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Photochemistry of (η^5-cyclopentadienyl)-tricarbonylmethylchromium in gas matrices and polymer films at 12–298 K: infrared spectroscopic evidence for reversible carbon monoxide ejection and α-H elimination from the methyl group

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Abstract

UV-Vis and infrared spectroscopic evidence, including ^{13}CO labelling and energy-factored force-field fitting, is presented which shows that photolysis of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ at high dilution in frozen gas matrices (Ar, CH_4, N_2, and CO) and poly(vinyl chloride) films at ca. 12 K affords the α-elimination product, *trans*-$(\eta^5\text{-}C_5H_5)Cr(CO)_2(=CH_2)H$, via the 16-electron species $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$. These reactions are thermally reversible at temperatures as low as 30 K with conversion of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(=CH_2)H$ to $(\eta^5\text{-}C_5H_5)Cr(CO)_2(L)CH_3$ complexes (L = CO and tetrahydrofuran) in poly(vinyl chloride) films. Irradiation of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in poly(vinyl chloride) films at 298 K yielded the dimer $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$ analogously to the solution photochemistry. The results are discussed in relation to the occurrence of α-H elimination reactions in general and the reactions of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in particular. It is suggested that the formation of the dimer $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$ in solution arises not from initial Cr–CH_3 bond cleavage or α-H elimination but from reactions of $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ or $(\eta^5\text{-}C_5H_5)Cr(CO)_2(\text{solvent})CH_3$ species with unreacted $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$.

Introduction

The complexes $(\eta^5\text{-}C_5H_5)M(CO)_3CH_3$ (M = Cr, Mo or W) and $(\eta^5\text{-}C_5H_5)M(CO)_3C_2H_5$ (M = Mo or W) are well known to undergo facile photosubstitution of CO by other lignads in solution [1–3] to form products of the type $(\eta^5\text{-}C_5H_5)M(CO)_2(L)CH_3$ and $\eta^5\text{-}C_5H_5)M(CO)_2(L)C_2H_5$, e.g. L = PPh_3. These reactions are thought [4] to involve a dissociative mechanism (cf. eqs. 1 and 2).

$$(\eta^5\text{-}C_5H_5)M(CO)_3CH_3 \xrightarrow[\lambda > 300\text{ nm}]{h\nu} (\eta^5\text{-}C_5H_5)M(CO)_2CH_3 + CO \tag{1}$$

$$(\eta^5\text{-}C_5H_5)M(CO)_2CH_3 \xrightarrow[\Delta]{L} (\eta^5\text{-}C_5H_5)M(CO)_2(L)CH_3 \tag{2}$$

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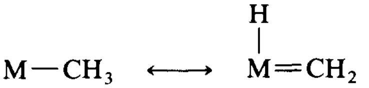
The CO dissociation reaction (eq. 1) has been observed directly (M = Mo and W) in frozen gas matrices [5], hydrocarbon glasses [6] and polymer films [7] at low temperatures, whilst thermal reactions of the $(\eta^5\text{-}C_5H_5)M(CO)_2CH_3$ species with ligands L (eq. 2) have been monitored on subsequently warming glasses and films [6,7]. Interestingly, irradiation of the $(\eta^5\text{-}C_5H_5)M(CO)_3CH_3$ complexes at room temperature in hydrocarbon solvents, in the absence of external ligands [8], leads to the formation of methane and the dimers $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$. The ethyl complexes $(\eta^5\text{-}C_5H_5)M(CO)_3C_2H_5$ also dealkylate [9] in these solvents, on irradiation, to form the hydride complexes $(\eta^5\text{-}C_5H_5)M(CO)_3H$. The latter dealkylation reactions have been shown to proceed via a β-hydrogen elimination pathway, where the photochemical and thermal reactivities of the intermediates (eqs. 3–5) have been studied in low temperature media [5–7].

$$(\eta^5\text{-}C_5H_5)M(CO)_3C_2H_5 \xrightarrow[-CO]{h\nu} (\eta^5\text{-}C_5H_5)M(CO)_2C_2H_5 \qquad (3)$$

$$(\eta^5\text{-}C_5H_5)M(CO)_2C_2H_5 \xrightarrow[\beta\text{-H elimination}]{h\nu \text{ or } \Delta} trans\text{-}(\eta^5\text{-}C_5H_5)M(CO)_2(C_2H_4)H \qquad (4)$$

$$trans\text{-}(\eta^5\text{-}C_5H_5)M(CO)_2(C_2H_4)H \xrightarrow[+CO]{h\nu \text{ or } \Delta} (\eta^5\text{-}C_5H_5)M(CO)_3H + C_2H_4 \qquad (5)$$

Reversible elimination of a hydrogen from carbons which are in β-positions relative to transition metals has been widely established to occur and is thought to be important in catalytic reactions, e.g. olefin isomerisation. Although less well documented, elimination involving carbons in the α-positions may also occur (eq. 6) and may be important in generating active intermediates in metal catalysed disproportionation reactions [10,11].



$$M{-}CH_3 \longleftrightarrow \overset{\displaystyle H}{\overset{|}{M}}{=}CH_2 \qquad (6)$$

As part of a general investigation of intermediates in photochemical reactions of transition metal alkyl complexes, we describe in this paper the photochemistry of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ seen in frozen gas matrices at 12–30 K and in poly(vinyl chloride) (PVC) films at 12–298 K. We present evidence for an α-hydrogen elimination pathway *.

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 [7,13,14]. The compound $(\eta^5\text{-}C_5H_5)Cr(CO)_3H_3$ was prepared according to the literature procedure [15] and purified by sublimation.

Results

(i) Electronic absorption spectrum of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$

The spectrum of $(\eta^5\text{-}C_5H_5)Cr(CO)_3H_3$ in PVC films (Fig. 1(a)) shows bands with maxima at 290 and 360 nm and is similar to the spectrum observed for this complex

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* A preliminary account of the work using gas matrices has been published elsewhere [12].

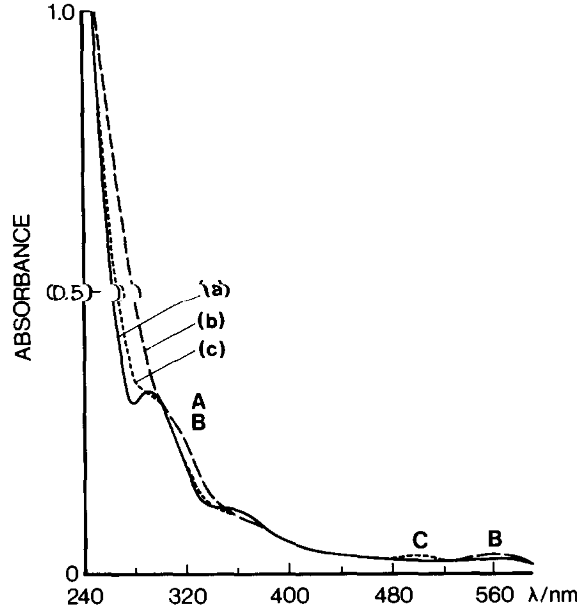

Fig. 1. UV-Vis spectra from an experiment with $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in a PVC film (cast from dichloroethane) at ca 12 K: (a) before irradiation, (b) after 20 min irradiation (300 < λ < 370 nm), and (c) after warming the film to ca 90 K and then recooling. Bands marked A, B and C are for products (see text).

in solution [2]. In this study, gas matrices and PVC films were irradiated with light at wavelengths corresponding to these absorption bands. Photosubstitution and photodealkylation reactions of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ have been observed in solution at room temperature under similar irradiation conditions [2,8].

(ii) Photolysis of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in CH_4, Ar, CO, N_2, 5% $^{13}CO/CH_4$ and 5% C_2H_4 doped CH_4 matrices

Infrared spectra from an experiment with $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ isolated at high dilution (ca 1 : 2000 to 1 : 5000) in a pure CO matrix at 12 K are shown in Fig. 2. The spectrum before photolysis (Fig. 2(a)) showed two strong bands in the terminal CO stretching region at 2012.5 (A') and 1935.6 ($A' + A''$) cm^{-1} (expected for molecule having a $Cr(CO)_3$ moiety with C_s local symmetry), together with weak bands (bands marked *) which arise from $(\eta^5\text{-}C_5H_5)Cr(^{12}CO)_2(^{13}CO)CH_3$ in natural abundance. Irradiation with visible light (λ > 430 nm) produced two new bands (A) at 2020.0 and 1938.5 cm^{-1} (Fig. 2(b)), the lower wavenumber band being overlapped by the parent band at 1935.6 cm^{-1}. Further irradiation with the same photolysis source enhanced the intensities of the new bands at the expense of the parent bands (Fig. 2(c)). Annealing the matrix to ca 30 K for two minutes and then re-cooling to 12 K resulted in a reduction in the intensities of the new product bands (A) and regeneration of the bands for the starting complex (Fig. 2(d)). Similar product bands, together with a band for free CO (at ca 2140 cm^{-1}) were observed on photolysis of the parent complex in CH_4 and Ar matrices (Table 1).

The high dilution used, the increasing and decreasing of the new bands with a constant relative intensity, and the reversibility of the primary photoreaction rule

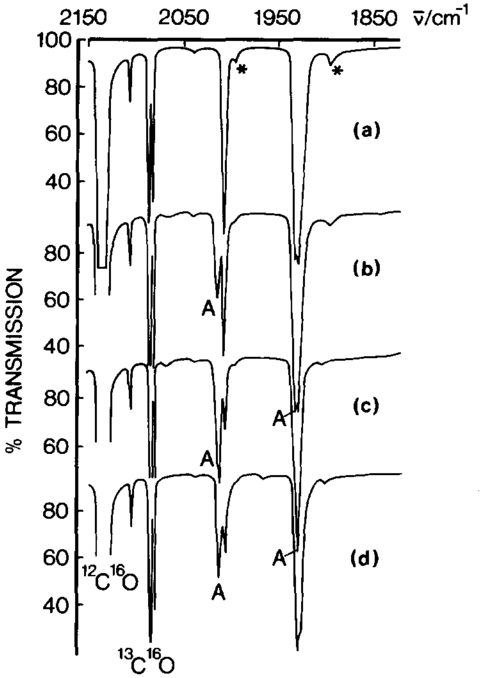

Fig. 2. Infrared spectra from an experiment with $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ isolated at high dilution in a CO matrix at ca 12 K: (a) after deposition, after 60 min photolysis with $\lambda > 430$ nm radiation, (c) after 180 min further photolysis using the same radiation, and (d) after annealing to ca 40 K for 2 min. Bands marked A are due to photoproduct (see text). Bands marked * are due to $(\eta^5\text{-}C_5H_5)Cr(^{12}CO)_2(^{13}CO)CH_3$ present in natural abundance.

out a polynuclear species and indicate a single new product (A) formed via a simple reaction process, viz. ejection of a CO ligand. The large shift to lower wavenumbers of the bands for $(\eta^5\text{-}C_5H_5)Mo(CO)_2CH_3$ (ν(CO) at 1966.0 and 1880.1 cm^{-1}; CH_4) compared with those for $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ (ν(CO) at 2023.9 and 1937.0 cm^{-1}; CH_4), observed previously [14], however, enables the coordinately unsaturated 16-electron species, $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ to be discounted. This species was observed to form in PVC films, under different irradiation conditions, as described below. Similarly, separate experiments with $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ (ν(CO) at 2016.7, 1943.6 and 1932.7 cm^{-1}) in CO matrices at 12 K ruled out this compound and its photoproducts, i.e. $(\eta^5\text{-}C_5H_5)Cr(CO)_3^{\cdot}$ (ν(CO) at 1986.3, 1910.4 and 1902.3 cm^{-1}) and $HCO^{\cdot}$ (ν(CO) at 1859.2 cm^{-1}) [16].

In order to establish the identity of the new metal-containing product experiments were carried out using 5% ^{13}CO doped CH_4 matrices. Initial brief irradiation caused some $^{13}CO/^{12}CO$ exchange in the parent complex but longer photolysis rapidly destroyed any $(\eta^5\text{-}C_5H_5)Cr(^{12}CO)_{3-n}(^{13}CO)_nCH_3$ complexes ($n = 0$–2) and produced new $^{13}CO/^{12}CO$ bands corresponding to the ^{12}CO enriched photoproduct. The $^{13}CO/^{12}CO$ enrichment bands were subjected to an energy-factored force-field fitting procedure for metal carbonyl fragments, which has been described elsewhere [17]. Comparison of the observed and calculated band positions for the new species revealed that the bands arose from a $Cr(CO)_2$ fragment rather than a

Table 1

Infrared band positions (cm^{-1}) observed in the CO stretching region for $(\eta^5\text{-}C_5H_5)M(CO)_3CH_3$ complexes (M = Cr, Mo, W) and their photoproducts in various gas matrices and PVC films at 12 K

Complex	CH_4	Ar	N_2	CO	5% C_2H_4/CH_4	PVC
$(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$	2013.5	2020.7	2015.5	2013.5	2011.3	2006
	1937.2	1946.3	1939.2	1936.6	1936.8	1925
$(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ [a]	2023.4	2030.7	2028.6	2025.8	2021.8	2016
	1937.9	1945.8	1941.4	1945.2 1938.8	1935.8	1924
$(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ [a]	2020.8	–	2024.7	2020.8	2020.0	2012
	1929.6	–	1933.8	1932.2 1928.5 [b]	1928.6	1910
$(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$	[d]	[d]	[d]	[d]	[d]	1951
						1863
$(\eta^5\text{-}C_5H_5)Mo(CO)_2CH_3$ [a]	1966.0	1972.0	1972.8	1962.4	1964.7	1949
	1880.1	1886.0	1884.4	1876.8 [c]	1876.5	1857
$(\eta^5\text{-}C_5H_5)W(CO)_2CH_3$ [a]	1953.8	–	1957.6	1950.8	1952.6	1939
	1861.0	–	1864.7	1861.3	1860.5	1840
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(THF)CH_3$ [f]			[e]			1915
						1835
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(THF)CH_3$ [a]			[e]			1920
						1820
$(\eta^5\text{-}C_5H_5)W(CO)_2(THF)CH_3$ [a]			[e]			1920
						1803
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(=CH_2)H$	2019.3	2023.8	2031.5	2020.0	2017.2	2014
	1938.3	1943.1	1940.2	1938.5	1937.2	1928

[a] Data from references 5, 7 and 14. [b] Matrix splitting. [c] Long photolysis time required. [d] Species not observed under irradiation conditions employed. [e] Species not studied in gas matrices. [f] Formed on warming films from 12 K.

$Cr(CO)_3$ fragment (Table 2), which is consistent with the observation of free CO in CH_4 and Ar matrices. In order to produce higher wavenumber bands than for $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ on ejection of a CO ligand some other π-acceptor ligand must have become coordinated to the metal. Since this ligand must have been previously coordinated to the metal in some form, it is proposed * that α-H elimination follows CO dissociation and that the new photoproduct is $(\eta^5\text{-}C_5H_5)Cr(CO)_2(=CH_2)H$. Comparison of the interaction force constant ($k_i = 66.6$ Nm^{-1}) with those for $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ ($k_{cis} = 43.8$ and $k_{trans} = 49.0$ N m^{-1}) suggests that CO ligands and the hydride and methylene ligands are *trans* to one another. Support for the *trans* configuration is afforded by the observation that on complete photodestruction of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ the lower band of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(=CH_2)H$ is more intense than the upper band, i.e. $I_{antisym}/I_{sym} > 1$.

Irradiation of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in reactive gas matrices e.g. N_2 and 5% C_2H_4 doped CH_4 matrices produced the same product $(\eta^5\text{-}C_5H_5)Cr(CO)_2(=CH_2)H$ (Table 1), i.e. no bands were observed for the photosubstitution products $(\eta^5\text{-}C_5H_5)Cr(CO)_2(N_2)CH_3$ and $(\eta^5\text{-}C_5H_5)Cr(CO)_2(C_2H_4)CH_3$.

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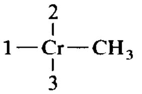
[*] It had been hoped to demonstrate the Cr–H bond using ν(Cr–H) and the appropriate isotopic shift on deuteriation. However, ν(Cr–H) bands in this species and $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ are extremely weak and so this means of verification proved impossible.

Table 2

Observed and calculated band positions (cm^{-1}) of terminal CO stretching bands in an experiment with (η^5-C_5H_5)Cr(CO)$_3$CH$_3$ in a 5% ^{13}CO doped CH$_4$ matrix at 12 K

Complex	ν(CO)	Observed	Calculated
(η^5-C_5H_5)Cr(^{12}CO)$_3$CH$_3$ [a]	A'	2011.5	2011.5
C_s	$A' + A''$	1935.7	1935.7
(η^5-C_5H_5)Cr(^{12}CO)$_2$(^{13}CO)CH$_3$	A'	[f]	2002.7
C_s [b]	A''	[g]	1935.5
	A'	[h]	1900.7
	A	1998.5	1996.3
C_1 [c]	A	[g]	1936.3
	A	[h]	1906.1
(η^5-C_5H_5)Cr(^{12}CO)(^{13}CO)$_2$CH$_3$	A	[i]	1992.8
C_1 [d]	A	[j]	1909.4
	A	[k]	1893.3
	A'	1985.2	1984.8
C_s [e]	A'	[l]	1917.9
	A''	[k]	1892.5
(η^5-C_5H_5)Cr(^{13}CO)$_3$CH$_3$	A'	[m]	1966.3
C_s	$A' + A''$	[m]	1892.1
(η^5-C_5H_5)Cr(^{12}CO)$_2$(=CH$_2$)H [n]	A'	2016.5	2015.6
C_s	A''	1933.0	1932.0
(η^5-C_5H_5)Cr(^{12}CO)(^{13}CO)(=CH$_2$)H	A	1998.5	1998.6
C_1	A	1905.8	1905.1
(η^5-C_5H_5)Cr(^{13}CO)$_2$(=CH$_2$)H	A'	1969.8	1970.4
C_s	A''	1888.0	1889.0



$$1-\underset{\substack{|\\3}}{\overset{\substack{2\\|}}{\mathrm{Cr}}}-\mathrm{CH_3}$$

$1 \neq 2 = 3$

[a] Refined energy-factored force constants for (η^5-C_5H_5)Cr(CO)$_3$CH$_3$: $K_1 = 1568.0$, $K_2 = 1546.7$, $k_{12} = 42.6$ and $k_{23} = 32.0$ Nm^{-1} as defined by the numbering above. [b] ^{13}CO in position 1. [c] ^{13}CO in position 2. [d] ^{12}CO in position 2. [e] ^{12}CO in position 1. [f] Unresolved band, obscured by the band of (η^5-C_5H_5)Cr(^{12}CO)(^{13}CO)(=CH$_2$)H at 1998.6 cm^{-1}. [g] Obscured by the lower parent band at 1935.7 cm^{-1}. [h] Obscured by the band of (η^5-C_5H_5)Cr(^{12}CO)(^{13}CO)(=CH$_2$)H at 1905.1 cm^{-1}. [i] Obscured by the band of (η^5-C_5H_5)Cr(^{12}CO)(^{13}CO)(=CH$_2$)H at 1998.6 cm^{-1}. [j] Obscured band. [k] Obscured band. [l] Very weak. [m] Very weak bands were observed for (η^5-C_5H_5)Cr(^{12}CO)(^{13}CO)$_2$CH$_3$, but no (η^5-C_5H_5)Cr(^{13}CO)$_3$CH$_3$ species was generated. [n] Refined energy-factored force constants for (η^5-C_5H_5)Cr(CO)$_2$(=CH$_2$)H: $K = 1574.6$ and $k_i = 66.6$ N m^{-1}.

(iii) Photolysis of (η^5-C_5H_5)Cr(CO)$_3$CH$_3$ in PVC films at 12 K

The infrared spectrum of the complex (η^5-C_5H_5)Cr(CO)$_3$CH$_3$ at 12 K in a PVC film (2 mg/500 mg) cast from a dichloroethane solution (298 K) showed bands at 2006 (A') and 1925 cm^{-1} ($A' + A''$) (Fig. 3(a)). Irradiation into the long wave UV absorption (λ_{max}: 360 nm, Fig. 1(a)) for the complex produced new bands in the electronic absorption spectrum in the region 260–340 nm and a much weaker band in the visible region (λ_{max}: 560 nm, Fig. 1(b)). During irradiation, new bands (A and B) grew in the infrared spectrum at ca 2014, 1951, ca 1928 and 1863 cm^{-1}, along with a band for free CO, whilst the parent bands decreased in intensity (Fig. 3(b)). The new bands (A) at 2014 and 1928 cm^{-1}, which were overlapped by the parent bands, were revealed on subtracting the parent bands from the spectrum (Fig. 3(c)). On subsequently warming the film from 12 K to ca 90 K, the bands (A) disappeared

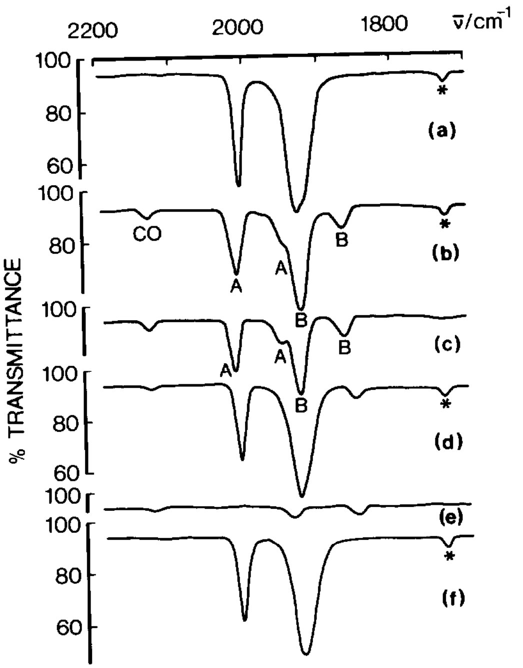
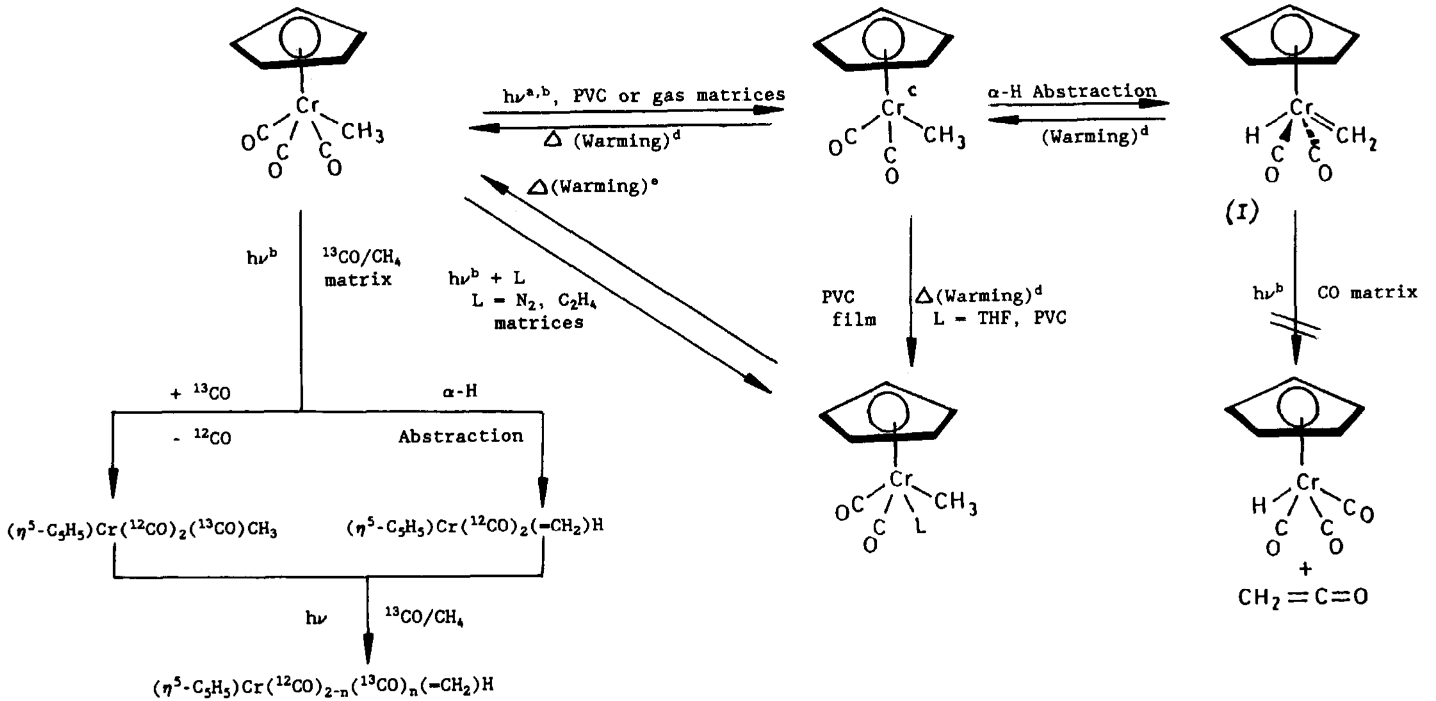


Fig. 3. Infrared spectra from an experiment with $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in a PVC film (cast from dichloroethane solution) at ca. 12 K: (a) before irradiation, (b) after 20 min irradiation ($300 < \lambda < 370$ nm), (c) spectral subtraction ($\{b\} - R\{a\}$, where R is a scaling factor), (d) after warming the film to ca 90 K and recooling to 12 K, (e) spectral subtraction ($\{d\} - S\{a\}$, where S is a scaling factor), (f) after warming the film to ca 130 K. Bands marked A and B are for products (see text) and that marked * is due to ketone groups in the PVC.

whilst the bands for the parent complex increased in intensity. At the same time, the other new bands (B) decreased and shifted to lower wavenumbers (ca 15 cm^{-1}) relative to the parent bands (Fig. 3(d)). The shift in the band (B) at 1951 cm^{-1} was revealed on subtracting the parent bands from the spectrum obtained on warming the film to ca 90 K and recooling to 12 K (Fig. 3(d)). At this stage, it was evident that the new visible absorption band, observed after irradiation had shifted to a shorter wavelength (*C*, λ_{nm}: 500 nm, Fig. 1(c)). This band and the shifted infrared bands (B) disappeared on subsequently warming the film from ca 100 to ca 130 K, which led to further regeneration of the parent complex $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ (Fig. 3(e)).

The main product infrared bands (A) seen at ca 2014 and ca 1922 cm^{-1}, in an intensity ratio of approximately 1 : 1.5 (Fig. 3(c)) are analogous to those observed on irradiation of the parent complex in the frozen gas matrices (see above) and are assigned to *trans*-$(\eta^5\text{-}C_5H_5)Cr(CO)_2(=CH_2)H$.

The product infrared bands (B) and the visible absorption (λ_{max}: 560 nm) observed after irradiation of the film at 12 K (Figs. 3(b) and 1(b)) are assigned to the 16-electron species $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$, produced via loss of a CO ligand from $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$, cf. the species $(\eta^5\text{-}C_5H_5)M(CO)_2CH_3$ (M = Mo or W) seen to form previously in PVC films at 12 K (Table 1). The observed shift to lower wavenumbers of the bands (B) and the blue shift of the visible absorption on



Scheme 1. (a) $300 < \lambda < 370$ nm; (b) $\lambda > 430$ nm; (c) observed in PVC films; (d) $12 < T < 50$ K; (e) $T > 100$ K for L = Cl and H in PVC and $T > 200$ K for L = THF.

warming and recooling the film are similar to the spectral changes observed for $(\eta^5\text{-}C_5H_5)M(CO)_2CH_3$ (M = Mo, W) in similar films [7,18] and may be interpreted in terms of the $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ fragment being coordinated at the metal by chlorine or hydrogen atoms (or impurity ketone groups) in the PVC.

Thermal conversion of the photogenerated species $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ and $(\eta^5\text{-}C_5H_5)Cr(CO)_2({=}CH_2)H$ to $(\eta^5\text{-}C_5H_5)Cr(CO)_2(THF)CH_3$ was observed on warming PVC films, doped with tetrahydrofuran (THF), from 12 to ca 80 K. The latter complex (Table 1), analogous to $(\eta^5\text{-}C_5H_5)W(CO)_2(THF)CH_3$ observed in a THF/hexane solution [19] at 196 K (ν(CO): 1912 and 1803 cm^{-1}), reacts thermally with CO in PVC films at temperatures above ca 200 K to form $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$.

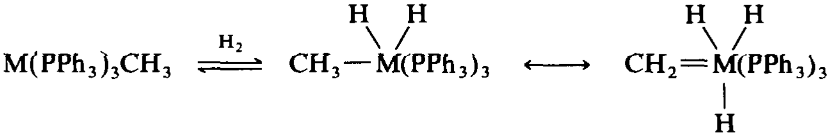
Irradiation ($290 < \lambda < 370$ nm) of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in PVC films (10 mg/500 mg) at room temperature (298 K) led to the formation of the dimer $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$. This product was identified from its infrared absorptions which were measured for an authentic sample of this complex in PVC films (ν(CO): 1944 and 1900 cm^{-1}) [20].

Discussion

The photoreactions of $(\eta^5\text{-}C_5H_5Cr(CO)_3CH_3$ observed in various gas matrices and in PVC films at 12 K are summarised in Scheme 1. Irradiation of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ leads to the formation of the carbene hydride complex *trans*-$(\eta^5\text{-}C_5H_5)Cr(CO)_2({=}CH_2)H$ (structure I) via photoinduced α-hydrogen abstraction from the methyl group in $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ both species being observed in PVC films under the irradiation conditions used in this study. In contrast, no evidence for a carbene complex was obtained [7,14] following irradiation of the molybdenum and tungsten analogues of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$, in gas matrices or PVC films at 12 K.

The fact that regeneration of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ from the carbene hydride complex was observed on annealing gas matrices to ca 30 K after irradiation and on warming PVC films to ca 50 K, indicates that α-hydrogen elimination in the species $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ is thermally reversible, cf. photochemically reversible β-elimination in $(\eta^5\text{-}C_5H_5)M(CO)_3C_2H_5$ in rigid media (eq. 4). Whether the thermal conversion of $(\eta^5\text{-}C_5H_5)Cr(CO)_2({=}CH_2)H$ to $(\eta^5\text{-}C_5H_5)Cr(CO)_2(L)CH_3$ (L = CO or THF) at such low temperatures (e.g. 50 K) actually proceeds via the 16-electron species $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ or via an associative mechanism, involving a reaction of the carbene complex with a ligand L in the immediate vicinity in the rigid medium, is not clear.

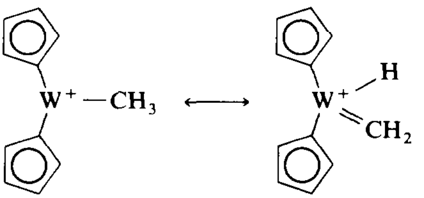
Reversible α-hydrogen abstraction from the methyl groups of $Co(PPh_3)_3CH_3$ and $Rh(PPh_3)_3CH_3$ involving intermediate carbene-hydride complexes, e.g. $(CH_2{=})MH_2(PPh_3)_3$ has recently been demonstrated [21] (eq. 7) (M = Co, Rh).



$$M(PPh_3)_3CH_3 \overset{H_2}{\rightleftharpoons} CH_3{-}\overset{H\ \ H}{\overset{\backslash\ /}{M}}(PPh_3)_3 \longleftrightarrow CH_2{=}\underset{H}{\overset{H\ \ H}{\overset{\backslash\ /}{M}}}(PPh_3)_3 \qquad (7)$$

Strong evidence for α-elimination is also provided by the isolation of $[(\eta^5\text{-}C_5H_5)_2W(CD_2)(P(C_6H_5)(CH_3)_2)D]^+$ from the reaction of $[(\eta^5\text{-}C_5H_5)_2W(\eta^2\text{-}$

$C_2H_4)CD_3]^+$ with $P(C_6H_5)(CH_3)_2$ [22]. It was proposed that the product arose via an equilibrium between two cationic intermediates (eq. 8).



(8)

Evidence for α-elimination in the chromium complexes $(C_6H_5CH_2CH_2CD_2CH_2)_3Cr \cdot 3$ THF and $(C_6H_5CH_2CH_2CH_2CD_2)_3Cr \cdot 3$ THF is inferred from the presence of $C_6H_5CH_2CH_2CD{=}CHD$ among the products. The presence of CH_2CD_2 and, after hydrolysis, of HD from the decomposition of $(CD_3)_3Cr \cdot 3$ THF also indicates a α-H elimination pathway [23]; a transitory carbene complex has been suggested as an intermediate [24].

A picosedond flash photolysis study of $(\eta^5\text{-}C_5H_5)W(CO)_3R$ (R = Me, Et) complexes in cyclohexane solution showed that the unsaturated CO-loss products, $(\eta^5\text{-}C_5H_5)W(CO)_2R$, were formed within 25 ps after the excitation pulse [25]. When $(\eta^5\text{-}C_5H_5)W(CO)_3Me$ was photolysed in cyclohexane with added tetrahydrofuran (THF; 0.002–1.0 *M*) the initially formed $(\eta^5\text{-}C_5H_5)W(CO)_2$ was found to be coordinated by THF and this was followed by the formation of a new intermediate. The degree to which this reaction occurred was found to be inversely dependent on [THF] while the rate of the reaction was independent of [THF]. It was proposed that the new product arises from α-elimination, i.e. a carbene is formed, e.g. $(\eta^5\text{-}C_5H_5)W(CO)_2({=}CH_2)H$ [25].

The $^{12}CO/^{13}CO$ exchange reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2({=}CH_2)H$ observed in matrices (Scheme 1) is consistent with the proposed CO dissociation of carbene complexes and reaction of the coordinatively unsaturated intermediates with ^{13}CO and olefins, and their roles in the olefin metathesis reactions, e.g. $(CO)_5W({=}C(C_6H_5)_2)$, $(CO)_5W({=}C(C_6H_5)H)$ and $(CO)_5M({=}C(OCH_3)C_6H_5)$ (M = Cr, Mo, W) complexes [26,27].

Irradiation of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in solution [1] in the presence of PPh_3 leads to the photosubstitution product $(\eta^5\text{-}C_5H_5)Cr(CO)_2(PPh_3)CH_3$. A subsequent step, in which migration of the methyl group from Cr to CO occurs followed by uptake of CO, leads to the formation of the acyl chromium complex $(\eta^5\text{-}C_5H_5)Cr(CO)_2(PPh_3)COCH_3$. Irradiation of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in frozen gas matrices (Scheme 1) in the presence of N_2 or C_2H_4 led only to the formation of the carbene complex $(\eta^5\text{-}C_5H_5)Cr(CO)_2{=}CH_2)H$; neither the photosubstitution products $(\eta^5\text{-}C_5H_5)Cr(CO)_2(L)CH_3$ (L = N_2 or C_2H_4) nor the acyl chromium complex $(\eta^5\text{-}C_5H_5)Cr(CO)_2(L)COCH_3$ were observed. In contrast, photolysis of the molybdenum and tungsten analogues of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in similar matrices [5] led to the complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)CH_3$ and $(\eta^5\text{-}C_5H_5)W(CO)_2(L)CH_3$. It is possible that the analogous chromium complexes are not photochemically stable under the irradiation conditions ($\lambda > 430$ nm) employed in this study.

Thermal generation of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(L')CH_3$ complexes (L' = THF, PVC) from $(\eta^5\text{-}C_5H_5)Cr(CO)_2({=}CH_2)H$ via $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ was, however, observed on warming the PVC films containing the potential ligands L'. Use of the polymer film media over the wide temperature range (12–298 K) permits the study of *secondary thermal reactions of photogenerated* $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ *and the* thermal reactivity of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(\text{solvent})CH_3$ (e.g. solvent = THF) which may *both be involved in the photosubstitution reactions of* $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ seen in solution [1,2].

No evidence was obtained for photoinduced cleavage of the Cr–CH$_3$ bond in $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ or $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ in gas matrices or PVC films at 12 K. In the 16-electron species, α-hydrogen elimination appears to be the dominant photoprocess. It is interesting to note, however, that no evidence for the photoconversion of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(=CH_2)H$ to the hydride $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ was observed in CO matrices (Scheme 1) which indicates that the α-elimination reaction in $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ does not provide a pathway for the dealkylation of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ (c.f. the β-hydrogen elimination in eqs. 3–5). The dealkylation of the methyl complex actually observed in PVC films at room temperature (eq. 9), also seen in hydrocarbon solvents, may arise from a thermal reaction between $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ and unreacted $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ molecules (eqs. 10–13).

$$2(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Cr_2(CO)_6 + C_2H_6 \tag{9}$$

$$(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3 + CO \tag{10}$$

$$(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Cr(CO)_2(=CH_2)H \tag{11}$$

$$(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3 + (\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3 \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)_2Cr_2(CO)_5 + 2\,CH_3^{\cdot} \tag{12}$$

$$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_5 + CO \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6 \tag{13}$$

Similar reaction steps (c.f. eqs. 12 and 13) have been proposed by Tyler et al. to be involved in the observed dealkylation of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ in solutions [19]. In the PVC films at room temperature large molecules appear to have sufficient mobility for bimolecular processes (cf. eq. 12) to occur. At low temperatures ($T < 200$ K), however, a back reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ with CO (eq. (10) appears to be a more facile process in the films.

In contrast to the flash photolysis report (UV-Vis dection) of the formation of $(\eta^5\text{-}C_5H_5)W(CO)_2(=CH_2)(H)$ by α-elimination from $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ no such process was observed at 12 K for either $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ or $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ isolated in gas matrices or dispersed in PVC films [5,7]. It is to be hoped that a future flash photolysis study coupled with infrared detection [28], which provides more definitive structural information than UV-Vis detection, can be carried out in order to characterise the species, especially the new tungsten species seen in cyclohexane solutions in the presence of THF.

Conclusions

The primary photoprocesses observed for $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ in frozen matrices and PVC films at 12 K is dissociative loss of a CO ligand to form the 16-electron species $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$. This species undergoes photo-induced ($\lambda > 430$ nm) α-hydrogen elimination to form the carbene hydride complex *trans-*

$(\eta^5\text{-}C_5H_5)Cr(CO)_2(=CH_2)H$. This process is thermally reversible at temperatures as low as 30 K with conversion of the carbene complex to $(\eta^5\text{-}C_5H_5)Cr(CO)_2(L)CH_3$ complexes (L = CO or THF) being seen in PVC films.

The photochemistry of the species $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ contrasts with that observed for the molybdenum and tungsten analogues in low temperature media where no evidence for α-hydrogen elimination was obtained. The conversion of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ to $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$ seen in PVC films and solutions irradiated at room temperature may result from a reaction between $(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3$ or $(\eta^5\text{-}C_5H_5)Cr(CO)_2(\text{solvent})CH_3$ species and unreacted molecules of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ rather than from photoinduced cleavage of the Cr–CH_3 bond or α-hydrogen abstraction.

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