Ethene Complexes of Chromium; the Generation and Characterisation of $[Cr(CO)_5(C_2H_4)]$ and *cis*- and *trans*-$[Cr(CO)_4(C_2H_4)_2]$ and their Relative Stabilities in Liquid Xenon Solution

Marion F. Gregory, Sarah A. Jackson, Martyn Poliakoff, and James J. Turner*

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.

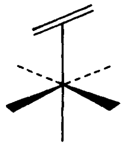
The unstable complexes $[Cr(CO)_5(C_2H_4)]$ and *cis*- and *trans*-$[Cr(CO)_4(C_2H_4)_2]$ are generated by photolysis of $[Cr(CO)_6]$ in C_2H_4-doped liquid xenon and are characterised by i.r. spectroscopy; these complexes are all unstable, even at −78 °C with the *cis*-$[Cr(CO)_4(C_2H_4)_2]$ complex being the least stable, decomposing with an enthalpy of activation, $\Delta H^{\ddagger}$, of ~60 kJ mol^{-1}.

Since alkene complexes of transition metals play an important role in many catalytic and photocatalytic reactions,[1] there has been considerable interest in their photochemistry.[2] In early experiments[3] $[W(CO)_5L]$ and $[W(CO)_4L_2]$ (L = propylene and η^2-butadiene) were isolated following photolytic generation from $[W(CO)_6]$ and the appropriate alkene in n-hexane solution. Several other alkene (and alkyne) compounds were identified by i.r. spectroscopy, notably the mono and bis C_2H_4 complexes of Mo and W;† the bis complexes were originally assigned the *trans*-structure on the basis of a single observed ν(C–O) band. The formation of a *trans*-compound is somewhat surprising since most photochemical substitution reactions[2] generate predominantly the *cis*-$[M(CO)_4L_2]$ compound, the theoretically preferred pathway [equation (1)].[4]

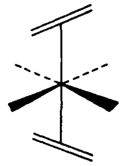
$$[M(CO)_5L] + L' \xrightarrow{h\nu} cis\text{-}[M(CO)_4LL'] + CO \quad (1)$$

Furthermore, matrix isolation experiments[5] suggest that in the primary photochemical step $[M(CO)_5(\text{alkene})]$ compounds lose a *cis* CO group.

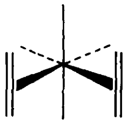
Until the recent photochemical preparation[6] of $[Cr(CO)_5(\eta^2\text{-}cis\text{-cyclo-octene})]$ and its subsequent thermal reactions to give $[Cr(CO)_5(tr\text{-cyo})]$ (*tr*-cyo = *trans*-cyclooctene) and the *trans*-disubstituted complexes, no complexes of Cr involving purely hydrocarbon alkene ligands had been reported. We have already shown,[7] using *liquid* noble gases as solvents in special high-pressure cells, that a wide variety of unstable organometallic species can be generated photolytically and studied by i.r. spectroscopy. In this communication we show that this technique can be used to generate *three* previously unknown ethene complexes of Cr, $[Cr(CO)_5(C_2H_4)]$ (M), *trans*-$[Cr(CO)_4(C_2H_4)_2]$ (T), and most significantly *cis*-$[Cr(CO)_4(C_2H_4)_2]$ (C). All the compounds



(M)



(T)



(C)

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† *trans*-$[W(CO)_4(C_2H_4)_2]$ has recently been isolated as a crystalline solid at room temperature; F-W. Grevels, personal communication.

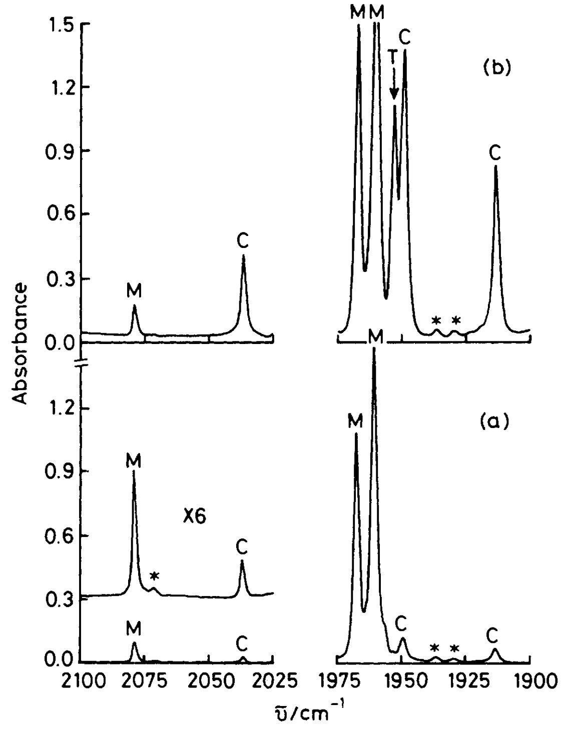

Figure 1. I.r. spectra in the ν(C–O) region following u.v. photolysis of $Cr(CO)_6$ in liquid xenon at −78 °C: (a) with a low pressure, ~2 atm, of C_2H_4 and (b) under a higher pressure, ~10 atm, of C_2H_4. The bands are labelled as follows; (M) $[Cr(CO)_5(C_2H_4)]$ and * natural abundance $[Cr(CO)_4(^{13}CO)(C_2H_4)]$; (C) *cis*-$[Cr(CO)_4(C_2H_4)_2]$; (T) *trans*-$[Cr(CO)_4(C_2H_4)_2]$. The high wavenumber region of spectrum (a) is also shown with a ×6 expanded absorbance scale. Note that the absorptions of dissolved C_2H_4 and $[Cr(CO)_6]$ have been removed by computer subtraction.

were thermally unstable under the conditions of our experiment, with (M) being the most stable and (C) the least.

Figure 1 shows the changes which occur in the ν(C–O) stretching region of the i.r. spectrum, after u.v. photolysis of a solution of $[Cr(CO)_6]$ in liquid Xe doped with C_2H_4 at −78 °C. Only the i.r. bands labelled (M) are observed with significant intensity after brief u.v. photolysis in a solution containing low concentrations of C_2H_4, Figure 1a. When higher concentrations of C_2H_4 are used, bands due to secondary photolysis products, (C) and (T), are observed, Figure 1b. These bands are due to two *different* photoproducts since, during photolysis, the band labelled (T) grows in intensity much more slowly than those labelled (C). The difference between these bands is further underlined by the changes observed when the solution was left to stand in the dark, Figure 2. Clearly, the band (C) decayed faster than (T), which in turn decayed faster than (M). There were also changes in the spectrum between 1600 and 1000 cm⁻¹ (not illustrated). This is a region associated with the vibrations of alkenes and these changes confirmed that photolysis was promoting substitution of CO by coordinated C_2H_4.

Table 1 lists the wavenumbers of the observed ν(C–O) bands. The bands of (M) and (T) are sufficiently close in frequency to those of $[Cr(CO)_5(tr\text{-cyo})]$ and *trans*-$[Cr(CO)_4(tr\text{-cyo})_2]$ for a preliminary assignment to mono-C_2H_4 and *trans*-bis-C_2H_4 complexes. Since *cis*-$[Cr(CO)_4(tr\text{-cyo})_2]$ is unknown, the bands of (C) can only be compared to those of a $[Cr(CO)_4(\text{diene})]$ complex. Nevertheless, the similarity of the spectra is striking, suggesting that (C) is *cis*-$[Cr(CO)_4(C_2H_4)_2]$.

Table 1. Wavenumbers, cm⁻¹, of ν(C–O) bands of the ethene complexes (M), (T), and (C) of chromium and related alkene complexes in liquid xenon solution at −78 °C.

$[Cr(CO)_5(C_2H_4)]$, (M)	$[Cr(CO)_5(tr\text{-cyo})]$	Assignment, C_{2v}
2078.9	2072.1	a_1
(1992.7)[a,b]	1992.4[b]	a_1
1967.4	1960.4	b_1
(1960.8)[a]	1957.6	a_1
1960.4	1953.6	b_2
trans- $[Cr(CO)_4(C_2H_4)_2]$, (T)	*trans*- $[Cr(CO)_4(tr\text{-cyo})_2]$	Assignment D_{2d}
1953.1	1937.1	e
	[1972.9][c]	b_2
cis- $[Cr(CO)_4(C_2H_4)_2]$,[d] (C)	*cis*- $[Cr(CO)_4(\text{nbd})]$[e]	Assignment C_{2v}
2036.8	2030.2	a_1
(1954.3)[f]	1955.7	a_1
1949.3	1944.2	b_1
1913.4	1913.2	b_2

[a] Calculated value using force constants, N m⁻¹: k_{ax} 1573.5; k_{eq} 1616.8; $k_{eq'}$ 1605.9; $k_{ax,eq} = k_{eq,eq}(cis)$ 29.9; and $k_{eq,eq}(trans)$ 52.7; r.m.s. error 0.3 cm⁻¹; 9 observed frequencies. See ref. 8. [b] I.r. inactive under C_{4v} symmetry. [c] Very weak, only observed in n-hexane at room temperature, ref. 6. [d] Mo analogue 2050, 1958, and 1914 cm⁻¹; W analogue 2050, 1957, and 1910 cm⁻¹. [e] n-Hexane solution room temperature from ref. 10; nbd = norbornadiene. [f] Calculated using force constants, N m⁻¹: k_1 1586.6; k_2 1529.6; k_{11} 51.6; k_{12} 29.7, and k_{22} 50.2; r.m.s. error 0.2 cm⁻¹; 7 observed frequencies. This a_1 band was presumably not observed because it is predicted to be almost co-incident with the e band of (T).

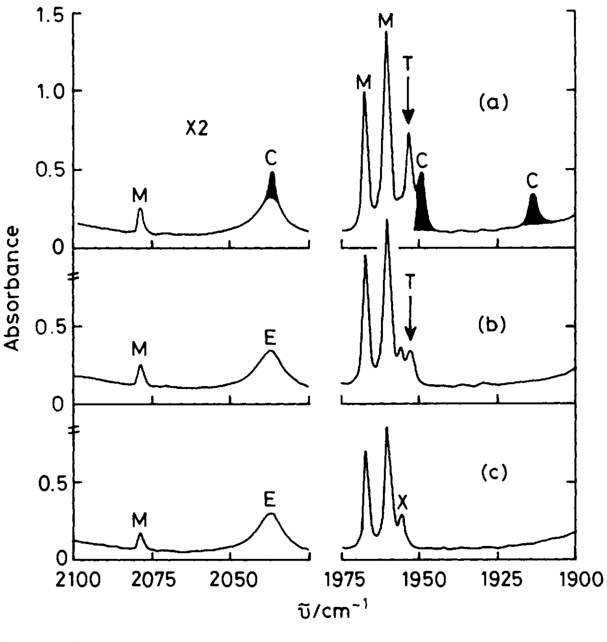

Figure 2. I.r. spectra illustrating the thermal decay of the chromium ethene complexes (M), (C), and (T) in liquid Xe at −78 °C: (a) after prolonged u.v. photolysis [note that band of (T) is now more intense than those of (C)], (b) after standing for 12 h during which time (C) has completely decayed, (c) after a further 18 h; (T) has now also completely decayed. Note that the high wavenumber region is plotted with ×2 absorbance expansion relative to the low frequency region. The broad band labelled E is due to dissolved C_2H_4, the band X is due to natural abundance $[Cr(CO)_5(^{13}CO)]$, and the other bands are labelled as in Figure 1.

The identities of (M), (C), and (T) were then confirmed by ^{13}CO enrichment and force-field calculations. The ^{13}CO-enriched species were generated by photolysis of $[Cr(CO)_5(^{13}CO)]$[6] and C_2H_4 in liquid xenon. The wavenumbers and relative intensities of the ν(C–O) bands were then fitted to particular geometries of the metal carbonyl moiety using a C–O factored force field.[9] These calculations show that (M) contains a $Cr(CO)_5$ moiety. Intuitively, one would expect this $Cr(CO)_5$ moiety to have local C_{4v} symmetry with the observed i.r. bands assigned $(2a_1 + e)$. In reality, we find that the co-ordinated C_2H_4 lowers the symmetry to C_{2v}, as already observed[6] for $[Cr(CO)_5(tr\text{-cyo})]$, and the band assignment is rather more complicated, see Table 1. The observed spectrum of ^{13}CO-enriched (C) is consistent with a C_{2v} $Cr(CO)_4$ moiety as expected for *cis*-$[Cr(CO)_4(C_2H_4)_2]$.

For (T), few ν(C–O) bands were observed even with ^{13}CO enrichment but, nevertheless, these were sufficient to confirm the presence of a pseudo-D_{4h} $Cr(CO)_4$ moiety, corresponding to *trans*-$[Cr(CO)_4(C_2H_4)_2]$, probably with D_{2d} symmetry like that of *trans*-$[W(CO)_4(tr\text{-cyo})_2]$.[6]

Similar experiments with $[Mo(CO)_6]$ and $[W(CO)_6]$ provided evidence for the formation not only of the known $[M(CO)_5(C_2H_4)]$ and *trans*-$[M(CO)_4(C_2H_4)_2]$ compounds, but also of the previously unknown Mo and W analogues of (C), *cis*-$[M(CO)_4(C_2H_4)_2]$. As illustrated in Figure 2, all three chromium complexes are unstable, although under the same conditions the corresponding Mo and W complexes are stable indefinitely.

We have studied the thermal decay of (C) in some detail.‡ Surprisingly, (C) does not appear to isomerize to (T). The decay is pseudo-first-order over several half lives and the rate of decay is inversely proportional to the concentration of dissolved C_2H_4, perhaps indicating a dissociative pathway. At −74 °C, under the conditions of Figure 2, (C) decayed with a pseudo-first-order rate constant of $1 \times 10^{-2}\ s^{-1}$ and over the temperature range −60 to −90 °C, the enthalpy of activation, $\Delta H^{\ddagger}$, is $60 \pm 5\ kJ\ mol^{-1}$.

The greater thermal stability of *trans*-bis-alkene complexes relative to the *cis* has previously been rationalised[11] in terms of 'd orbital sharing.' A CO group has two orthogonal π acceptor orbitals while C_2H_4 has only one. This means that there will always be competition for π-bonding d electrons between C_2H_4 and a CO group *trans* to it. However, there will be no competition between the two *trans* C_2H_4 groups, oriented with their C=C bonds at right angles as in (T). Thus, a *trans* CO group would be expected to weaken the M–alkene bond and (C) will be less stable than (T). The same argument suggests that $[M(CO)_5(C_2H_4)]$, which has a *trans* CO group, should be *less* stable than *trans*-$[M(CO)_4(C_2H_4)_2]$, which does not. It is therefore surprising to note that in our experiments with Cr, (M) is *more* stable than (T).

We are now extending our experiments in liquid xenon to reactions of $[Cr(CO)_5(alkene)]$ complexes with H_2 in an attempt to prepare mixed H_2–alkene complexes.

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‡ The liquid Xe contains a mixture of species [*i.e.* unphotolysed $Cr(CO)_6$, (M), (C), and (T)] but there is no indication that the decay of either (C) or (T) is catalysed by other species.