Matrix Isolation Evidence for Reversible α-Elimination of Hydrogen from a Chromium Methyl Compound to give a Chromium Methylene Hydride Species

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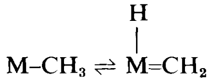
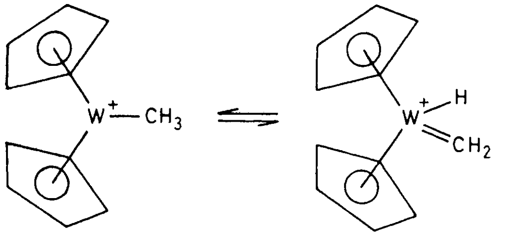
I.r. spectroscopic evidence, including ^{13}CO labelling and energy-factored force-field fitting, is presented to show that photolysis of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3]$ in gas matrices at 12 K leads to a methylene hydride species, $[(\eta^5\text{-}C_5H_5)Cr(CO)_2(CH_2)H]$, following CO dissociation and α-H elimination reactions and that this process is reversible.

Reversible elimination of hydrogens from carbons which are in β-positions relative to transition metals has been widely established to occur and to be important in catalytic reactions, *e.g.* olefin isomerisation. Although less well documented, elimination involving hydrogens in the α-position may also occur [equation (1)] and may be important in generating active intermediates in metal catalysed disproportionation reactions.[1,2] Strong evidence for α-elimination is the isolation of



$$\mathrm{M{-}CH_3} \rightleftharpoons \overset{\displaystyle \mathrm{H}}{\overset{|}{\mathrm{M}}}\mathrm{{=}CH_2} \qquad (1)$$

$[(\eta^5\text{-}C_5H_5)_2W(CD_2PPhMe_2)D]^+$ from the reaction of $[(\eta^5\text{-}C_5H_5)_2W(\eta^2\text{-}C_2H_4)CD_3]^+$ with $PPhMe_2$.[3] It was proposed that the product arose *via* an equilibrium between two cationic intermediates [equation (2)]. Evidence for α-elimination for the chromium complexes $[(PhCH_2CH_2CD_2CH_2)_3Cr{\cdot}3thf]$ (thf = tetrahydrofuran) and $[(PhCH_2CH_2CH_2CD_2)_3Cr{\cdot}3thf]$ is inferred from the presence of $PhCH_2CH_2CD{=}CHD$ among the products. The presence of CH_2CD_2 and, after hydrolysis, of HD from the decomposition of $[(CD_3)_3Cr{\cdot}3thf]$ also indicates a α-H elimination pathway;[4] a transitory carbene complex has been suggested as an intermediate.[5] In this communication we report matrix isolation evidence for a reversible process which is interpreted as involving a chromium methylene hydride species.



(2)

I.r. 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 Figure 1. The spectrum before photolysis [Figure 1(a)] showed two strong bands in the terminal CO stretching region at 2012.5 and 1935.6 cm^{-1} together with weak 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 at 2020.0 and 1938.5 cm^{-1} [Figure 1(b)]. Further irradiation with the same photolysis source enhanced the intensities of the new bands at the expense of the parent bands [Figure 1(c)]. Annealing the matrix to *ca.* 30 K for two minutes and then recooling to 12 K resulted in a reduction in the intensities of the new product bands and regeneration of the bands of the starting complex [Figure 1(d)]. Similar bands together with a band due to 'free' CO were observed for CH_4, Ar, N_2, and even 5% C_2H_4 doped CH_4 matrices, in which the analogous Mo and W complexes gave $[(\eta^5\text{-}C_5H_5)M(CO)_2(C_2H_4)CH_3]$ complexes (M = Mo, W).[7]

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 out a polynuclear species and indicate a single new product 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),[6] however, enables the co-ordinatively unsaturated 16 electron species, $[(\eta^5\text{-}C_5H_5)Cr(CO)_2CH_3]$ to be discounted. 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 $[(\eta^5\text{-}C_5H_5)Cr(CO)_3{\cdot}]$ (ν_{CO} at 1986.3, 1910.4, and 1902.3 cm^{-1}) and $HCO{\cdot}$ (ν_{CO} at 1859.2 cm^{-1}).[7] 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—3) and produced new $^{13}CO/^{12}CO$ bands corresponding to the ^{12}CO 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.[8,9] 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 $[Cr(CO)_3]$ fragment (Table 1), 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 co-ordinated to the metal. Since this ligand must have been previously co-ordinated to the metal in some form, it is proposed that α-H elimination follows CO dissociation and that the new photoproduct is $[(\eta^5\text{-}C_5H_5)Cr(CO)_2(CH_2)H]$‡ (Scheme 1). Comparison of the interaction force constant (k_I = 66.6 $N\,m^{-1}$)

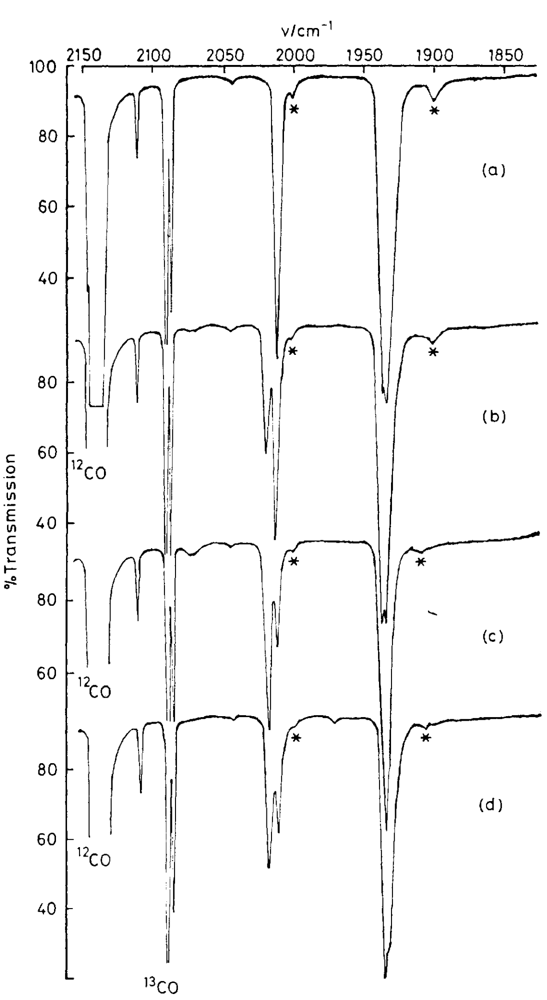


Figure 1. Infrared spectra from an experiment with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3]$ isolated at high dilution in a CO matrix at 12 K: (a) after deposition, (b) after 60 min photolysis with λ >430 nm radiation, (c) after 180 min further photolysis using the same radiation, and (d) after annealing for 2 min. Bands marked (*) are due to $[(\eta^5\text{-}C_5H_5)Cr(^{12}CO)_2(^{13}CO)CH_3]$ present in natural abundance.

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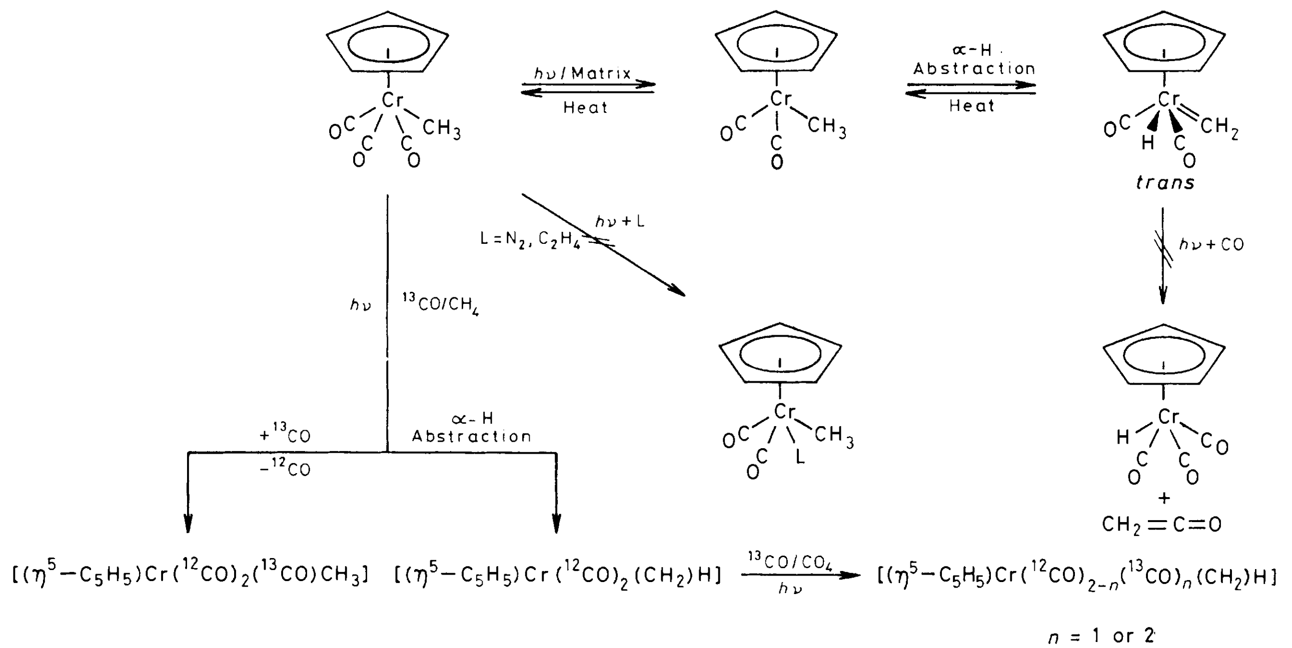
† Details of the 12 K cryostat and vacuum system, techniques for achieving high dilution matrices, i.r. spectrometers, the photolysis lamp and filters to effect wavelength-selective photolysis, and matrix gases have been described previously.[6]

‡ 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} in this species and $[(\eta^5\text{-}C_5H_5)Cr(CO)_3H]$[7] is extremely weak and so this means of verification proved impossible.



Scheme 1

Table 1. Observed and calculated[a] band positions (cm^{-1}) of terminal CO stretching modes for the photolysis products formed from [(η^5-C_5H_5)Cr(CO)$_3$CH$_3$] in 5% ^{13}CO doped CH$_4$ matrices at 12 K.

Complex	CO	Observed	Calculated
[(η^5-C_5H_5)Cr(^{12}CO)$_2$(CH$_2$)H]	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

[a] Refined energy-factored stretching (K) and interaction (k_i) 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}.

with those for [(η^5-C_5H_5)Mo(CO)$_3$CH$_3$] (k_{cis} = 43.8 and k_{trans} = 49.0 N m^{-1})[6] 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 [(η^5-C_5H_5)Cr(CO)$_3$CH$_3$] the lower band of [(η^5-C_5H_5)Cr(CO)$_2$(CH$_2$)H] is more intense than the upper band, *i.e.* $I_{\text{antisym}}/I_{\text{sym}} > 1$.

This work provides the *first* direct evidence for reversible elimination of α-hydrogen and sets proposed carbene hydride reaction intermediates on a firmer basis, *e.g.* equation (2).

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