(CO)_3}]$ *in mthf.**—This was very similar to that of $[\mathrm{Mn(cp)(CO)_3}]$, with a marked temperature shift of ν(CO) on cooling, the formation of a four-band spectrum assignable to two rotamers, the higher-frequency spectrum being weaker and disappearing first on warming, and extensive regeneration of starting material (Table, Figure 4). We could find no evidence for displacement of benzene by mthf.

$[\mathrm{Fe(cp)(CO)_2I}]$ *in mthf.*—Like other workers,[14] we find evidence (Table) for formation of $[\mathrm{Fe(cp)(CO)(mthf)I}]$. The band assigned to this species was slightly broader than the A'' band of the parent, suggesting the presence of rotamers. Even extensively filtered light (GG420) caused photolysis, but the rate of photolysis increased markedly on going from WG350- through WG305-filtered to unfiltered light. We found no evidence for photoreversal, but there was some secondary photolysis to a carbonyl-free species, and incomplete regeneration of parent on warming.

$[\mathrm{Mn(cp)(CO)_2(CS)}]$ *in Methylcyclohexane–Isopentane* (4 : 1).—This substance showed the usual shift of the two ν(CO) bands to lower frequency on cooling. The

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* Single run only.

only species formed directly by photolysis with unfiltered light was assignable as [Mn(cp)(CO)(CS)], but, when the photolysed glass was rapidly warmed (in about 10 min) to room temperature, regeneration of starting material was incomplete and a weak but real new band was observed at the known[15] frequency of [Mn(cp)(CO)$(CS)_2$] (Table, Figure 5). A little [Mn(cp)$(CO)_2$] was formed, most probably from [Mn(cp)$(CO)_3$] impurity, since on other evidence[16] direct CS loss seems unlikely.

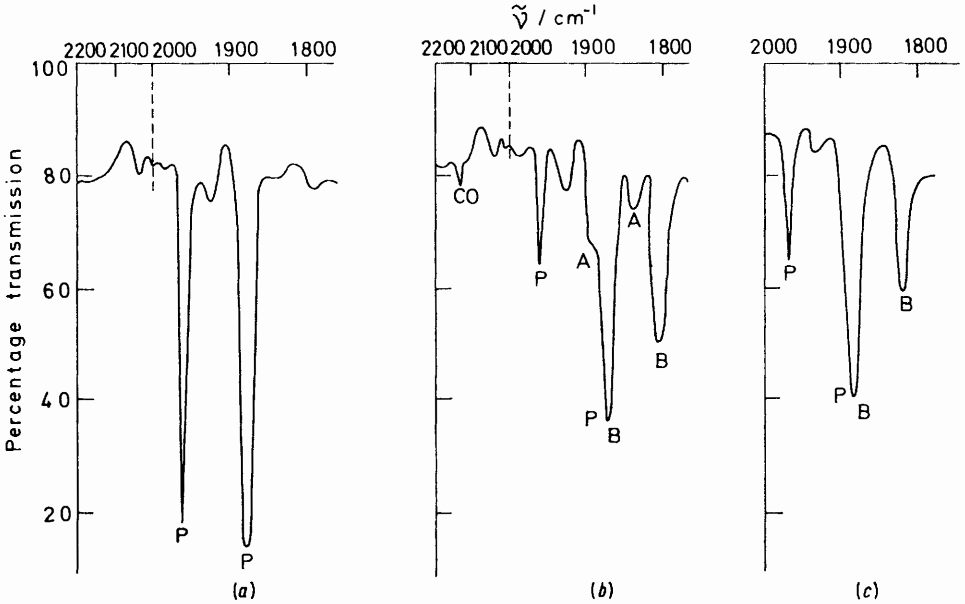

FIGURE 4 Photolysis of [$Cr(C_6H_6)(CO)_3$] in mthf: (*a*) at 77 K (reference at room temperature, hence baseline peaks); (*b*) as (*a*), after irradiation (unfiltered) for 40 min; (*c*) as (*b*), during warm-up [CO still present as in (*b*)]. Peaks: P, parent; A and B, rotamers of [$Cr(C_6H_6)(CO)_2$(mthf)]

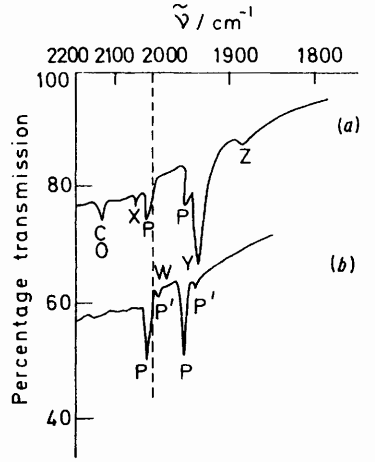

FIGURE 5 Photolysis of [Mn(cp)$(CO)_2$(CS)] in methylcyclohexane–isopentane (4 : 1): (*a*) after irradiation (unfiltered) for 75 min; (*b*) on warm-up (curve displaced for clarity). Peaks: P, [Mn(cp)$(CO)_2$(CS)]; P′, [Mn(cp)$(CO)_3$] impurity; Y, [Mn(cp)(CO)(CS)]; Z, [Mn(cp)$(CO)_2$] (presumably from P′); X, unidentified; W, [Mn(cp)(CO)$(CS)_2$]

[Mn{$C_4(CF_3)_4S(C_6F_5)$}$(CO)_3$][17] *in mthf.*—The spectroscopic and photochemical properties of this substance reflected the low symmetry of the non-carbonyl ligand. Thus the lower-frequency ν(CO) peak of the parent was broad even at room temperature, and split into two components on cooling (Table, Figure 6). Irradiation with Pyrex-filtered or (more rapidly) with unfiltered light gave rise to a poorly resolved spectrum clearly containing several new bands, and to an overall loss of intensity suggesting extensive destruction. The new bands disppeared on warming, and some starting material was regenerated. The complexity of the spectrum is consistent with the expected existence of isomers (as well as, we must presume, rotamers) of [Mn{$C_4(CF_3)_4S(C_6F_5)$}$(CO)_2$(mthf)]. Attempted studies of the parent, and of the related species [Mn{$C_4(CF_3)_4S(CF_3)$}$(CO)_3$], in hydrocarbon media failed because of poor solubility.

Conclusions.—Like the d^6 metal hexacarbonyls, the d^6 metal tricarbonyl half-sandwich complexes studied here showed photolytic CO loss, photoreversal, uptake of ethers or alcohols by the photolytic fragments, and (in our sealed systems) eventual displacement of these oxygen donors by CO. Photolysis was slower than for the hexacarbonyls, and there are many possible reasons for this. There was no evidence for aquation of fragments in hydrocarbon glasses, even though such aquation is important in hexacarbonyl chemistry.[1,5] Ether complexes may be formed and trapped in a metastable conformation that disappears rapidly on warming. The spectra of [Mn(cp)$(CO)_2$] and [Mn(mcp)$(CO)_2$] have been analysed in some detail assuming effective two-fold symmetry of the Mn$(CO)_2$ fragment. This assumption could be tested by ^{13}CO labelling which would require a degree of resolution obtainable in vapour-deposited

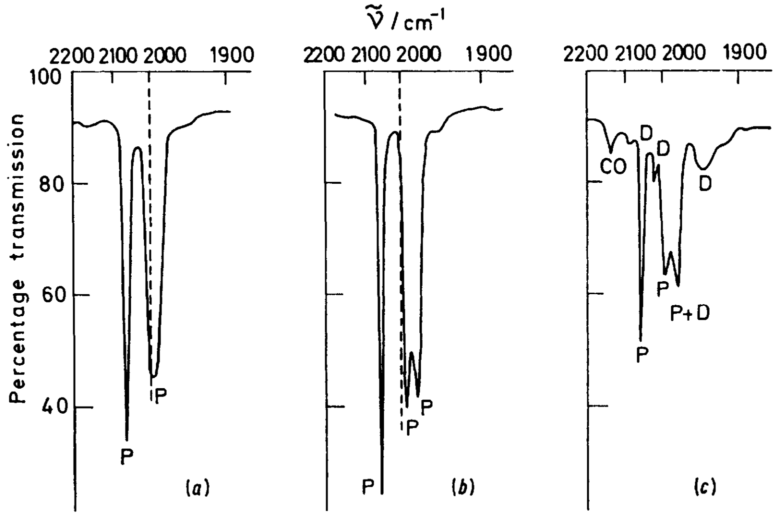

FIGURE 6 Spectra of $[Mn\{C_4(CF_3)_4S(C_6F_5)\}(CO)_3]$ in mthf: (*a*) at room temperature; (*b*) as (*a*), but at 77 K; (*c*) as (*b*), after irradiation (unfiltered) for 30 min. Peaks: P, parent; D, daughter

matrices (see, for example, refs. 7 and 10) but not in our solvent glasses.

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