Photochemistry of Some (η^5-Cyclopentadienyl)carbonylchloro Complexes of Molybdenum, Tungsten, Iron, and Ruthenium in Frozen Gas Matrices at *ca.* 12 K and in Poly(vinyl chloride) Films at *ca.* 12—298 K†

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Infrared spectroscopic evidence including ^{13}CO substitution and energy-factored force-field fitting is presented to show that photolysis of $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ complexes (M = Mo or W) in argon, methane, nitrogen, carbon monoxide, and 5% C_2H_4–CH_4 matrices at *ca.* 12 K yields ejection of CO and formation of the 16-electron species $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ as the primary process. This process is reversible. In nitrogen and 5% C_2H_4–CH_4 matrices the $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ species react with N_2 and C_2H_4 to give *cis*-$[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)Cl]$ and *cis*-$[M(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)Cl]$ (M = Mo or W) respectively. In carbon monoxide matrices the ejection of CO is suppressed and the photolysis products are proposed to be the species $[M(\eta^5\text{-}C_5H_5)(CO)_3]^+Cl^-$ (M = Mo or W), indicative of metal–chlorine bond heterolysis. Irradiation of $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ complexes (M = Fe or Ru) in methane, nitrogen, and carbon monoxide matrices and in poly(vinyl chloride) films at *ca.* 12 K produced only the 16-electron species $[M(\eta^5\text{-}C_5H_5)(CO)Cl]$ and CO indicating that dissociation, rather than cleavage of the metal–chlorine bond, is the principal reaction pathway. The primary process can be reversed thermally in the polymer films by virtue of their wider working temperature range (*ca.* 12—298 K). For the iron complex reversal occurred by *ca.* 60 K, whereas the ruthenium complex needed a higher temperature of annealing (*ca.* 80 K). The results of the low-temperature studies are discussed in relation to the thermal and photochemical reactions of complexes of Mo, W, Fe, and Ru in solution at ambient temperatures.

Previous investigations have demonstrated that the $[M(\eta^5\text{-}C_5H_5)(CO)_3X]$ complexes (M = Mo or W; X = Cl, Br, or I) react with a variety of ligands in solution to yield derivatives of two types.

(*i*) Reactions in which CO only is replaced photochemically by a variety of two-electron donor ligands [equation (1)].

$$[M(\eta^5\text{-}C_5H_5)(CO)_3X] + L \xrightarrow{h\nu} [M(\eta^5\text{-}C_5H_5)(CO)_2(L)X] + CO \quad (1)$$

Examples of such monosubstituted products are $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(L)Cl]$ (L = PPh_3, $AsPh_3$, or $SbPh_3$) and $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(L)I]$ (L = PEt_3, PPh_3, $AsPh_3$, $AsMePh_2$, or $SbPh_3$).[1] Substituted derivatives of $[M(\eta^5\text{-}C_5H_5)(CO)_3X]$ have also been prepared by thermal reactions with two-electron donor ligands.[2,3] Disubstituted complexes of general formula $[M(\eta^5\text{-}C_5H_5)(CO)L_2X]$ have been obtained by prolonged irradiation of $[M(\eta^5\text{-}C_5H_5)(CO)_3X]$ with excess of ligand,[1] which suggests that the monosubstituted complexes are themselves susceptible to photosubstitution [equation (2)]. Similarly

$$[M(\eta^5\text{-}C_5H_5)(CO)_2(L)X] + L \xrightarrow{h\nu} [M(\eta^5\text{-}C_5H_5)(CO)L_2X] + CO \quad (2)$$

$[M(\eta^5\text{-}C_5H_5)(CO)_3X]$ complexes are reported to react photochemically with the bidentate ligands $Me_2P(CH_2)_2PMe_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$, ejecting two CO ligands and forming $[M(\eta^5\text{-}C_5H_5)(CO)(L\text{–}L)X]$ complexes.[4]

(*ii*) Reactions in which the halide ion is displaced to yield ionic products, *e.g.* $[M(\eta^5\text{-}C_5H_5)(CO)_3]^+X^-$ [equation (3)].

$$[M(\eta^5\text{-}C_5H_5)(CO)_3X] \xrightarrow{h\nu} [M(\eta^5\text{-}C_5H_5)(CO)_3]^+ + X^- \quad (3)$$

For example, $[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ reacts with ammonia or hydrazine to afford the ionic derivatives $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(am)]^+X^-$ (am = NH_3 or N_2H_4).[5] The tungsten complex $[W(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ reacts with triphenyl- and triethylphosphine to afford $[W(\eta^5\text{-}C_5H_5)(CO)_2(PR_3)_2]^+Cl^-$ complexes (R = Ph or Et), where ionisation and CO substitution has occurred.[6] Irradiation of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ also promotes the formation of the ionic substitution compounds $[Mo(\eta^5\text{-}C_5H_5)(CO)_2L_2]^+Cl^-$ where [L = PEt_3, PPh_3, or L_2 = dppe ($Ph_2PCH_2CH_2PPh_2$)].[7]

The primary photochemical process for $[Fe(\eta^5\text{-}C_5H_5)(CO)_2X]$ complexes (X = Cl, Br, or I) is similarly claimed to be dissociative loss or exchange of a carbon monoxide ligand.[8] For example, irradiation of the bromo- or iodo-derivatives in the presence of PPh_3 leads to the formation of the covalent complexes $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)X]$ (X = Br or I)[8] [equation (4)]. Photolysis of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2X]$ (X = Cl, Br, or I) in

$$[Fe(\eta^5\text{-}C_5H_5)(CO)_2X] + PPh_3 \xrightarrow[-CO]{h\nu\,(\lambda\,\approx\,300\text{ nm})} [Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)X] \quad (4)$$

benzene solutions saturated with ^{13}CO yields $[Fe(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)X]$. Other authors, however, have shown that irradiation of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ results in the formation of $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$[9] together with Fe^{2+}, Cl^-, and ferrocene,[10] depending upon the experimental conditions. It should be noted that $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ reacts rapidly with PPh_3 in the dark at room temperature to produce a mixture of the covalent $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Cl]$ and ionic $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)]^+Cl^-$ derivatives, precluding a detailed study of the photochemical substitution reactions of this complex.[8]

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† *Non-S.I. unit employed:* Torr ≈ 133 Pa.

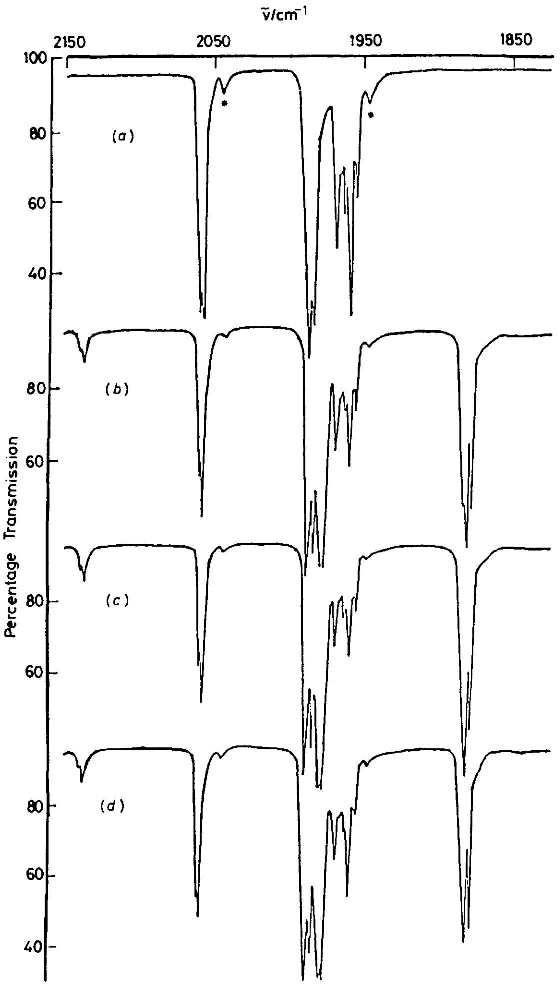


Figure 1. Infrared spectra (Grubb Parsons Spectromajor) from an experiment with [Mo(η^5-C_5H_5)(CO)$_3$Cl] isolated at high dilution in an argon matrix at 12 K: (*a*) after deposition, (*b*) after 10 min of photolysis ($\lambda > 410$ nm), (*c*) after 5 min more of photolysis using the same radiation, and (*d*) after 2 min of annealing. Bands marked * are due to [Mo(η^5-C_5H_5)(^{12}CO)$_2$(^{13}CO)Cl] in natural abundance

This paper describes an investigation of the photochemistry of [M(η^5-C_5H_5)(CO)$_3$Cl] (M = Mo or W) and of [M′(η^5-C_5H_5)(CO)$_2$Cl] (M′ = Fe or Ru) complexes in low-temperature media to determine whether dissociation of CO is the dominant photoprocess or whether cleavage of the M–Cl bond occurs as a major photoprocess in low-temperature media at 12 K. The results are related to the mechanisms of thermal and photochemical solution reactions, *cf.* the proposal that CO photosubstitution reactions of [Fe(η^5-C_5H_5)(CO)$_2$Cl] involve the 16-electron species [Fe(η^5-C_5H_5)(CO)Cl].[8] The application of polymer film media has enabled the thermal reactivity of unstable species to be monitored over wider temperature ranges than those covered in previous studies using frozen gas matrices or paraffin waxes.

Experimental

The low-temperature equipment, spectrometers, photolysis lamp, matrix gases, isotopically labelled CO, casting of polymer films, and details of spraying on matrices or mounting films have been described previously.[11] Compounds for this study were made from [Fe$_2$(η^5-C_5H_5)$_2$(CO)$_4$] and [Mo$_2$(η^5-C_5H_5)$_2$(CO)$_6$] or were gifts from Professor M. Herberhold and Dr. H. G. Alt {[W(η^5-C_5H_5)(CO)$_3$Cl] and [Ru(η^5-C_5H_5)(CO)$_2$Cl]}. Enrichment with ^{13}CO was achieved by photochemical exchange in solution.[12]

Gas matrices were prepared by the slow spray-on technique[13] with samples vaporising at constant temperatures and being condensed with excess of matrix gas: [Mo(η^5-C_5H_5)(CO)$_3$Cl] (50 °C), [W(η^5-C_5H_5)(CO)$_3$Cl] (50 °C), [Fe(η^5-C_5H_5)(CO)$_2$Cl] (40 °C), and [Ru(η^5-C_5H_5)(CO)$_2$Cl] (50 °C).

Wavelength-selective photolysis was achieved using the following combinations of absorbing materials: filter A, $\lambda > 370$ nm, Corning colour glass CS 0-51 (3 mm thick); filter B, $\lambda > 410$ nm, Corning colour glass CS 3-74 (3 mm thick); filter C, $320 < \lambda < 390$ nm, Corning colour glass CS 7-39 (3 mm thick); filter D, $290 < \lambda < 370$ nm, quartz gas cell (pathlength 300 mm) containing Br_2 gas (300 Torr) + Pyrex disc (3 mm thick).

Results

(*i*) *Photolysis of* [M(η^5-C_5H_5)(CO)$_3$Cl] *Complexes* (M = Mo *or* W) *in Argon and Methane Matrices at* ca. 12 K.—The i.r. spectra of [Mo(η^5-C_5H_5)(CO)$_3$Cl] isolated at high dilution in argon and methane matrices (*ca.* 1:2 000—1:5 000) at 12 K were very similar. The spectrum in Figure 1(*a*) shows that the [Mo(CO)$_3$Cl] fragment has a C_s symmetry, with three i.r. bands in the terminal CO stretching region at 2 062.5 (A'), 1 989.4 (A'), and (1 973.4, 1 964.6) (A'') cm^{-1} (Table 1). Irradiation of [Mo(η^5-C_5H_5)(CO)$_3$Cl] in argon matrices using visible light ($\lambda > 410$ nm) produced free CO (*ca.* 2 138 cm^{-1}) and two new bands at 1 981.2 and 1 883.5 cm^{-1} [Figure 1(*b*) and (*c*)]. The production of these two bands was accompanied by a decrease in the bands of the parent and an increase in the band due to free CO. Annealing the matrix for 2 min caused a decrease in the intensities of the new photoproduct bands at 1 981.2 and 1 883.5 cm^{-1} with the regeneration of bands due to the starting material, [Mo(η^5-C_5H_5)(CO)$_3$Cl] [Figure 1(*d*)]. The relative intensities of the new terminal CO stretching bands remained constant under a variety of photolysis conditions (time and wavelength of radiation), indicating that the bands arose from a single product species. This species may be assigned as [Mo(η^5-C_5H_5)(CO)$_2$Cl] on the basis that the elimination of carbon monoxide from [Mo(η^5-C_5H_5)(CO)$_3$Cl] could be reversed by annealing the matrix to *ca.* 35 K. Similar results were obtained for the methane matrices.

The assignment of the new bands to the 16-electron species [Mo(η^5-C_5H_5)(CO)$_2$Cl] was confirmed by an experiment in which [Mo(η^5-C_5H_5)(CO)$_3$Cl] was photolysed in a 5% ^{13}CO–CH$_4$ matrix. Initially rapid exchange occurred to produce bands due to the range of species [Mo(η^5-C_5H_5)(^{12}CO)$_{3-n}$(^{13}CO)$_n$Cl] (n = 0—3) but then further bands appeared assigned to the ^{13}CO-substituted 16-electron species [Mo(η^5-C_5H_5)(^{12}CO)$_m$(^{13}CO)$_{2-m}$Cl] (m = 0—2). Satisfactory correspondence between observed and calculated band positions was found for both [Mo(η^5-C_5H_5)(^{12}CO)$_{3-n}$(^{13}CO)$_n$Cl] (n = 0—3) and [Mo(η^5-C_5H_5)(^{12}CO)$_{2-m}$(^{13}CO)$_m$Cl] (m = 0—2) species using the energy-factored force-field approach[14] (Table 2).

Photolysis of [W(η^5-C_5H_5)(CO)$_3$Cl] in methane matrices similarly led to the formation of a CO-loss product, *i.e.* [W(η^5-C_5H_5)(CO)$_2$Cl] (Table 1) though the photoreaction proceeded more slowly than for Mo.

(*ii*) *Photolysis of* [M(η^5-C_5H_5)(CO)$_3$Cl] *Complexes* (M = Mo *or* W) *in Nitrogen Matrices at* ca. 12 K.—Infrared spectra from an experiment with [Mo(η^5-C_5H_5)(CO)$_3$Cl] isolated at high dilution in a nitrogen matrix at 12 K are shown in Figure 2. Before photolysis the spectrum shows three strong bands in the terminal CO stretching region at 2 058.0 (A'), 1 983.7 (A'), and 1 969 (A'') cm^{-1}.

Table 1. Infrared band positions (cm^{-1}) observed in the CO stretching region for [M(η^5-C_5H_5)(CO)$_3$Cl] (M = Mo or W) and for [M(η^5-C_5H_5)(CO)$_2$Cl] (M = Fe or Ru) complexes and their photoproducts in various gas matrices and pvc films at *ca.* 12 K

Complex	CH_4	Ar	CO	N_2	5% C_2H_4–CH_4	pvc
[Mo(η^5-C_5H_5)(CO)$_3$Cl]	2 057.2	2 062.5	2 058.0	2 058.0	2.056.3	—
	1 983.0	1 989.4	1 982.7	1 983.7	1 982.7	—
	1 959.2	1 973.4 1 964.6 [a]	1 963.5	1 969.0	1 969.3	—
[W(η^5-C_5H_5)(CO)$_3$Cl]	2 050.7	—	2 052.0	2 052.3	2 049.3	
	1 967.0	—	1 966.0	1 968.3	1 966.1	—
	1 950.8	—	1 951.2	1 955.2	1 948.4	—
[Mo(η^5-C_5H_5)(CO)$_2$Cl]	1 976.7	1 981.2	*b*	1 980.3	1 979.2	—
	1 880.3	1 883.5	—	1 883.4	1 881.5	—
[W(η^5-C_5H_5)(CO)$_2$Cl]	1 963.0	—	1 964.8	1 967.0	1 962.4	—
	1 863.0	—	1 865.0	1 867.0	1 861.4	—
[Mo(η^5-C_5H_5)(CO)$_2$(N_2)Cl][c]	—	—	—	1 999.4	—	—
	—	—	—	1 938.5	—	—
[Mo(η^5-C_5H_5)(CO)$_2$(C_2H_4)Cl]	—	—	—	—	2 015.5	—
	—	—	—	—	1 953.4	—
[W(η^5-C_5H_5)(CO)$_2$(C_2H_4)Cl]	—	—	—	—	2 011.8	—
	—	—	—	—	1 945.4	—
[Mo(η^5-C_5H_5)(CO)$_3$]$^+$	—	—	2 057.8	—	—	—
	—	—	1 987.0	—	—	—
	—	—	1 955.2	—	—	—
[W(η^5-C_5H_5)(CO)$_3$]$^+$	—	—	2 052.0	—	—	—
	—	—	1 972.8	—	—	—
	—	—	1 946.5	—	—	—
[Fe(η^5-C_5H_5)(CO)$_2$Cl][d]	2 054.2	—	2 054.3	2 056.1	—	2 050
	2 010.2	—	2 010.6	2 013.7	—	2 000
[Ru(η^5-C_5H_5)(CO)$_2$Cl][e]	2 056.2	—	2 056.3	2 058.6	—	2 052
	2 009.2	—	2 009.5	2 010.3	—	1 998
[Fe(η^5-C_5H_5)(CO)Cl][f]	1 977.1	—	1 974.5	1 979.2	—	1 975
[Fe(η^5-C_5H_5)(CO)(thf)Cl][g]	—	—	—	—	—	1 963
[Ru(η^5-C_5H_5)(CO)Cl][h]	1 967.7	—	1 966.0	1 969.5	—	1 965
[Ru(η^5-C_5H_5)(CO)(thf)Cl][g]	—	—	—	—	—	1 955

[a] Matrix splitting. [b] Irradiation of [Mo(η^5-C_5H_5)(CO)$_3$Cl] in CO matrices produced complete conversion to the cationic species [Mo(η^5-C_5H_5)(CO)$_3$]$^+$ whereas the W complex gave a mixture of the cationic species together with the co-ordinatively unsaturated 16-electron species [W(η^5-C_5H_5)(CO)$_2$Cl] (see text). [c] ν(N≡N) at 2 240.8 cm^{-1}. [d] $\lambda_{max.}$(pvc) at 330 and 380 nm. [e] $\lambda_{max.}$(pvc) at 290 and 340 nm. [f] Only observed to form at *ca.* 12 K; $\lambda_{max.}$ at 440 nm (pvc). [g] Observed to form on warming films after irradiation at 12 K. [h] Only observed to form at *ca.* 12 K; $\lambda_{max.}$ at 405 nm (pvc).

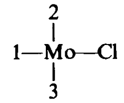
Visible irradiation with $\lambda > 410$ nm produced new i.r. bands at 2 240.8, 2 138.0, 1 999.4, 1 938.5, and 1 883.4 cm^{-1} [Figure 2(*b*)], of which the band at 2 138.0 cm^{-1} corresponds to free CO. Prolonged photolysis with light of the same energy showed a further increase in free CO, increases in all the new bands, and decreases in the parent bands [Figure 2(*b*) and (*c*)]. In these photolyses it was observed that the lower band of [Mo(η^5-C_5H_5)(CO)$_3$Cl] at 1 983.7 cm^{-1} decreased more slowly than the other two bands, indicating the growth of a new product band close to the position of a decreasing parent band [Figure 2(*c*)]. Warming the matrix to 35 K and then re-cooling to 12 K caused increases in the intensities of the new photoproduct bands at 2 240.8, 1 999.4, and 1 938.5 cm^{-1}, decreases in the intensities of bands at 1 989.3 and 1 883.4 cm^{-1}, and little change in the parent band intensities [Figure 2(*d*)]. Comparison of the growth and disappearance of bands at various times of photolysis identified two pairs of new terminal CO stretching bands: (I) at 1 999.4 and 1 938.5 cm^{-1} and (II) at 1 980.3 and 1 883.4 cm^{-1}. The pair (II) may be assigned to the co-ordinatively unsaturated 16-electron species [Mo(η^5-C_5H_5)(CO)$_2$Cl] by virtue of the reversal on annealing and the correspondence of the band positions with those of the species obtained on photolysis of [Mo(η^5-C_5H_5)(CO)$_3$Cl] in argon and methane matrices. The pair (I) also correlate with a band at 2 240.8 cm^{-1} which may be assigned as a ν(N≡N) stretching mode of a end-on co-ordinated dinitrogen ligand by analogy with bands for [Ni(CO)$_3$(N_2)] [ν(NN) at 2 266 cm^{-1}, nitrogen matrix],[15] [Mo(η^5-C_5H_5)(CO)$_2$(N_2)Me] [ν(NN) at 2 190.8 cm^{-1}, nitrogen matrix],[16] and, [RhH(N_2)(PPr$^i_3$)$_2$] [ν(NN) at 2 140 cm^{-1}, hexane].[17] The second new product therefore contains at least two CO ligands and one NN ligand and may be assigned as [Mo(η^5-C_5H_5)(CO)$_2$(N_2)Cl]. Photolysis of ^{13}CO-enriched [Mo(η^5-C_5H_5)(CO)$_3$Cl] in a N_2 matrix gave bands attributable to the species [Mo(η^5-C_5H_5)(^{12}CO)$_{2-m}$(^{13}CO)$_m$(N_2)Cl] (m = 0—2, Table 2), confirming the structural assignment of product (I) as [Mo(η^5-C_5H_5)(CO)$_2$(N_2)Cl]. Calculation of the OC–Mo–CO bond angle ($\theta = 78°$) from relative band intensities[14] suggests that the two CO ligands in [Mo(η^5-C_5H_5)(CO$_2$)(N_2)Cl] are *cis* to one another. The tungsten analogue, however, showed photoejection of a CO ligand in nitrogen matrices to give *only* the 16-electron species [W(η^5-C_5H_5)(CO)$_2$Cl], *i.e.* no bands were observed for a [W(η^5-C_5H_5)(CO)$_2$(N_2)Cl] species.

(*iii*) *Photolysis of* [M(η^5-C_5H_5)(CO)$_3$Cl] *Complexes* (M = Mo *or* W) *in* 5% C_2H_4–CH_4 *Matrices at* ca. 12 K.—Infrared spectra from an experiment with [W(η^5-C_5H_5)(CO)$_3$Cl] isolated at high dilution in a 5% C_2H_4–CH_4 matrix are shown in Figure 3. Before photolysis the spectrum shows three bands in the CO stretching region at 2 049.3, 1 966.1, and 1 948.4 cm^{-1} [Figure 3(*a*)].

Irradiation of the matrix using long-wavelength radiation ($\lambda > 410$ nm) produced new bands at 2 138.0, 2 011.8, 1 945.4, and 1 861.4 cm^{-1} of which the band at 2 138.0 cm^{-1} corresponds to CO liberated during photolysis [Figure 3(*b*)]. Longer times of irradiation with the same energy wavelength ($\lambda > 410$ nm) revealed a band growing at 1 962.4 cm^{-1}, which was formerly obscured by the bands of the parent molecule at 1 966.1 cm^{-1},

Table 2. Observed and calculated[a] band positions (cm^{-1}) of terminal CO bands in an experiment with a ^{13}CO-enriched sample of [Mo(η^5-C_5H_5)(CO)$_3$Cl] in a nitrogen matrix at 12 K

Complex	ν(CO)	Observed	Calculated
[Mo(η^5-C_5H_5)(^{12}CO)$_3$Cl][a]	*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]	*A′*	2 053.5	2 052.2
(C_s)[b]	*A″*	1 969.2	1 968.5
	A′	*d*	1 944.2
(C_1)[c]	*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)(^{13}CO)$_2$Cl]	*A*	2 037.8	2 036.5
(C_1)[e]	*A*	1 948.5	1 949.0
	A	*d*	1 934.9
(C_s)[f]	*A′*	2 025.6	2 025.7
	A′	1 970.3	1 969.6
	A″	1 924.3	1 924.8
[Mo(η^5-C_5H_5)(^{13}CO)$_3$Cl]	*A′*	2 011.3	2 011.8
(C_s)	*A′*	1 938.7	1 939.2
	A″	1 924.3	1 924.8
[Mo(η^5-C_5H_5)(^{12}CO)$_2$Cl]	*A′*	1 980.3	1 980.3
(C_s)	*A″*	1 883.4	1 883.4
[Mo(η^5-C_5H_5)(^{12}CO)(^{13}CO)Cl]	*A*	*d*	1 962.8
(C_1)	*A*	1 857.2	1 857.9
[Mo(η^5-C_5H_5)(^{13}CO)$_2$Cl][g]	*A′*	*d*	1 936.3
(C_1)	*A″*	1 841.0	1 841.6
[Mo(η^5-C_5H_5)(^{12}CO)$_2$(N_2)Cl][h]	*A*	1 999.4	1 999.4
(C_1)	*A*	1 938.5	1 938.5
[Mo(η^5-C_5H_5)(^{12}CO)(^{13}CO)(N_2)Cl]	*A*	*d*	1 984.3
(C_1)	*A*	*d*	1 909.9
[Mo(η^5-C_5H_5)(^{13}CO)$_2$(N_2)Cl]	*A*	*d*	1 955.0
(C_1)	*A*	1 895.3	1 895.5



i.e. $1 \neq 2 = 3$

[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 in the diagram above. [b] ^{13}CO in position 1. [c] ^{13}CO in position 2. [d] Obscured bands. [e] ^{12}CO in position 2. [f] ^{12}CO in position 1. [g] Refined energy-factored force constants for [Mo(η^5-C_5H_5)(CO)$_2$Cl]: K = 1 508.7 and k_i = 75.6 N m^{-1}. [h] Refined energy-factored force constants for [Mo(η^5-C_5H_5)(CO)$_2$(N_2)Cl]: K = 1 566.7 and k_i = 48.5 N m^{-1}.

and caused all the new product bands to increase in intensity while those of the parent molecule [W(η^5-C_5H_5)(CO)$_3$Cl] decreased [Figure 3(*c*)]. Annealing the matrix showed that the bands at 1 962.4 and 1 861.5 cm^{-1} were not related to those at 2 011.8 and 1 945.4 cm^{-1} because the former decreased in intensity whereas the latter increased, while there was little or no change in the relative intensities of the parent bands [Figure 3(*d*)]. The pair of bands at 1 962.4 and 1 861.5 cm^{-1} [bands (III)] which reversed on annealing can be assigned to the co-ordinatively unsaturated 16-electron species [W(η^5-C_5H_5)(CO)$_2$Cl] by comparison with those observed in a methane matrix (Table 1) and their analogous reversal behaviour. The pair of bands at higher wavenumbers [2 011.8 and 1 945.4 cm^{-1}, bands (IV)] are typical of a situation where a CO ligand has been replaced by another ligand, *e.g.* [W(η^5-C_5H_5)(CO)$_2$(C_2H_4)Ph] (1 990.2 and 1 922.5 cm^{-1}) compared with [W(η^5-C_5H_5)(CO)$_2$Ph] (1 951.5 and 1 861.5 cm^{-1}). The two CO ligands in [W(η^5-C_5H_5)(CO)$_2$(C_2H_4)Cl] are probably *cis* to one another, because the upper band of [W(η^5-C_5H_5)(CO)$_2$(C_2H_4)Cl] is more intense than the lower band, *i.e.* $I_{asym}/I_{sym} < 1$.[14]

Analogous results were obtained with [Mo(η^5-C_5H_5)(CO)$_3$Cl] isolated at high dilution in a 5% C_2H_4–CH_4 matrix.

(*iv*) *Photolysis of* [M(η^5-C_5H_5)(CO)$_3$Cl] *Complexes* (M = Mo *or* W) *in Carbon Monoxide Matrices at* ca. 12 K.—The i.r. spectrum of [Mo(η^5-C_5H_5)(CO)$_3$Cl] isolated at high dilution in a carbon monoxide matrix is shown in Figure 4. Before photolysis, the spectrum [Figure 4(*a*)] showed bands in the CO stretching region at 2 058.0, 1 982.7, and 1 963.5 cm^{-1} (matrix-split doublet) (Table 1).

An extended period of irradiation with visible light ($\lambda > 410$ nm) or a shorter period of irradiation with u.v. light ($320 < \lambda > 390$ nm) produced at least three new bands ν(CO) at 2 057.8, 1 987.0, and 1 955.2 cm^{-1} [Figure 4(*b*)]. Annealing the matrix for 2 min caused a rapid disappearance of the new photoproduct bands [bands (V)] with the regeneration of the bands due to the starting material [Mo(η^5-C_5H_5)(CO)$_3$Cl] [Figure 4(*c*)]. The relative intensities of the new terminal CO stretching bands remained constant under a variety of photolysis conditions (time and wavelength of radiation), indicating that the bands arose from a single mononuclear product species. Interestingly these new photoproduct bands are at different wavenumbers from those obtained for irradiation of [Mo(η^5-C_5H_5)(CO)$_3$Cl] in methane and argon matrices.

Irradiation of [W(η^5-C_5H_5)(CO)$_3$Cl] in carbon monoxide matrices and under the same conditions produced two bands at 1 964.8 and 1 865.0 cm^{-1} which may be assigned to [W(η^5-C_5H_5)(CO)$_2$Cl] (Table 1). Longer times of irradiation caused a

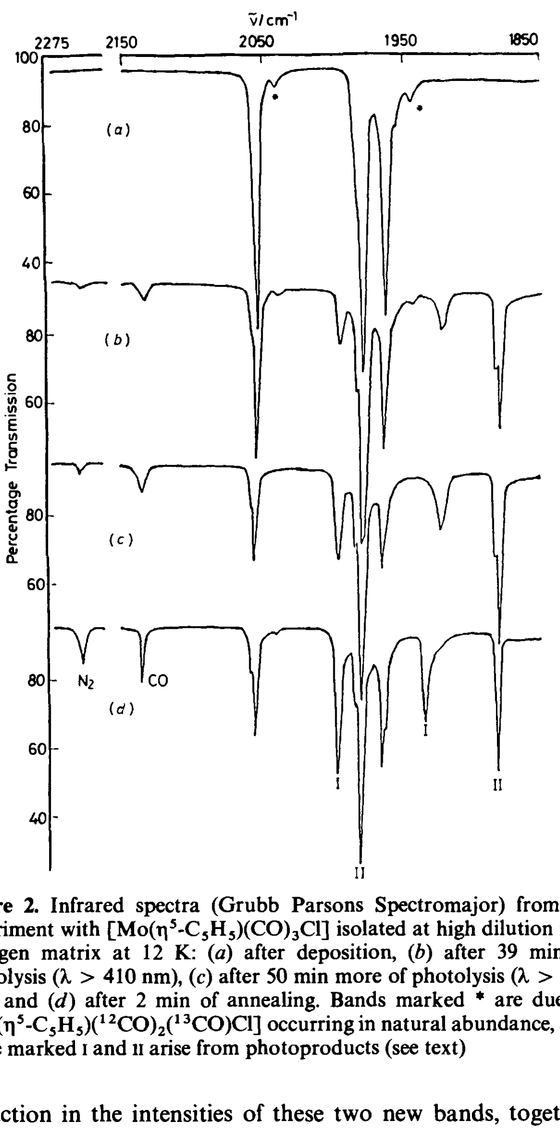


Figure 2. Infrared spectra (Grubb Parsons Spectromajor) from an experiment with $[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ isolated at high dilution in a nitrogen matrix at 12 K: (*a*) after deposition, (*b*) after 39 min of photolysis ($\lambda > 410$ nm), (*c*) after 50 min more of photolysis ($\lambda > 410$ nm), and (*d*) after 2 min of annealing. Bands marked * are due to $[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)Cl]$ occurring in natural abundance, and those marked I and II arise from photoproducts (see text)

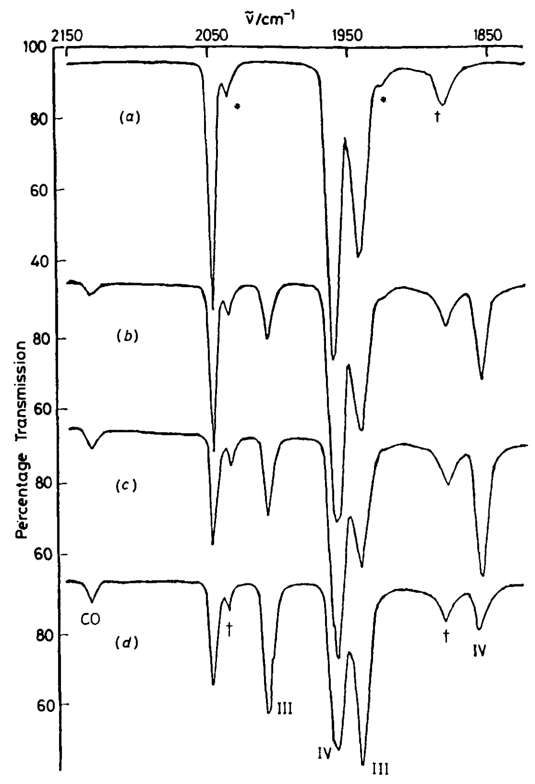


Figure 3. Infrared spectra (Grubb Parsons Spectromajor) from an experiment with $[W(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ isolated at high dilution in a 5% C_2H_4–CH_4 matrix at 12 K: (*a*) after deposition, (*b*) after 60 min of photolysis ($\lambda > 410$ nm), (*c*) after 70 min more of photolysis ($\lambda > 410$ nm), and (*d*) after 2 min of annealing. Bands marked * are due to $[W(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)Cl]$ in natural abundance, those marked † are due to C_2H_4, and III and IV arise from photoproducts (see text)

reduction in the intensities of these two new bands, together with the appearance of three other new bands at 2 052.0, 1 972.8, and 1 946.5 cm^{-1}, *cf.* the bands obtained on irradiation of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ in carbon monoxide matrices.

There are three possible photochemical processes relevant to assigning the new photoproduct bands at 2 057.8, 1 987.0, and 1 955.2 cm^{-1}, and at 2 052.0, 1 972.8, and 1 946.5 cm^{-1}, obtained from the irradiation of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ and $[W(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ complexes in carbon monoxide matrices, respectively [equations (5)—(7)].

$$[M(\eta^5\text{-}C_5H_5)(CO)_3Cl] \overset{h\nu}{\rightleftharpoons} [Mo(\eta^5\text{-}C_5H_5)(CO)_3]^{\bullet} + Cl^{\bullet} \tag{5}$$

$$[M(\eta^5\text{-}C_5H_5)(CO)_3Cl] \xrightarrow{h\nu} [M(\eta^3\text{-}C_5H_5)(CO)_3Cl] \xrightarrow{+CO} [M(\eta^3\text{-}C_5H_5)(CO)_4Cl] \tag{6}$$

$$[M(\eta^5\text{-}C_5H_5)(CO)_3Cl] \overset{h\nu}{\rightleftharpoons} [M(\eta^5\text{-}C_5H_5)(CO)_3]^+ + Cl^- \xrightarrow{+CO} [M(\eta^5\text{-}C_5H_5)(CO)_4]^+ + Cl^- \tag{7}$$

Formation of the radical species $[M(\eta^5\text{-}C_5H_5)(CO)_3]^{\bullet}$ [equation (5)] can be eliminated because the bands attributed to these species in carbon monoxide matrices are known $\{[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^{\bullet}$, 2 009.9 and 1 912.2 cm^{-1}; and $[W(\eta^5\text{-}C_5H_5)(CO)_3]^{\bullet}$, 1 999.3 and 1 898.4 cm$^{-1}\}$.[18a] The ring-slippage process [equation (6)] can also be eliminated because of the rapid and complete reversal of the new photoproduct bands to the starting material $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ on annealing the matrix from 12 to 35 K. If this process occurred it might also have led to the generation of the hexacarbonyl complexes $[M(CO)_6]$ (M = Mo or W), *cf.* the generation of $[M(CO)_6]$ on irradiation of the $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$ complexes (M = Cr, Mo, or W) in carbon monoxide matrices.[18b] However, no bands attributable to $[M(CO)_6]$ were observed during irradiation of the $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ complexes in carbon monoxide matrices. Therefore, the new bands probably arise from the cationic species $[M(\eta^5\text{-}C_5H_5)(CO)_x]^+$ (x = 3 or 4) as a result of heterolytic cleavage of the metal–halogen bond. The ionic species $[M(\eta^5\text{-}C_5H_5)(CO)_4]^+X^-$ (M = Mo or W) were first reported by Fischer *et al.*;[19] subsequently the related η-ethylene derivatives $[M(\eta^5\text{-}C_5H_5)(CO)_3(\eta\text{-}C_2H_4)]^+X^-$ (M = Mo or W) were described.[5]

Comparison of the new bands at 2 057.8, 1 987.0, and 1 955.2 cm^{-1} obtained upon irradiation of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ in a carbon monoxide matrix with those of $[Mo(\eta^5\text{-}C_5H_5)(CO)_4]^+$ [ν(CO) bands at 2 129, 2 041, and 1 980 cm^{-1}; solution] and the new bands at 2 052.0, 1 972.8, and 1 946.5 cm^{-1} obtained upon irradiation of $[W(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ in a carbon monoxide matrix with those of $[W(\eta^5\text{-}C_5H_5)(CO)_4]^+$ [ν(CO) bands at 2 128, 2 028, and 1 965 cm^{-1}; solution] showed a poor correlation between the band positions in solution and those in carbon monoxide matrices. In solution, however, it was also

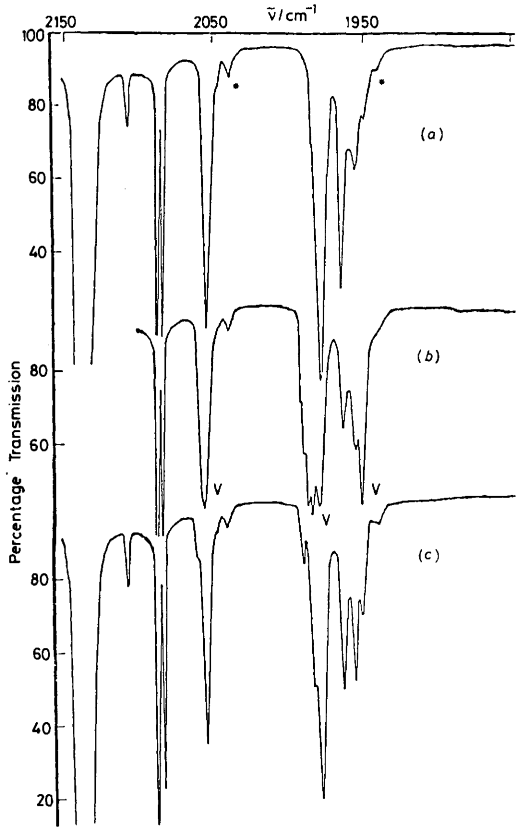


Figure 4. Infrared spectra (Grubb Parsons Spectromajor) from an experiment with [Mo(η^5-C_5H_5)(CO)$_3$Cl] isolated at high dilution in a carbon monoxide matrix at 12 K: (*a*) after deposition, (*b*) after 20 min of photolysis (320 < λ < 390 nm), and (*c*) after annealing the matrix for 2 min. Bands marked v are due to [Mo(η^5-C_5H_5)(CO)$_3$]$^+$, those marked * are due to [Mo(η^5-C_5H_5)(^{12}CO)$_2$(^{13}CO)]$^+$ present in natural abundance

suggested[20] that the loss of halide anions from [W(η^5-C_5H_5)(CO)$_3$Cl] would result in formation of the 16-electron cationic complexes [W(η^5-C_5H_5)(CO)$_3$]$^+$ which should recombine rapidly to give the starting complexes[20] [equation (7)]. In the presence of free carbon monoxide or PPh$_3$, the cations would be expected to react to give the co-ordinatively saturated complexes [M(η^5-C_5H_5)(CO)$_4$]$^+$ or [M(η^5-C_5H_5)(CO)$_3$(PPh$_3$)]$^+$.[19,21] If the reaction [equation (7)] went to completion in matrices, however, it is unlikely that the modest thermal energy afforded by annealing the CO matrix would effect the reversal, *i.e.* replacement of CO by Cl$^-$.

It seems probable, therefore, that the new photoproduct bands resulting from irradiation of [M(η^5-C_5H_5)(CO)$_3$Cl] complexes (M = Mo or W) in carbon monoxide matrices are in fact due to the formation of the 16-electron cationic species [M(η^5-C_5H_5)(CO)$_3$]$^+$ rather than the 18-electron [M(η^5-C_5H_5)(CO)$_4$]$^+$. The use of ^{13}CO isotopic labelling to support this assignment was not feasible because of the large number of bands in the spectrum due to the range of species [Mo(η^5-C_5H_5)(^{12}CO)$_{3-n}$(^{13}CO)$_n$Cl] (n = 0—3) (Table 2) and the overlapping of these bands with those of the cationic photoproduct species.

(*v*) *Photolysis of* [M(η^5-C_5H_5)(CO)$_2$Cl] *Complexes* (M = Fe *or* Ru) *in Methane, Nitrogen, Carbon Monoxide, and* 5% ^{13}CO–CH$_4$ *Matrices at* ca. 12 K.—The i.r. spectrum of [Fe(η^5-C_5H_5)(CO)$_2$Cl] isolated at high dilution in a methane matrix shows in the CO stretching region two bands at 2 054.2 and 2 010.2 cm^{-1} (Figure 5). These bands correspond to the symmetric (*A*′) and antisymmetric (*A*″) modes expected for a molecule with C_s symmetry together with two very weak bands (marked with an asterisk) arising from [Fe(η^5-C_5H_5)(^{12}CO)(^{13}CO)Cl] present in natural abundance.

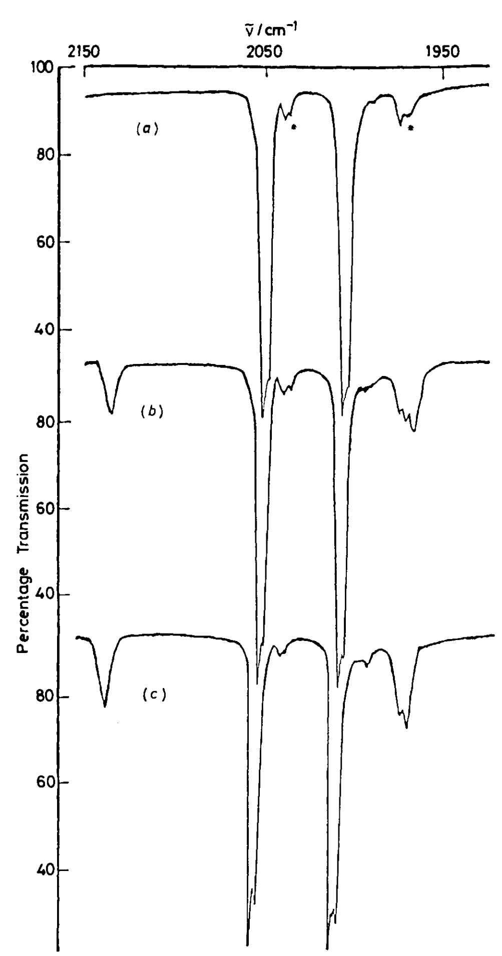


Figure 5. Infrared spectra (Grubb Parsons Spectromajor) from an experiment with [Fe(η^5-C_5H_5)(CO)$_2$Cl] isolated at high dilution in a methane matrix at 12 K: (*a*) after deposition, (*b*) after 30 min of photolysis (290 < λ < 370 nm), and (*c*) after 2 h more of photolysis with the same energy source. Bands marked * are due to [Fe(η^5-C_5H_5)(^{12}CO)(^{13}CO)Cl] present in natural abundance

Irradiation of the matrix with u.v. light (290 < λ < 370 nm) produced a single band at 1 977.1 cm^{-1} in addition to a band for free CO at 2 138 cm^{-1} [Figure 5(*b*)]. Longer times of irradiation with the same photolysis source led to increases in the single band at 1 977.1 cm^{-1} and the band of free CO [Figure 5(*c*)]. The band at 1 977.1 cm^{-1} could be assigned to the unsaturated 16-electron [Fe(η^5-C_5H_5)(CO)Cl] species on the basis that elimination of carbon monoxide from the parent complex [Fe(η^5-C_5H_5)(CO)$_2$Cl] was found to be reversible on annealing the matrix to higher temperatures (*ca.* 30 K). The validity of this assignment was demonstrated when [Ru(η^5-C_5H_5)(CO)$_2$Cl] was photolysed in a 5% ^{13}CO–CH$_4$ matrix [Figure 6(*a*) and (*b*)]. Initially rapid exchange occurred to produce [Ru(η^5-C_5H_5)(^{12}CO)(^{13}CO)Cl] and [Ru(η^5-C_5H_5)(^{13}CO)$_2$Cl] but on further photolysis bands assigned to [Ru(η^5-C_5H_5)(^{12}CO)Cl] and [Ru(η^5-C_5H_5)(^{13}CO)Cl] occurred. Satisfactory correspondence between observed and calculated band positions was found for ^{13}CO-enriched [Ru(η^5-C_5H_5)(CO)$_2$Cl] and [Ru(η^5-C_5H_5)(CO)Cl] (Table 3) using the energy-factored force-field approach.[14]

Irradiation of [M(η^5-C_5H_5)(CO)$_2$Cl] complexes (M = Fe or Ru) in nitrogen and carbon monoxide matrices was expected

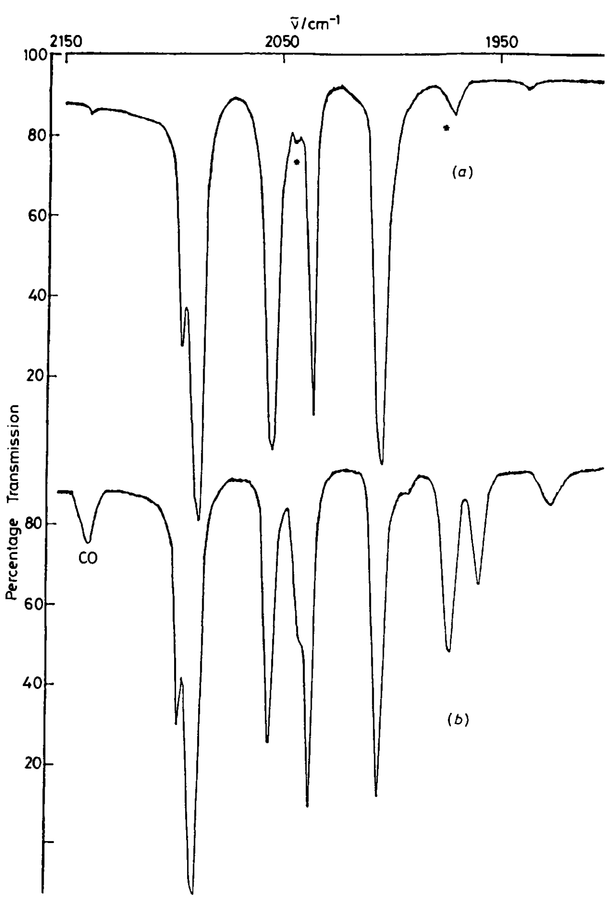


Figure 6. Infrared spectra (Grubb Parsons Spectromajor) from an experiment with [Ru(η^5-C_5H_5)(CO)$_2$Cl] isolated at high dilution in a 5% ^{13}CO–CH_4 matrix at 12 K: (*a*) after deposition and (*b*) after 2 h of photolysis (290 < λ < 370 nm). Bands marked * are due to [Ru(η^5-C_5H_5)(^{12}CO)(^{13}CO)Cl] present in natural abundance

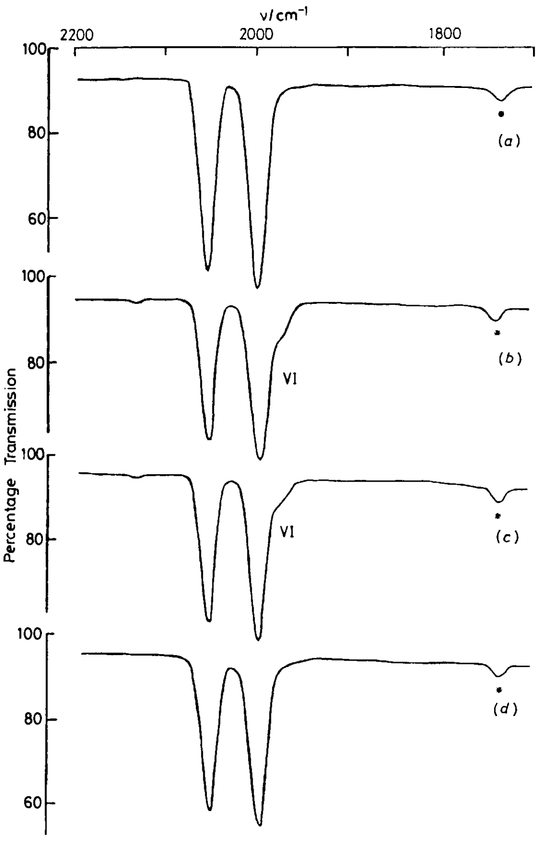


Figure 7. Infrared spectra (Nicolet 7199 Fourier-transform i.r. spectrometer) from an experiment with [Ru(η^5-C_5H_5)(CO)$_2$Cl] in a pvc film (cast from a 1,2-dichloroethane solution) at 12 K: (*a*) before irradiation, (*b*) after 60 min of irradiation (300 < λ < 370 nm), (*c*) after warming the film to *ca.* 100 K, and (*d*) after warming to *ca.* 130 K. Band VI is due to the photoproduct and that marked * is due to ketone groups in the pvc

to lead to the formation of [M(η^5-C_5H_5)(CO)(N_2)Cl] and [M(η^5-C_5H_5)(CO)$_2$]$^+$Cl$^-$ respectively. However, only [M(η^5-C_5H_5)(CO)Cl] was seen to be formed. Spectroscopic data for the new species are given in Table 1.

(*vi*) *Photolysis of* [M(η^5-C_5H_5)(CO)$_2$Cl] *Complexes* (M = Fe *or* Ru) *in Poly*(*vinyl chloride*) (*pvc*) *Films at* 12—298 K.—The i.r. spectrum of the complex [Ru(η^5-C_5H_5)(CO)$_2$Cl] at 12 K in a pvc film (2 mg:500 mg) cast from a 1,2-dichloroethane solution (298 K) showed two terminal CO stretching bands at 2 052 (A') and 1 998 (A'') cm^{-1} [Figure 7(*a*)]. The electronic absorption spectrum of the film showed a band at 290 nm and another much weaker band at *ca.* 340 nm [Figure 8(*a*)]. On irradiating the film with light corresponding to these bands, a new band (VI) appeared in the spectrum at *ca.* 405 nm [Figure 8(*b*)]. At the same time, a new band (VI) grew in the i.r. spectrum at *ca.* 1 965 cm^{-1}, along with a band for free CO at 2 133 cm^{-1}, whilst the parent bands decreased in intensity [Figure 7(*b*)]. No change was observed in the spectrum on subsequently warming the film to *ca.* 80 K. Further warming the film to *ca.* 100 K, however, led to reductions in the product band (VI) and the band for free CO, whilst the parent bands increased in intensity [Figure 7(*c*)]. Reversal of the photoreaction observed at 12 K occurred on warming the film to *ca.* 130 K [Figure 7(*d*)]. It is evident from the observation of free CO that the photoproduct (VI) arises from loss of a CO ligand from the parent compound. The thermal reversibility of the photoreaction at low temperatures and the fact that the product i.r. absorption band occurs at a lower wavenumber than for the parent bands suggest that the product is the 16-electron species [Ru(η^5-C_5H_5)(CO)Cl], *cf.* gas matrices (Table 1).

Irradiation (300 < λ < 370 nm) of the complex [Fe(η^5-C_5H_5)(CO)$_2$Cl] [ν(CO) 2 050 and 2 000 cm^{-1}] at 12 K in a pvc film (2 mg:500 mg) cast from a 1,2-dichloroethane solution [Figure 9(*a*) and (*b*)] led to the formation of free CO and a monocarbonyl species (VII) having an i.r. absorption band at *ca.* 1 975 cm^{-1}. The position of this band was revealed on subtracting the parent bands from the spectrum [Figure 9(*c*)]. The photoproduct (VII) was observed to recombine completely with CO on warming the film to *ca.* 60 K [Figure 9(*d*)]. The product, which is analogous to the CO-loss product generated on photolysis of [Fe(η^5-C_5H_5)(CO)$_2$Cl] [*cf.* bands in methane matrices (Table 1)], is proposed to be [Fe(η^5-C_5H_5)(CO)Cl]. This species was also seen to form on irradiation of the complex [Fe(η^5-C_5H_5)(CO)$_2$Cl] at 12 K in a pvc film cast from a tetrahydrofuran solution (thf). Warming this film to *ca.* 60 K led to the formation of a new monocarbonyl species [ν(CO): 1 963 cm^{-1}]. Thermal conversion of this product into the parent compound [Fe(η^5-C_5H_5)(CO)$_2$Cl] was observed on subsequently warming the film to above *ca.* 200 K. The product is most probably the complex [Fe(η^5-C_5H_5)(CO)(thf)Cl], formed in a reaction of the species [Fe(η^5-C_5H_5)(CO)Cl] with residual thf solvent in the film: *cf.* [M(CO)$_6$] $\rightleftharpoons$ [M(CO)$_5$] + CO $\underset{\text{thf}}{\rightleftharpoons}$ [M(CO)$_5$(thf)] (M = Cr, Mo, or W).[11a] An analogous product [ν(CO) 1 955 cm^{-1}] was seen to form from the species

Table 3. Observed and calculated[a] band positions (cm^{-1}) of [Ru(η^5-C_5H_5)(CO)$_2$Cl] and its photoproducts in a 5% ^{13}CO–CH_4 matrix

Complex	Point group	ν(CO)	Observed	Calculated
[Ru(η^5-C_5H_5)(^{12}CO)$_2$Cl]	C_s	A'	2 056.2	2 056.2
		A''	2 009.2	2 009.2
[Ru(η^5-C_5H_5)(^{12}CO)(^{13}CO)Cl]	C_1	A	2 043.2	2 042.5
		A	1 977.5	1 977.7
[Ru(η^5-C_5H_5)(^{13}CO)$_2$Cl]	C_s	A'	2 011.0[b]	2 010.5
		A''	1 964.5	1 964.6
[Ru(η^5-C_5H_5)(^{12}CO)Cl]	C_s	A'	1 967.7[c]	1 967.7[d]
[Ru(η^5-C_5H_5)(^{13}CO)Cl]	C_s	A'	1 923.2	1 923.0

[a] Refined energy-factored force constants for [Ru(η^5-C_5H_5)(CO)$_2$Cl], K = 1 669.5 and k_i = 38.6 N m^{-1}; for [Ru(η^5-C_5H_5)(CO)Cl], K = 1 563.6 N m^{-1}. [b] Band obscured under the lower band of [Ru(η^5-C_5H_5)(^{12}CO)$_2$Cl]. [c] Band obscured under the lower band of [Ru(η^5-C_5H_5)(^{13}CO)$_2$Cl]; it is calculated to be at 1 967.7 cm^{-1} compared with that in a methane matrix. [d] Experimental band used for calculation.

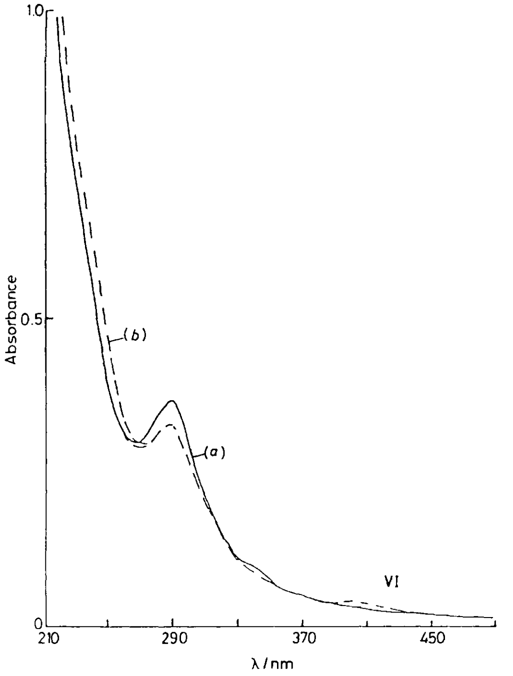


Figure 8. Ultraviolet–visible spectra (Pye Unicam SP1800B) from an experiment with [Ru(η^5-C_5H_5)(CO)$_2$Cl] in a pvc film (cast from a 1,2-dichloroethane solution) at 12 K: (*a*) before irradiation, (*b*) after 60 min of irradiation (300 < λ < 370 nm). The band VI is due to the photoproduct

[Ru(η^5-C_5H_5)(CO)Cl] on warming films, cast from thf solutions, from *ca.* 80 to 130 K. Spectroscopic data for the species are given in Table 1.

No photoproducts were observed on irradiation (300 < λ < 370 nm) of the complexes [Fe(η^5-C_5H_5)(CO)$_2$Cl] and [Ru(η^5-C_5H_5)(CO)$_2$Cl] in pvc films at room temperature.

Discussion

The photoreactions of [M(η^5-C_5H_5)(CO)$_3$Cl] complexes (M = Mo or W), in frozen gas matrices (Ar, CH_4, N_2, CO, or 5% C_2H_4-doped CH_4), are summarised in Scheme 1.

Previous investigations of the photolysis of [M(η^5-C_5H_5)(CO)$_3$X] complexes (M = Mo or W; X = Cl, Br, or I) in solution in the presence of PPh_3 have observed the formation of the monosubstituted complexes [M(η^5-C_5H_5)(CO)$_2$(PPh_3)X].[2,3] Kinetic studies of the thermal substitution reactions of [Mo(η^5-C_5H_5)(CO)$_3$X] with PPh_3 have shown[22,23] that the reactions proceed by a dissociative mechanism, with loss of carbon monoxide as the rate-determining step [equations (8) and (9)].

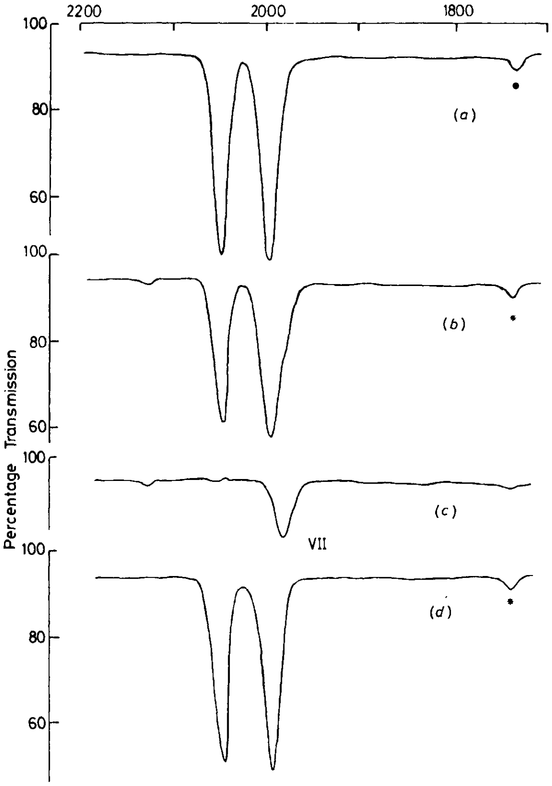
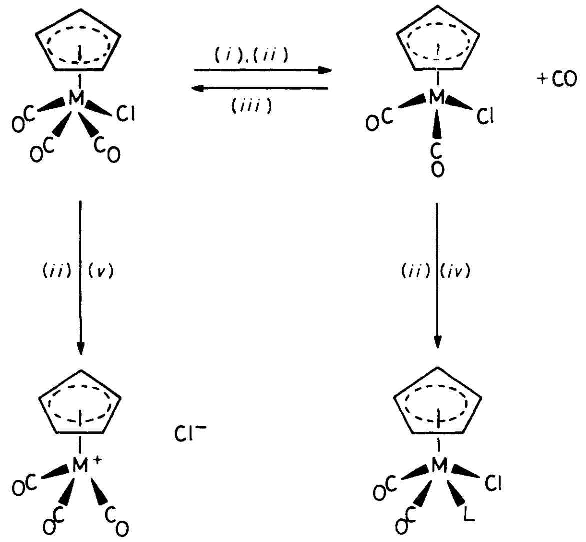


Figure 9. Infrared spectra (Nicolet 7199 Fourier-transform i.r. spectrometer) from an experiment with [Fe(η^5-C_5H_5)(CO)$_2$Cl] in a pvc film (cast from a 1,2-dichloroethane solution) at *ca.* 12 K: (*a*) before irradiation, (*b*) after 60 min of irradiation (300 < λ < 370 nm), (*c*) spectral subtraction, (*b*) – *N*(*a*), where *N* is a scaling factor, and (*d*) after warming the film to *ca.* 60 K. Band VII is due to photoproduct and that marked * is due to ketone groups in the pvc

$$[M(\eta^5\text{-}C_5H_5)(CO)_3X] \xrightarrow{\text{slow}} [M(\eta^5\text{-}C_5H_5)(CO)_2X] + CO \quad (8)$$

$$[M(\eta^5\text{-}C_5H_5)(CO)_2X] + PPh_3 \xrightarrow{\text{fast}} [M(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)X] \quad (9)$$

The matrix-isolation studies of [M(η^5-C_5H_5)(CO)$_3$Cl] complexes (M = Mo or W) in different non-reactive gas matrices, *e.g.* CH_4 and Ar, have demonstrated the dissociative loss of one CO ligand and the formation of the unsaturated 16-electron species [M(η^5-C_5H_5)(CO)$_2$Cl] as proposed[22,23] in equation (8). Exchange of ^{13}CO for ^{12}CO during the photolysis of [M(η^5-



Scheme 1. (*i*) CH_4 or Ar; (*ii*) $h\nu$ ($\lambda > 410$ nm); (*iii*) $h\nu$ ($\lambda > 520$ nm) or annealing; (*iv*) M = Mo, L = N_2 or C_2H_4; M = W, L = C_2H_4; (*v*) CO

$C_5H_5)(CO)_3Cl]$ complexes (M = Mo or W) in ^{13}CO-doped methane matrices at 12 K confirms that photoinduced dissociation and exchange of CO ligands is taking place and indicates that similar processes occur during the irradiation in solution.

Irradiation of $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ complexes (M = Mo or W) in nitrogen matrices affords the $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)Cl]$ derivative, however no reaction was observed for the $[W(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ analogue. An interesting feature of the $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)Cl]$ complex is the *cis* stereochemistry deduced on the basis of OC–M–CO bond-angle calculations ($\approx 78°$)[14] [equation (10)]. This stereochemistry may be related

$$[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl] + N_2 \xrightarrow{h\nu/CO} cis\text{-}[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)Cl] \quad (10)$$

to the photolysis of $[M(\eta^5\text{-}C_5H_5)(CO)_3X]$ complexes in the presence of PPh_3 to yield the monosubstituted complexes $[M(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)X]$. Although both *cis* and *trans* isomers of these derivatives are possible,[20,24] complexes with the *cis* geometry are formed stereospecifically by photosubstitution reactions [equation (11)], but *cis*- and *trans*-

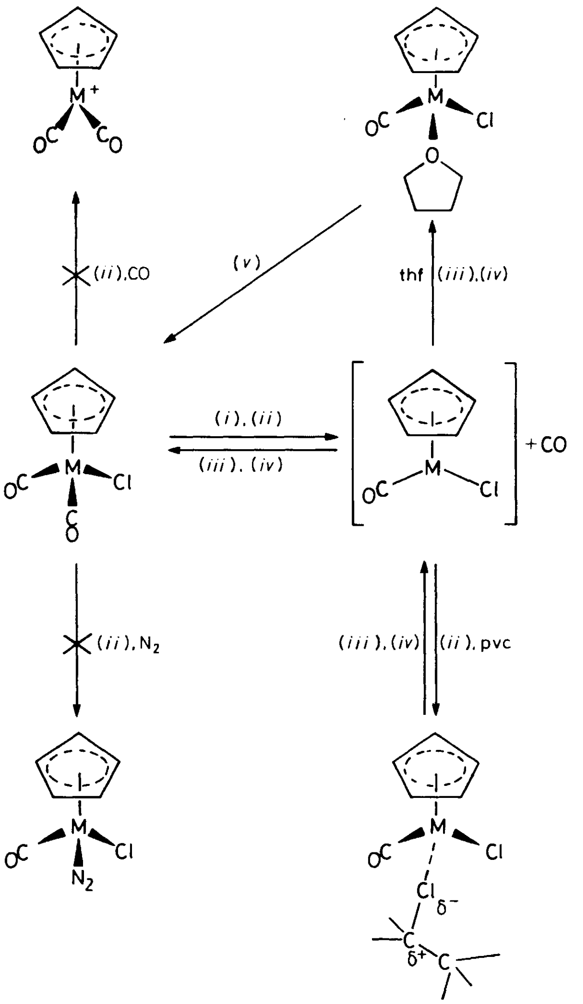
$$[M(\eta^5\text{-}C_5H_5)(CO)_3X] + PPh_3 \xrightarrow[-CO]{h\nu} cis\text{-}[M(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)S] \quad (11)$$

$[M(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)X]$ complexes (M = Mo, X = Br or I; M = W, X = I) undergo geometric isomerisation upon photolysis at 336 and 436 nm in benzene solutions [equation (12)]. It is noteworthy, however, that the chloro complexes

$$cis\text{-}[M(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)X] \xrightarrow[h\nu']{h\nu} trans\text{-}[M(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)X] \quad (12)$$

cis-$[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)Cl]$ does not undergo photochemical isomerisation in benzene solutions to produce the *trans* isomer.

The photolysis of $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ complexes (M = Mo or W) in 5% C_2H_4–CH_4 matrices led to the formation of $[M(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)Cl]$ complexes *via* the co-ordinatively unsaturated 16-electron species $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ [equation (13)]. Overlapping of bands made it impossible to



(A)

Scheme 2. M = Fe or Ru: (*i*) CH_4, CO, N_2, or pvc films, (*ii*) $h\nu$ ($300 < \lambda < 400$ nm) at 12 K; (*iii*) warming pvc film from 12 to *ca.* 60 K (M = Fe); (*iv*) warming film from *ca.* 80 to *ca.* 130 K (M = Ru); (*v*) warming pvc film to above *ca.* 200 K, +CO, −thf

$$[M(\eta^5\text{-}C_5H_5)(CO)_3Cl] + C_2H_4 \xrightarrow{h\nu} cis\text{-}[M(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)Cl] \quad (13)$$

calculate the bond angle OC–M–CO but a careful examination of the symmetric and antisymmetric band intensities of $[M(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)Cl]$ showed that the two CO groups are in a *cis* position ($I_{asym}/I_{sym} < 1$). Similarly *cis*-$[M(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)Me]$ and *cis*-$[W(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)Ph]$ were generated when the complexes $[M(\eta^5\text{-}C_5H_5)(CO)_3Me]$ (M = Mo or W) and $[W(\eta^5\text{-}C_5H_5)(CO)_3Ph]$ respectively were photolysed in 5% C_2H_4–CH_4 matrices.[13a] The reactivity of the $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ species toward the nitrogen ligand is less than that with the ethylene ligand as demonstrated by the higher yield of the latter photoproduct for the molybdenum derivatives. The high value of $\nu(N\equiv N)$ (2 240.8 cm^{-1}) probably reflects a weak M–N_2 bond, *cf.* $\nu(N\equiv N)$ = 2 169 cm^{-1} for $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)]$ which can be prepared by a conventional bench synthesis.[25]

Previous investigations have illustrated that the $[M(\eta^5\text{-}C_5H_5)(CO)_3X]$ derivatives of molybdenum and tungsten can react with a variety of ligands to yield a second type of derivative in which the halide ion is displaced to yield an ionic product, *e.g.* equation (3). The loss of halide anions from $[M(\eta^5\text{-}C_5H_5)(CO)_3X]$ is proposed to result in formation of the 16-electron cationic complexes $[M(\eta^5\text{-}C_5H_5)(CO)_3]^+$ [equation (3)] which can capture a ligand (L = CO or PPh_3) to yield the 18-electron complexes $[M(\eta^5\text{-}C_5H_5)(CO)_4]^+$ and $[M(\eta^5\text{-}C_5H_5)(CO)_3(PPh_3)]^+$ respectively[19,21] [equation (14)].

$$[M(\eta^5\text{-}C_5H_5)(CO)_3]^+ + X^- \xrightarrow[L\,=\,CO\text{ or }PPh_3]{h\nu} [M(\eta^5\text{-}C_5H_5)(CO)_3L]^+ + X^- \quad (14)$$

In contrast to the formation of the 16-electron species $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$, in methane, nitrogen, and argon matrices, an alternative reaction path to CO ejection is observed in carbon monoxide matrices which probably involves heterolytic cleavage of the metal–halogen bond [equations (15)—(17)]. Comparing the photochemical reactivity of the

$$[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl] \xrightleftharpoons[heat]{h\nu/+CO} [Mo(\eta^5\text{-}C_5H_5)(CO)_3]^+ + Cl^- \quad (15)$$

molybdenum and tungsten complexes in carbon monoxide matrices reveals that the generation of the $[M(\eta^5\text{-}C_5H_5)(CO)_3]^+$ cation is faster for Mo than for W using the same light source and the same period of irradiation. This suggests that the W–Cl bond may be stronger than the Mo–Cl bond.

$$[W(\eta^5\text{-}C_5H_5)(CO)_3Cl] \xrightleftharpoons{h\nu/+CO} [W(\eta^5\text{-}C_5H_5)(CO)_3]^+ + Cl \quad (16)$$

$$[W(\eta^5\text{-}C_5H_5)(CO)_3Cl] \xrightleftharpoons{h\nu/-CO} [W(\eta^5\text{-}C_5H_5)(CO)_2Cl] \quad (17)$$

The photoreactions of the $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ complexes (M = Fe or Ru) observed in gas matrices (CH_4, N_2, and CO) and in pvc films at 12 K are summarised in Scheme 2 together with the thermal reactions occurring on warming the films to *ca.* 130 K. The primary photochemical process for $[Fe(\eta^5\text{-}C_5H_5)(CO)_2X]$ complexes (X = Cl, Br, or I) in solution is dissociative loss of a CO ligand,[8] *cf.* equation (4).

The low-temperature media studies of $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ complexes (M = Fe or Ru) (Scheme 2, CH_4, N_2 or CO) have demonstrated the dissociative loss of one CO ligand and the formation of the unsaturated 16-electron species $[M(\eta^5\text{-}C_5H_5)(CO)Cl]$, as is proposed to occur in solutions.[8]. In a 5% $^{13}CO\text{–}CH_4$ matrix $[Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ shows rapid ^{13}CO exchange leading to $[Ru(\eta^5\text{-}C_5H_5)(^{12}CO)_{2-n}(^{13}CO)_nCl]$ (n = 1 or 2) species together with $[Ru(\eta^5\text{-}C_5H_5)(^{12}CO)Cl]$ and $[Ru(\eta^5\text{-}C_5H_5)(^{13}CO)Cl]$. This confirms that photoinduced dissociation and exchange of CO ligands takes place during u.v. irradiation of $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ (M = Fe or Ru) in low temperature matrices at 12 K.

Irradiation of $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ complexes (M = Fe or Ru) in reactive nitrogen matrices also produced the 16-electron intermediate $[M(\eta^5\text{-}C_5H_5)(CO)Cl]$ but no reaction with nitrogen was observed. The failure of $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ to react photochemically with nitrogen on irradiation at low temperatures may be because the nitrogen ligand competes less effectively than the CO for the $[M(\eta^5\text{-}C_5H_5)(CO)Cl]$ fragment.[26–28]

In previous studies it has been proposed[8] that loss of the halide anion from $[Fe(\eta^5\text{-}C_5H_5)(CO)_2X]$ might occur leading to the formation of the 16-electron cationic complexes $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^+X^-$. These complexes have been proposed to be susceptible to nucleophilic attack by two-electron donor ligands[29] and should efficiently react with CO to produce the 18-electron cationic complexes $[Fe(\eta^5\text{-}C_5H_5)(CO)_3]^+X^-$. No evidence for the formation of cations was found on photolysis of $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ complexes in carbon monoxide matrices.

An alternative pathway involves breaking the iron–halogen bond homolytically. Homolytic cleavage of the metal–halogen bond would produce the radical species $[M(\eta^5\text{-}C_5H_5)(CO)_2]^\bullet$ and $X^\bullet$ and these radicals would yield the dimers $[\{M(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ and X_2 in solution. Indeed Kemp and co-workers[9] have reported that the principal product on irradiation ($\lambda > 280$ nm) of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ in the donor solvents pyridine and dimethyl sulphoxide is $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$, but no reaction was observed in cyclohexane or diethyl ether. Irradiation of $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ complexes (M = Fe or Ru) in carbon monoxide matrices only resulted in CO ejection and the production of co-ordinatively unsaturated $[M(\eta^5\text{-}C_5H_5)(CO)Cl]$ species. This strongly suggests that neither homolytic nor heterolytic iron–halogen bond cleavage is an important pathway for the $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ complexes. The dimer $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ was not expected nor observed in gas matrices nor in pvc films because of the high dilution used in the experiments.

It is interesting that whilst the CO-loss product formed on irradiation of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ is thermally reactive towards CO or thf solvent molecules in pvc films at temperatures below *ca.* 60 K, the ruthenium analogue is only seen to be reactive at temperatures above *ca.* 80 K. It is possible that the 16-electron species $[Fe(\eta^5\text{-}C_5H_5)(CO)Cl]$ and $[Ru(\eta^5\text{-}C_5H_5)(CO)Cl]$, photogenerated in the films at 12 K, are co-ordinated by a hydrogen or chlorine atom in the pvc [*cf.* structure (A), Scheme 2] and that the difference in reactivities of the iron and ruthenium species reflects the relative strengths of the metal–polymer interactions. The fact that the $[Fe(\eta^5\text{-}C_5H_5)(CO)Cl]$ species reacts with CO or with thf in films at lower temperatures than the ruthenium analogue suggests that any bond which exists between the pvc and the iron species at its vacant co-ordination site is weaker than that formed between the polymer and the ruthenium species.

The complex $[Fe(\eta^5\text{-}C_5H_5)(CO)(thf)Cl]$, formed on warming pvc films containing thf is, in fact, analogous to the CO-substitution products seen to form in the solution reactions.

Conclusions

The photoreactions of $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ complexes (M = Mo or W) in argon, methane, nitrogen, and 5% $C_2H_4\text{–}CH_4$ matrices at *ca.* 12 K indicate that the principal intermediate in the thermal and photochemical solution substitution reactions is the co-ordinatively unsaturated 16-electron species $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$. The reaction is reversible [equation (18)].

$$[M(\eta^5\text{-}C_5H_5)(CO)_3Cl] \xrightleftharpoons[heat]{h\nu\ (\lambda\,\approx\,300\text{ nm})} [M(\eta^5\text{-}C_5H_5)(CO)_2Cl] + CO \quad (18)$$

Irradiation of $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ complexes (M = Mo or W) in carbon monoxide matrices can suppress the CO-loss photoreaction pathway and allow a second pathway to be observed [equation (19)]. The formation of $[M(\eta^5\text{-}C_5H_5)(CO)_3]^+$ and Cl^- ions is indicative of photo-induced metal–chlorine bond heterolysis.

$$[M(\eta^5\text{-}C_5H_5)(CO)_3Cl] \xrightleftharpoons[heat]{h\nu/+CO} [M(\eta^5\text{-}C_5H_5)(CO)_3]^+ + Cl^- \quad (19)$$

Irradiation ($300 < \lambda < 400$ nm) of $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ complexes (M = Fe or Ru) in methane, nitrogen, and carbon monoxide matrices, and in pvc films at *ca.* 12 K produced only the 16-electron species [equation (20)] indicating that CO

$$[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{Cl}] \underset{\text{heat}}{\overset{h\nu}{\rightleftarrows}} [\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})\mathrm{Cl}] + \mathrm{CO} \quad (20)$$

dissociation rather than cleavage of the M–Cl bond is the principal reaction pathway. On warming pvc films to *ca.* 60 K after irradiation, the species $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})\mathrm{Cl}]$ reacts completely with CO or with thf in the films to regenerate $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{Cl}]$ or form the complex $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{thf})\mathrm{Cl}]$, respectively. The ruthenium species, however, is only reactive towards CO or thf on warming films to above *ca.* 80 K. This suggests that the $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})\mathrm{Cl}]$ species (M = Fe or Ru) seen to form in films at *ca.* 12 K may be co-ordinated by the pvc with the metal–polymer interaction for ruthenium being stronger than that for iron.

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