Photochemistry of Tricarbonyl (η^5-cyclopentadienyl)(trifluoroacetyl)-molybdenum in a Variety of Frozen Gas Matrices at *ca.* 12 K: Infrared Spectroscopic Evidence for Carbon Monoxide Ejection and Difluorocarbene Formation by α-F Elimination

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Infrared spectroscopic evidence including ^{13}CO labelling is presented which shows that photolysis of $[Mo(\eta^5-C_5H_5)(CO)_3(COCF_3)]$ in frozen gas matrices (argon, methane, carbon monoxide, or nitrogen) at *ca.* 12 K affords stepwise ejection of CO to yield $[Mo(\eta^5-C_5H_5)(CO)_3(CF_3)]$ *via* the 16-electron species $[Mo(\eta^5-C_5H_5)(CO)_2(COCF_3)]$. Subsequent photolysis of $[Mo(\eta^5-C_5H_5)(CO)_3(CF_3)]$ produces further CO ejection reversibly to give the 16-electron species $[Mo(\eta^5-C_5H_5)(CO)_2(CF_3)]$, which in nitrogen matrices undergoes a reversible reaction to produce *cis*-$[Mo(\eta^5-C_5H_5)(CO)_2(CF_3)(N_2)]$, while in other matrices a novel fluorocarbene species, *trans*-$[Mo(\eta^5-C_5H_5)(CO)_2(CF_2)F]$, corresponding to α-F elimination is observed for the *first* time. The mechanisms of the various photolysis steps are discussed in relation to the growing chemistry of metal–halogeno-carbene complexes.

Early interest in the synthesis and properties of perfluoroalkyl transition metal species stemmed from their use as model compounds for the chemically and thermally less stable hydroalkyl transition metal species.[1,2] For example, $[Co(CO)_4(CF_3)]$ is a pale yellow liquid which can be prepared at room temperature and boils at 91 °C,[3] whilst $[Co(CO)_4(CH_3)]$ decomposes at *ca.* -20 °C.[4]

Much of the early research on transition-metal perfluoroalkyl species was directed towards explaining their increased stability in terms of differing bonding as compared to hydroalkyl species. Structural studies using *X*-ray crystallography[5,6] indicated that the M–C bond lengths were shorter for $M-C_F$ species than for $M-C_H$ species implying stronger bonding to the metal centre for the perfluoroalkyl species. The same studies also showed that the C_α fluorines, *i.e.* those on the carbon atom bonded directly to the metal centre, showed longer than expected C–F bond distances. These results were supported by an examination of the i.r. stretching frequencies of various C–F bonds. It was found that C–F vibrations of the C_α fluorines, were *ca.* 100 cm^{-1} lower than for species not directly bound to a transition metal centre, *e.g.* $M(COCF_3)$ fluoroacetyl species or CF_3I.[7–11] Corroborative evidence was also provided by ^{19}F n.m.r. studies,[8,12] which demonstrated a large shift to lower field for C_α fluorines relative to C_β and C_γ resonances, *i.e.* for fluorine nuclei on carbon atoms not directly bound to the metal centre.

Four different bonding arguments were put forward to explain the strengthening of the fluoroalkyl M–C bond and the weakening of the C–F bonds with CF_3 species being used as the model: (*i*) a contraction of the metal *d*-orbitals, brought about by the high electronegativity of the perfluoroalkyl ligand;[13] (*ii*) the involvement of the 'no-bond' structures such as $[M-CF_3] \longleftrightarrow [M{=}CF_2]^+ F^-$;[7] (*iii*) a lowering in energy of the C–F σ^* antibonding orbital to an extent whereby it could participate in $d\pi$ backbonding from the metal;[8–10,14] (*iv*) a perturbation of the orbitals on the α-carbon away from sp^3 hybridization due to the electronegativity of the fluorine substituents. The result of this change was proposed to be an increase in the *s*-character of the carbon σ-bonding orbital and a higher induced positive charge on the metal, both effects resulting in a stronger M–C bond.[13,15] The weakening of the C–F bonds was also explained on these grounds since the M–C σ-bonding orbital is antibonding in the C–F region.[15]

Of these bonding arrangements (*iii*) and (*iv*) were viewed as the most likely although a number of authors objected to proposal (*iii*).[6,11,15,16] This objection was based chiefly on the results of a CO force constant study of $[MnL(CO)_5]$, where L represented a large number of substituents including CH_3 and CF_3.[16] The results of this study indicated that CH_3 and CF_3 were both equally poor π-electron acceptors.

In addition to bonding arguments, another factor which must be taken into account when considering the additional stability of perfluoroalkyl species over hydroalkyl ones, is the lack of decomposition pathways involving atom transfer in the former case. The classic case for alkyls is β-hydride transfer to give M–H and an olefin,[17] but as yet no such processes have been reported for fluoroalkyl species.

Interest in the chemistry of trifluoromethyl species has recently undergone an upsurge with the discovery that they readily undergo halogen exchange to give other trihalomethyl complexes, [equation (1)][18,19] and more importantly are useful

$$[Mn(CO)_5(CF_3)] + BCl_3 \xrightarrow[\text{Pentane}]{-78\,^{\circ}C} [Mn(CO)_5(CCl_3)] + BF_3 \qquad (1)$$

precursors in the synthesis of dihalogenocarbene complexes.[19,20] The first dihalogenocarbene species, a dichlorocarbene complex of tetraphenylporphinatoiron(II) was synthesized by Brault *et al.* in 1977,[21] with the first difluorocarbene being reported not long afterwards.[22] Such compounds have come to play an important part in the understanding of transition metal carbene structure and reactivity,[19] a field which opened with the discovery of the first carbene by Schrock in 1975.[23] Interest in transition metal carbenes has been stimulated by the fact that they are synthetically useful in organic[24] and organometallic chemistry,[19] and have also long been proposed as reaction intermediates in a number of catalytic cycles.[25]

In order to investigate the chemistry of transition metal trifluoroacetyl and trifluoromethyl species more fully [Mo(η^5-

Table 1. Infrared band positions (cm^{-1})[a] for [Mo(η^5-C_5H_5)(CO)$_3$($COCF_3$)] (1) and its photoproducts[b] in the terminal CO stretching region in argon, methane, and carbon monoxide matrices at *ca.* 12 K

Complex	ν(CO)	Ar	CH_4	CO
(1) [Mo(η^5-C_5H_5)(CO)$_3$($COCF_3$)]	A'	2 049.0s	2 046.5s	2 048.5s
C_s	A'	1 979.5m	1 977.0m	1 977.5m
	A''	1 965.0vs	1 962.0s	1 963.5s
	A'	1 657.0w	1 653.0w	1 654.0w
(3) [Mo(η^5-C_5H_5)(CO)$_3$(CF_3)]	A'	2 058.0m	2 056.5m	2 057.5m
C_s	A'	1 980.0s	1 976.0s	1 979.0s
	A''	1 974.5 (sh)	1 970.5 (sh)	1 971.5 (sh)
(4) [Mo(η^5-C_5H_5)(CO)$_2$(CF_3)]	A'	1 997.5w	1 995.0w	1 995.5w
C_s	A''	1 915.0vw	1 910.0vw	1 912.5vw
(5) [Mo(η^5-C_5H_5)(=CF_2)(CO)$_2$F][c]	A'	2 063.5w	2 063.0w	2 064.0w
C_s	A''	2 000.5m	1 998.0m	2 000.0m

[a] Relative intensities: w = weak, m = medium, s = strong, v = very, and sh = shoulder. [b] Bands for the 16-electron CO-loss product [Mo(η^5-C_5H_5)(CO)$_2$($COCF_3$)] (2), *cf.* other analogous acyl species, were too weak to be observed. [c] *Trans* isomer.

Table 2. Infrared band positions (cm^{-1})[a] for [Mo(η^5-C_5H_5)(CO)$_3$($COCF_3$)] (1) and its photoproducts[b] in the CF stretching region in argon, methane, and carbon monoxide matrices at *ca.* 12 K

Complex	Ar	CH_4	CO
(1) [Mo(η^5-C_5H_5)(CO)$_3$($COCF_3$)]	1 240.5s	1 240.0s	1 239.5m
C_s	1 195.0s	1 194.0s	1 194.0s
	1 148.5s	1 147.0s	1 147.5s
(3) [Mo(η^5-C_5H_5)(CO)$_3$(CF_3)]	1 058.5s	1 057.0s	1 058.5s
C_s	1 036.0m	1 031.0m	1 034.0m
	1 024.0w	1 020.5w	1 023.5w
(4) [Mo(η^5-C_5H_5)(CO)$_2$(CF_3)]	1 067.5 (sh)	1 067.0 (sh)	1 068.0 (sh)
C_s	1 050.0w	1 047.5w	1 049.3w
	c	*c*	*c*
(5) [Mo(η^5-C_5H_5)(=CF_2)(CO)$_2$F][d]	1 182.0w	1 181.5w	1 181.0 (sh)
C_s	1 176.5m	1 176.0m	1 176.0m

[a] Relative intensities: w = weak, m = medium, s = strong, v = very, and sh = shoulder. [b] Bands for the 16-electron CO-loss product [Mo(η^5-C_5H_5)(CO)$_2$($COCF_3$)] (2), *cf.* other analogous acyl species, were too weak to be observed. [c] Band obscured by the bands of species (3). [d] *Trans* isomer; ν(Mo–F), a weak broad band at 693.0 (Ar), 690.5 (CH_4), and 692.0 cm^{-1} (CO).

C_5H_5)(CO)$_3$($COCF_3$)] was photolysed in a variety of low temperature matrices.

Experimental

Details of the 12 K cryostat and vacuum system, the spectrometers, the photolysis lamp and matrix gases have been described previously.[26]

[Mo(η^5-C_5H_5)(CO)$_3$($COCF_3$)], (1), was prepared according to the standard literature procedure[8] and used without further purification.

Matrices containing (1) were prepared by subliming the complex (25 °C for 300 min) and co-condensing it with a large excess of matrix gas, *i.e.* the slow spray-on technique.

Wavelength selective photolysis was achieved using broad band filters: filter A, $\lambda > 375$ nm, Corning glass filter no. 3060 (2 mm thick); and filter B, $\lambda > 460$ nm, Corning glass filter no. 3385 (2 mm thick).

Results

(*a*) *Photolysis of* [Mo(η^5-C_5H_5)(CO)$_3$($COCF_3$)], (1), *isolated at High Dilution in Argon, Methane, and Carbon Monoxide Matrices at* ca. 12 K *with Infrared Spectroscopic Monitoring in the Terminal* CO, CF, *and* MoF *Stretching Regions.*—Analogous results were obtained in all three matrix gases. The results in the argon matrix are presented in detail here and are representative of the photochemistry in all three cases. A comparison of the respective band positions is given in Tables 1 and 2.

The i.r. spectrum of [Mo(η^5-C_5H_5)(CO)$_3$($COCF_3$)] (1), in the CO stretching region is shown in Figure 1(*a*), whilst the CF stretching region is shown in Figure 2(*a*). Both regions show three bands as expected for a C_s symmetry with the acyl CO stretch appearing at 1 657 cm^{-1}. The solution u.v.–visible spectrum of (1) showed three absorptions (n-hexane) at 260 (ε = 10 500), 310 (shoulder, ε *ca.* 3 700), and 370 nm (shoulder, ε *ca.* 1 550 dm^3 mol^{-1} cm^{-1}). The 260 nm absorption maximum appeared in good agreement with previously reported spectra,[8] and has been assigned to a metal-to-ligand charge transfer (m.l.c.t.) involving the acyl group, whilst the weaker absorptions have been assigned to metal-centred transitions.

Initial photolysis (filter A, 30 min) at $\lambda > 375$ nm led to a decrease in the intensities of the i.r. bands attributed to complex (1) and the appearance of new bands at 2 139.5, 2 058.0, 1 980.0, 1 974.5, 1 058.5, 1 036.0, and 1 024.0 cm^{-1} [Figures 1(*b*) and 2(*b*)]. The band at 2 139.5 cm^{-1} was due to 'free CO' whilst the other bands correspond to those reported for [Mo(η^5-C_5H_5)(CO)$_3$(CF_3)], (3).[8] The three bands observed in the terminal CO-stretching region at 2 058.0, 1 980.0, and 1 974.5 cm^{-1} agreed well with the literature values reported for species (3) as a halogenocarbon oil mull at 2 054 and 1 976 cm^{-1}, except that the lower-wavenumber band was resolved into two bands in the low-temperature matrix, as expected for a molecule with C_s symmetry. The bands in the CF stretching region at 1 058.5, 1 036.0, and 1 024.0 cm^{-1} showed the expected 100 cm^{-1} shift for a trifluoromethyl group bound directly to a metal centre. A range of long-wavelength photolyses failed to produce any changes in the i.r. spectrum indicating that the initial reaction

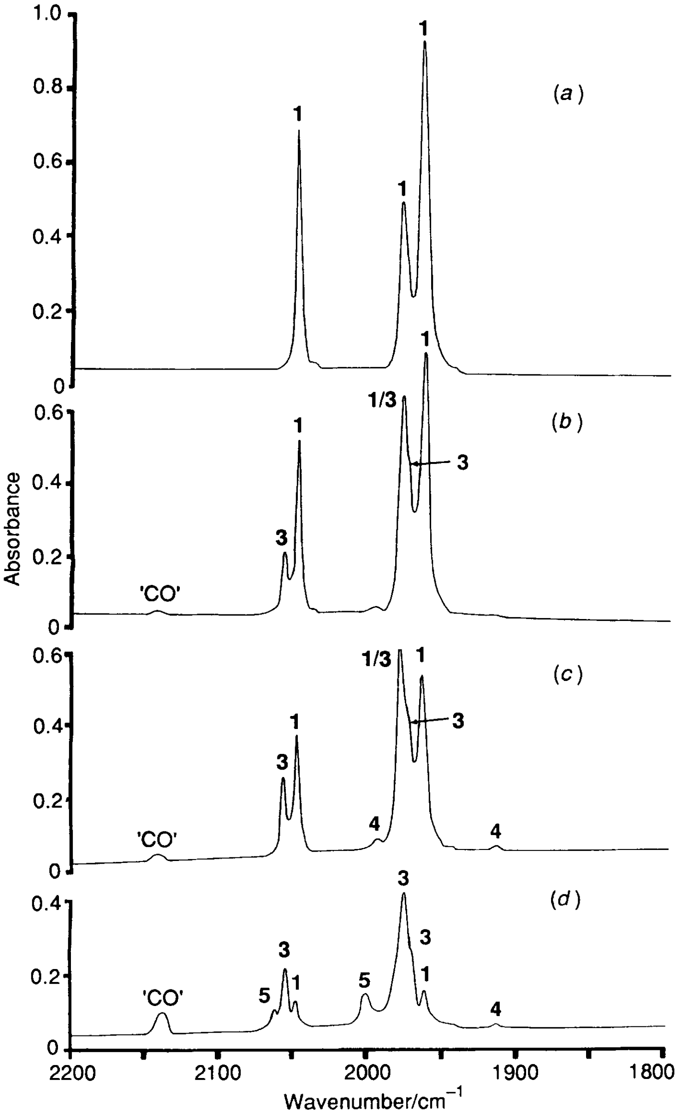

Figure 1. Infrared spectra (Nicolet 7199 Fourier-transform i.r. spectrometer; terminal CO stretching region) from an experiment with [Mo(η^5-C_5H_5)(CO)$_3$($COCF_3$)] isolated at high dilution in an argon matrix at *ca.* 12 K: (*a*) at start, (*b*) after 30 min, (*c*) after 60 min, and (*d*) after 240 min irradiation using filter A. Bands marked (**1**)—(**5**) correspond to species discussed in the text

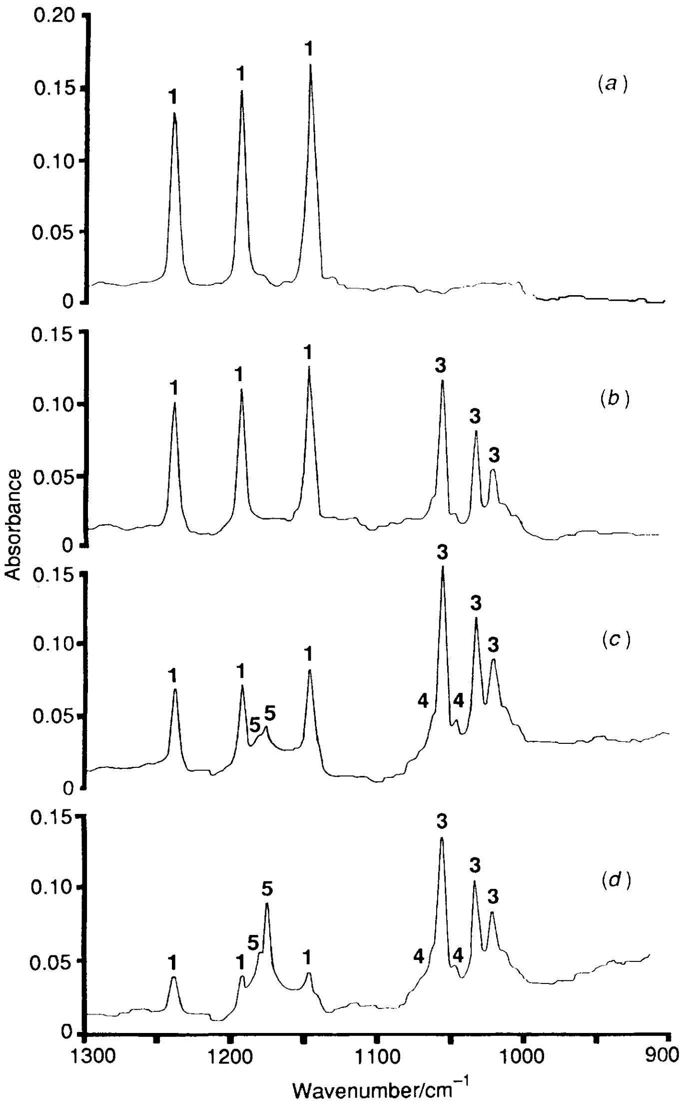

Figure 2. Infrared spectra (Nicolet 7199 Fourier-transform i.r. spectrometer; terminal CF stretching region) from an experiment with [Mo(η^5-C_5H_5)(CO)$_3$($COCF_3$)] isolated at high dilution in an argon matrix at *ca.* 12 K: (*a*) at start, (*b*) after 30 min, (*c*) after 60 min, and (*d*) after 240 min irradiation using filter A. Bands marked (**1**)—(**5**) correspond to species discussed in the text

step was photochemically irreversible. No spectroscopic evidence was observed for the only reasonable intermediate between (**1**) and (**3**), the 16-electron carbonyl-loss species [Mo(η^5-C_5H_5)(CO)$_2$($COCF_3$)], (**2**). Such intermediates have, however, been observed in low-temperature matrices previously, for example, [Mn(CO)$_4$($COCH_3$)] which was detected upon photolysis of [Mn(CO)$_5$($COCH_3$)] in mechanistic ^{13}CO-labelling studies.[27] The failure to detect any i.r. bands due to the initial CO-loss species implied that CO extrusion from (**2**) was a rapid process even at *ca.* 12 K, and hence the concentration of (**2**) was insufficient for its band positions to be successfully located.

Further photolysis (filter A, total 60 min), resulted in the continuing increase in the intensities of the bands associated with (**3**) and 'free CO,' and in addition a number of new weak bands at 1 997.5, 1 915.0, 1 067.5, and 1 050.0 cm^{-1} * appeared [Figures 1(*c*) and 2(*c*)]. At this stage a period of long-wavelength photolysis (filter B, 30 min), resulted in the virtual disappearance of the new weak bands, a decrease in the intensity of the band due to 'free CO' and an increase in the intensities of the bands due to (**3**). The rate of this reversal was enhanced in a pure carbon monoxide matrix. The bands due to (**1**) were observed not to change in intensity and hence the weak new bands were assigned to the CO-ejection product [Mo(η^5-C_5H_5)(CO)$_2$(CF_3)], (**4**) which was formed reversibly from (**3**).

Continued photolysis with filter A (total 240 min) resulted in the virtual disappearance of the bands due to (**1**), a slight decrease in the bands due to (**3**) and (**4**) and the appearance of five new bands at 2 063.5, 2 000.5, 1 182.0, 1 176.5, and 693.0 cm^{-1}. The new bands all grew at the same rate and maintained the same relative intensities, which led to them being assigned to one photoproduct, (**5**). A series of subtractions showed that the appearance of (**5**) was accompanied by an increase in the band due to 'free CO' at 2 139.5 cm^{-1}, and a decrease in the intensities of the bands due to (**3**). The dicarbonyl species (**4**) was

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* One C–F band was obscured by the bands of (3).

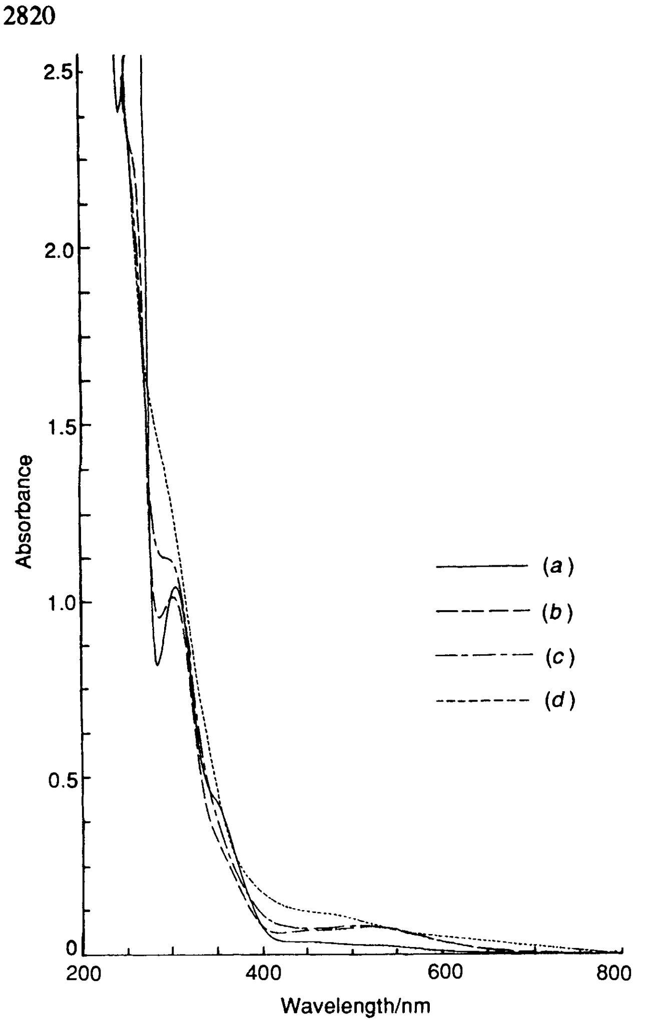


Figure 3. U.v.–visible spectra (Perkin-Elmer Lambda 7) from an experiment with $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(COCF_3)]$ isolated at high dilution in an argon matrix at *ca.* 12 K: (*a*) at start, (*b*) after 30 min, (*c*) after 60 min, and (*d*) after 240 min irradiation using filter A

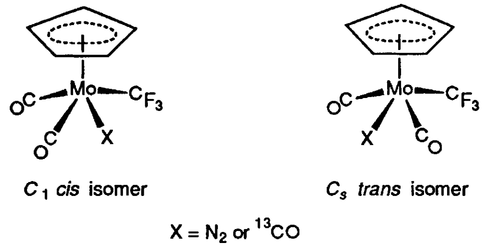
confirmed as an intermediate between species (**3**) and (**5**) on the basis of reversal experiments performed at this stage. As before, a period of long-wavelength photolysis (filter B, 30 min) led to the virtual disappearance of the bands due to (**4**) and reversal to (**3**) by CO uptake. On subsequent forward photolysis with filter A, however, no increase was observed in the intensities of the bands due to (**5**) until a significant quantity of (**4**) had once again been formed (*ca.* 45 min).

On the basis of its formation from (**4**) and its i.r. band positions, the final photoproduct (**5**) was assigned to the difluorocarbene species $[Mo(\eta^5\text{-}C_5H_5)({=}CF_2)(CO)_2F]$, produced by fluorine migration from the CF_3 group to the metal centre to give an 18-electron species. The relative intensities of the terminal CO stretching vibrations, *i.e.* $I_{\text{antisym.}}/I_{\text{sym.}} > 1$ led to this species being assigned as the C_s *trans*-dicarbonyl isomer. Similar cationic molybdenum difluorocarbene species have been reported, *e.g.* $[Mo(\eta^5\text{-}C_5H_5)({=}CF_2)(CO)_3]SbF_6$,[22] but have not been isolated in a pure form. Infrared data for other neutral transition metal difluorocarbene species, indicates that the carbonyl bands at 2 063.5 and 2 000.5 cm^{-1} and the C–F stretching bands at 1 182.0 and 1 176.5 were in the expected region for these types of compounds.[19] The band at 693 cm^{-1} which was weak and only appeared clearly in subtractions was *ca.* 30 cm^{-1} lower than the 'ring modes' and was assigned to the Mo–F stretching mode by comparison with the band positions for other transition-metal carbonyl fluoride species.[28]

Analogous results were obtained in a preliminary study starting from $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CF_3)]$ but an inferior spectrometer was used.[29]

No products were observed during any stage of the photolysis resulting from the ejection of $CF_3^{\bullet}$ which has been isolated in low-temperature matrices previously.[30,31] This species has reported band positions in an argon matrix at 1 249—1 251vvs, 1 087ms, and 703 mw cm^{-1}.

(*b*) *Photolysis of* $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(COCF_3)]$, (**1**), *isolated at High Dilution in Nitrogen and* ^{13}CO*-doped Methane Matrices at* ca. 12 K *as monitored by Infrared Spectroscopy in the* CO, CF, *and* MoF *Stretching Regions.*—Photolysis of complex (**1**) in a pure nitrogen matrix at *ca.* 12 K using filter A led to identical photochemistry to that seen in other matrices, with only small differences in the band positions due to differing matrix solvent effects and packing (Table 3). However, an additional species was produced upon long-wavelength photolysis of (**4**) (filter B). This new species showed three weak bands at 2 260.0, 2 018.0, and 1 938.0 cm^{-1}, and was assigned to the dinitrogen substituted complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CF_3)(N_2)]$, (**6**). No bands were observed in the C–F or Mo–F stretching regions for this species presumably because they were too weak to be detected, or were obscured by the bands of the other species present. Only one set of new bands was observed, although there were two possible isomers for (**6**), with either C_s *trans*-or C_1 *cis*-carbonyl groups.



The two weak terminal carbonyl bands were of approximately equal intensities and hence appeared to be due to the statistically favoured *cis* geometry. Concurrent periods of forward photolysis (filter A) followed by reversal (filter B) failed to produce any significant increase in the intensities of the bands due to (**6**) since the periods of forward photolysis resulted in photoreaction of (**6**) presumably to regenerate (**4**).

Photolysis of (**1**) in a 5% ^{13}CO-doped methane matrix again followed the familiar pattern of reaction established in other matrices. As with the situation in pure nitrogen matrices, the only differences were in the photochemistry of species (**4**). In the ^{13}CO-doped matrix a period of long-wavelength photolysis (filter B, 30 min) led to the regeneration of (**3**) and to two new weak bands in the terminal CO stretching region at 2 041.0 and 1 940.5 cm^{-1}. These new bands were assigned to the *mono*-^{13}CO-substituted isomer of (**3**), $[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)(CF_3)]$. A comparison of the band positions for this species with those reported by Rest and co-workers for $[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ (Table 4)[29,32] and its ^{13}CO-substituted isomers showed good agreement. As with the dinitrogen-substituted analogue above, two isomers of the *mono*-^{13}CO-substituted isomer were possible (see above), but only one was observed, from the force-field fitting comparison, assigned to the statistically favoured *cis*-^{12}CO geometry with the bands due to the *trans*-^{12}CO isomer being too weak to be observed. The small quantity of species present in this study meant that repeated periods of forward photolysis (filter A) followed by revesal (filter B) led only eventually to photochemical decomposition of all the species ($t > 360$ min). Photochemical reversal of (**4**) to give *mono*-^{13}CO-substituted (**3**) in a 5% ^{13}CO-doped methane matrix was,

Table 3. Infrared band positions (cm^{-1})[a] for [Mo(η^5-C_5H_5)(CO)$_3$(COCF$_3$)] (**1**) and its photoproducts[b] in the terminal CO and CF stretching regions in a pure nitrogen matrix at *ca.* 12 K

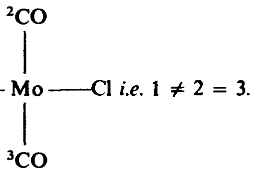
Complex		ν(CO)	ν(CF)
(**1**) [Mo(η^5-C_5H_5)(CO)$_3$(COCF$_3$)]	*A′*	2 049.0m	1 241.0m
C$_s$	*A′*	1 978.0m	1 194.5s
	A″	1 963.5	1 145.0s
	A′	1 656.5w	
(**3**) [Mo(η^5-C_5H_5)(CO)$_3$(CF$_3$)]	*A′*	2 060.0m	1 057.0m
C$_s$	*A′*	1 980.5s	1 032.5m
	A″	1 974.0 (sh)	1 021.0w
(**4**) [Mo(η^5-C_5H_5)(CO)$_2$(CF$_3$)]	*A′*	1 997.0w	1 068.0 (sh)
C$_s$	*A″*	1 914.5vw	1 050.5w
			c
(**5**) [Mo(η^5-C_5H_5)(=CF$_2$)(CO)$_2$F][d]	*A′*	2 066.0w	1 183.0w
C$_s$	*A″*	2 000.0m	1 176.5m
			e
(**6**) [Mo(η^5-C_5H_5)(CO)$_2$(CF$_3$)(N$_2$)][f]	*A*	2 018.0vw	*g*
C$_1$	*A*	1 938.0vw	*g*

[a] Relative intensities: w = weak, m = medium, s = strong, v = very, and sh = shoulder. [b] Bands for the 16-electron CO-loss product [Mo(η^5-C_5H_5)(CO)$_2$(COCF$_3$)] (**2**), *cf.* other analogous acyl species, were too weak to be observed. [c] Band obscured by the bands of species (**3**). [d] *Trans* isomer. [e] ν(Mo–F) too weak to be observed. [f] *Cis* isomer observed; ν(NN) at 2 260.0 cm^{-1}. [g] Too weak to be observed.

Table 4. Observed and calculated[a] wavenumbers (cm^{-1}) of terminal infrared CO stretching bands produced following photolysis of [Mo(η^5-C_5H_5)(CO)$_3$Cl] in 5% ^{13}CO-doped methane matrices at *ca.* 12 K, compared to those produced upon photolysis of [Mo(η^5-C_5H_5)(CO)$_3$(CF$_3$)] under identical conditions

Compound	ν(CO)	Observed	Calculated
[Mo(η^5-C_5H_5)(^{12}CO)$_3$Cl][b]	*A′*	2 058.0	2 057.3
C$_s$	*A′*	1 983.7	1 983.2
	A″	1 969.0	1 968.5
[Mo(η^5-C_5H_5)(^{12}CO)$_2$(^{13}CO)Cl][b]	*A′*	2 053.5	2 052.2
Trans C$_s$[c]	*A″*	1 969.2	1 968.5
	A′	*d*	1 944.2
Cis C$_1$[e]	*A*	2 044.1	2 043.6
	A	1 981.4	1 981.6
	A	1 938.7	1 939.4
[Mo(η^5-C_5H_5)(^{12}CO)$_3$(CF$_3$)]	*A′*	2 059.5	
C$_s$	*A′*	1 980.0	
	A″	1 973.0	
[Mo(η^5-C_5H_5)(^{12}CO)$_2$(^{13}CO)(CF$_3$)]	*A*	2 041.0	
Cis C$_1$[e]	*A*	*f*	
	A	1 940.5	

[a] Refined energy-factored force constants for [Mo(η^5-C_5H_5)(CO)$_3$Cl]: $K_1 = 1\,610.4$, $K_2 = 1\,627.2$, $k_{12} = 32.7$, and $k_{23} = 61.7$ N m^{-1} as defined by the numbering:



$$\begin{array}{c} {}^{2}\mathrm{CO} \\ | \\ {}^{1}\mathrm{CO}\text{——}\mathrm{Mo}\text{——}\mathrm{Cl}\ \ \textit{i.e.}\ 1 \neq 2 = 3. \\ | \\ {}^{3}\mathrm{CO} \end{array}$$

[b] Observed and calculated band positions from ref. 32. [c] ^{13}CO in position 1. [d] Band obscured. [e] ^{13}CO in position 2. [f] Bands obscured by the bands of [Mo(η^5-C_5H_5)(^{12}CO)$_3$(CF$_3$)].

however, a useful confirmation of the assignment of (**4**) as the CO-ejection product, [Mo(η^5-C_5H_5)(CO)$_2$(CF$_3$)].

(*c*) *U.V.–Visible Spectra obtained Following the Photolysis of* [Mo(η^5-C_5H_5)(CO)$_3$(COCF$_3$)] *isolated at High Dilution in Argon, Methane, Carbon monoxide, and Nitrogen Matrices at* ca. 12 K.—The u.v.–visible spectrum of complex (**1**), isolated at high dilution in an argon matrix is shown in Figure 3(*a*). The strong m.l.c.t. absorption involving the acyl moiety appeared at 258 nm, whilst the two bands which appeared as shoulders in the solution spectrum were observed in the matrix under conditions of greater resolution at 304 and 360 nm.

Initial photolysis (filter A, totals 30 and 60 min) led to a situation where the 258 nm band decreased in intensity, as did the absorption at 360 nm, and a number of new absorptions appeared [Figures 3(*b*) and (*c*)]. These new absorptions were centred at *ca.* 295 and 510 nm and from an examination of the i.r. spectrum at this stage in the photolysis, they were assigned to species (**3**). The band at *ca.* 295 nm has been reported previously for (**3**) in cyclohexane solution at 308 nm,[8] whilst the 510 band was presumably too weak to be observed under these conditions. At this stage a period of long-wavelength photolysis (filter B, 30 min) resulting in (**4**) ——→ (**3**) reversal, led to a slight decrease in the absorbance in the 480 nm region. This indicated that (**4**) showed a weak absorption in this region and correlated well with the observation that it was photolysis in the visible region which produced photochemical reversal.

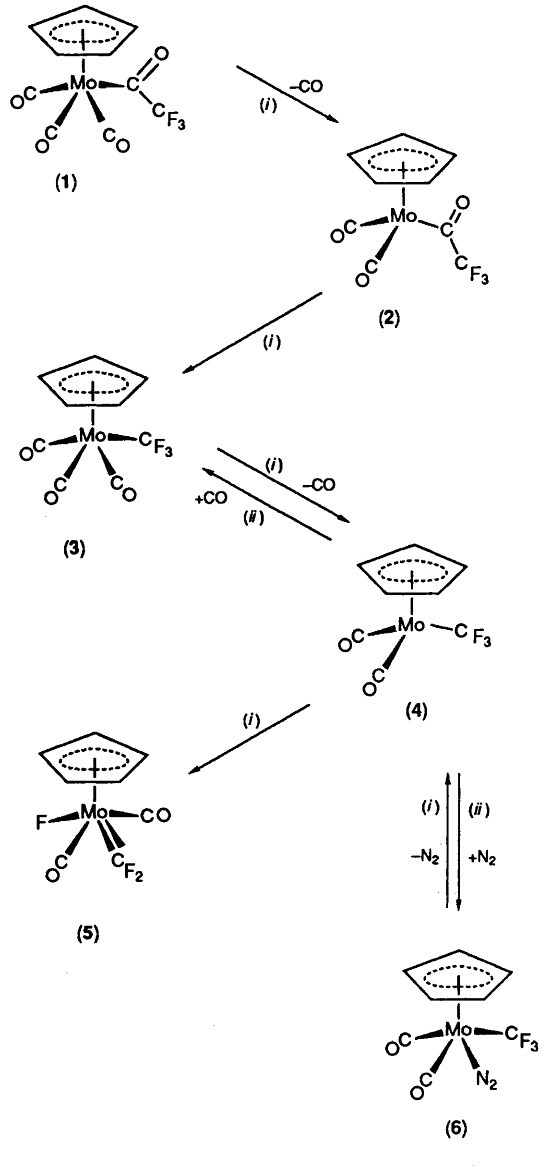
Continued photolysis (filter A, total 240 min) resulted in a featureless spectrum, which tailed strongly into the visible region [Figure 3(*d*)] but with no absorptions which were clearly attributable to the new species, (**5**).

Discussion

The photoreactions of [Mo(η^5-C_5H_5)(CO)$_3$(COCF$_3$)] and its photoproducts isolated at high dilution in a variety of matrices are summarised in the Scheme.

As with the manganese acyl species [Mn(CO)$_5$(COCH$_3$)],[27] the photochemistry of complex (**1**) was initiated by ejection of a terminal CO, followed by migration of the CF$_3$ group to give the stable trifluoromethyl species (**3**). Such carbonyl ejection/alkyl migration reactions have been well documented,[27,33] but it was interesting to note in this case that the reaction was extremely rapid, since no bands for the intermediate species (**2**) were observed. The rapidity of the reaction is most probably due to the thermodynamic stability of the product (**3**).

The matrix photoreactions of (**3**) can be likened very much to those of the analogous chromium methyl complex [Cr(η^5-C_5H_5)(CO)$_3$(CH$_3$)]. Photochemical matrix studies on the chromium species yielded evidence for an α-elimination reaction,[34] leading to a methylene hydride species, [Cr(η^5-C_5H_5)(=CH$_2$)(CO)$_2$H]. This species was assigned a *trans*-



Scheme. (*i*) *h*v, filter A; (*ii*) *h*v, filter B

dicarbonyl geometry on the basis of a force-field fitting study, and on the relative intensities of the two carbonyl stretching bands, *i.e.* $I_{\text{antisym.}}/I_{\text{sym.}} > 1$. A similar band intensity pattern was observed for species (**5**) [Figure 3(*d*)] and hence this species has also been formulated as the *trans*-dicarbonyl isomer (Scheme), rather than the expected *cis* isomer. The predominance of the *trans* isomer was presumably due to rapid photolytic rearrangement of the *cis* isomer as it formed in the α-fluorine elimination reaction. Rapid intramolecular isomerization reactions have been observed to take place for other transition-metal carbonyl species without accompanying CO ejection, both in low-temperature media, *e.g.* $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{H}_2]$,[35] and in solution, *e.g.* $[\text{Mo}(\text{CO})_4\{\text{P}(\text{C}_4\text{H}_9)_3\}_2]$.[36]

The observation of an α-fluorine elimination reaction upon prolonged photolysis, was illustrative of the relatively weak C–F bonds of the C_α carbon atom when directly bound to a transition metal centre, as opposed to other perfluoroalkyl environments. The fact that for the 16-electron species (**4**) the C–F stretching modes were observed to shift upwards by *ca.* 10 cm^{-1} also has relevance to the mode of bonding in perfluoromethyl species. Such an upward shift was in direct contrast to that expected for a bonding arrangement where the CF_3 group was involved in *d*π backbonding from the metal centre, one of the bonding arrangements proposed earlier [mode (*iii*)]. Under these circumstances a reduction in the number of ligands would have been expected to lead to a reduction, not an increase in the C–F stretching frequencies. An upward shift was, however, in line with the bonding arguments based purely on a change in hybridization of the carbon atom, and the electron withdrawal due to the electronegativity of the CF_3 group [mode (*iv*)]. This was because electron withdrawal would be expected to be reduced in the 16-electron species (**4**).

Conclusions

Difluorocarbene complexes such as the final photoproduct reported here, (**5**), have been formed previously by fluoride abstraction from trifluoromethyl complexes. This study, however, represents the ***first*** example of such species being formed by an α-elimination reaction. As such the study again illustrates the usefulness of the matrix-isolation technique in elucidating new reaction mechanisms, especially in cases where the products are far too unstable to be isolated at ambient temperatures. It seems unlikely that the α–F elimination route could be used synthetically for the production of difluorocarbene species at ambient temperatures since similar routes using fluoride abstraction have led to products that were not isolable. Such routes may well be viable at lower temperatures, however, or at least warrant the investigation of this possibility.

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