Organometallics **1997,** *16,* 5260−5268

Matrix Isolation Study into the Mechanism of Photoinduced Cyclization Reactions of Chromium Carbenes

M. Louise Gallagher, J. Barry Greene, and A. Denise Rooney*

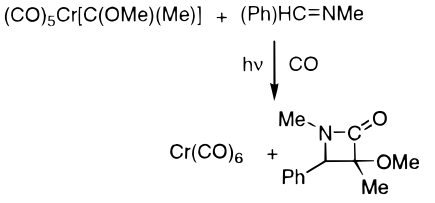
Department of Chemistry, National University of Ireland, Maynooth, County Kildare, Ireland

Received June 11, 1997[⊗]

The complex $(CO)_5Cr[C(OMe)(Me)]$ is known to react photochemically with *N*-benzylidenemethylamine ($CH_3NC(Ph)H$) to form a β-lactam (1,3-dimethyl-3-methoxy-4-phenyl-2-azetidinone), whereas our study shows that $(CO)_5W[C(OMe)(Me)]$ does not. Irradiation of the complexes in argon and nitrogen matrices ($\lambda > 390$ nm) resulted in a geometrical isomerization and the trapping of the *syn* isomers. There was no evidence from the matrix isolation experiments for the formation of a metal−ketene complex, a likely intermediate in the solution photochemistry of $(CO)_5Cr[C(OMe)(Me)]$ with respect to β-lactam formation. Three differences were observed in the matrix and solution photochemistry of $(CO)_5Cr[C(OMe)(Me)]$ and $(CO)_5W[C(OMe)(Me)]$. (i) $(CO)_5Cr[C(OMe)(Me)]$ undergoes CO loss upon irradiation with UV light more readily than its tungsten analogue. (ii) Upon UV irradiation of $(CO)_5Cr[(C(OMe)(Me)]$ in a nitrogen matrix bands were observed in the IR spectrum which indicated that two $(CO)_4(N_2)Cr[C(OMe)(Me)]$ isomers were formed, whereas irradiation of $(CO)_5W[C(OMe)(Me)]$ under the same conditions produced only one nitrogen adduct. (iii) Irradiation of $(CO)_5Cr[C(OMe)(Me)]$ in solution and in a solid CO matrix showed that this complex underwent loss of the carbene ligand more readily than the tungsten analogue. These findings are consistent with the proposal that, upon irradiation of chromium carbenes, a ketene transient could be formed by a cleavage of the chromium−carbene σ bond and intramolecular nucleophilic attack by the carbene on a metal carbonyl. The photochemistry of the complex $(CO)_5Cr(OMe)(biphenyl)$ was studied in both argon and nitrogen matrices. This complex underwent CO loss very readily, and it is likely that this step is involved in at least one pathway of its solution photochemistry.

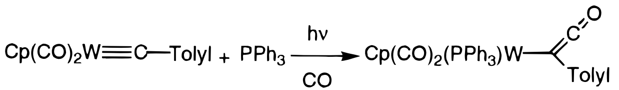
Introduction

In recent years there has been much interest in the activity of Fischer carbenes, $(CO)_5Cr[C(X)(Y)]$, with respect to their ability to act as reagents for the synthesis of organic compounds.[1] Complexes of this type have been shown to be photochemically reactive, forming a range of compounds including β-lactams from imines (eq 1), cyclobutanones from alkenes, esters from alcohols, and the products of intramolecular benzannulation reactions.[1c,2−4]



(1)

The excited state of the carbene complex believed to be involved in these reactions is the metal-to-ligand charge-transfer (MLCT) state.[2,5] It was proposed that excitation into this state resulted in the formation of a metal-ketene transient formed by insertion of one of the CO ligands into the chromium−carbene bond.[5,6] Studies on $Cp(CO)_2W[C(tolyl)]$ have shown that migration of CO from the metal onto the carbyne carbon upon MLCT excitation was possible.[7] Irradiation of this complex in the presence of a phosphine resulted in the formation of the η^1-ketenyl complex $Cp(CO)_2(PPh_3)W[\eta^1\text{-}C(tolyl)CO]$ (eq 2). It would seem reasonable that the chromium−ketene transient formed upon irradiation of the chromium carbenes could be formed by a mechanism similar to that proposed for the formation of $Cp(CO)_2(PPh_3)W[\eta^1\text{-}C(tolyl)CO]$ (Scheme 1).



$$\mathrm{Cp(CO)_2W{\equiv}C{-}Tolyl} + \mathrm{PPh_3} \xrightarrow[\mathrm{CO}]{h\nu} \mathrm{Cp(CO)_2(PPh_3)W{-}C({=}C{=}O)(Tolyl)} \qquad (2)$$

A mechanism such as CO loss and the formation of a metallacycle, which has been proposed for many of the thermal reactions of chromium carbenes, was discounted due to the following observations for the β-lactam formation. CO loss is also a known thermal reaction of carbene complexes, but no β-lactam was formed upon the reaction of the chromium−carbene complexes with imines under thermal conditions.[2] It

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) For reviews see: (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (c) Hegedus, L. S. *Acc. Chem. Res.* **1995**, *28*, 299.

(2) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680.

(3) Sierra, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1989**, *111*, 2335.

(4) Merlic, C. A.; Xu, D.; Khan, S. I. *Organometallics* **1992**, *11*, 412.

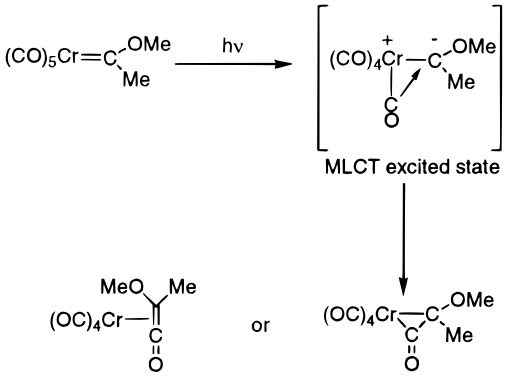
(5) Hegedus, L. S.; de Weck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.

(6) Hegedus, L. S. *Pure Appl. Chem.* **1990**, *62*, 691.

(7) Sheridan, J. B.; Pourreau, D. B.; Geoffroy, G. L. *Organometallics* **1988**, *7*, 289.

S0276-7333(97)00495-0 CCC: $14.00

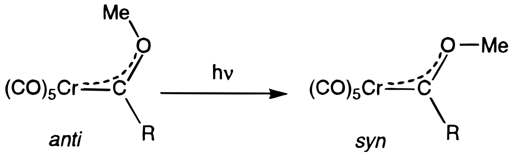
Scheme 1. Proposed Mechanism for the Formation of a Chromium−Ketene Transient from Promotion into the MLCT Excited State of $(CO)_5Cr[C(OMe)(Me)]$



was also observed that high yields of the β-lactam products were obtained when the photochemical reaction was carried out under high pressures of CO.[8] This finding would tend to argue against a mechanism which required CO dissociation. Moreover, in the case of compounds of the type $(CO)_5Cr[C(OMe)(R)]$ (R = Ph, Me) it was shown that the reaction with imine went efficiently upon irradiation with visible light.[2,9] From this observation it was deduced that the reaction did not require excitation into the higher energy ligand field (LF) excited state from which CO loss occurs but, rather, into the lower energy MLCT excited state. Previous studies had shown that CO loss is not associated with MLCT excitation.[10] Moreover, the ratios of the products formed for a series of photoinduced reactions between imines, alkenes, and dienes and chromium carbenes were the same as for the thermal reactions between these compounds and the analogous uncoordinated ketene.[8,11,12]

Studies have shown that complexes of the type $(CO)_5W[C(X)(Y)]$ have three low-lying empty orbitals with symmetry labels $2b_1$, $2a_1$, and $3a_1$, respectively.[13] Transitions from the HOMO to each of these orbitals results in the bands observed in the near-UV−visible region of the absorption spectra of these complexes. These are assigned as a metal to carbene ligand charge-transfer band (${}^1A_1$ (b_2^2) → ${}^1A_2$ ($b_2^1 2b_1^1$)) which generally masks the lower energy LF band (${}^1A_1$ (b_2^2) → ${}^1B_2$ ($b_2^1 3a_1^1$)) and a higher energy LF band (${}^1A_1$ (b_2^2) → ${}^1B_2$ ($b_2^1 3a_1^1$)). Experiments in solution have shown that steady-state irradiation into the higher energy LF band results in substitution of a CO ligand, generally at the *cis* position.[10,14] Excitation into the lower energy LF excited state would be expected to result in dissociation of the carbene ligand or a CO ligand at the *trans* position, and there is some evidence that carbene loss does occur upon irradiation of $(CO)_5W[C(Ph)_2]$ in solution.[15] However, this complex is thermally very unstable; therefore, it is difficult to separate its thermal and photochemical reactions in solution. Studies on the complexes $(CO)_5W[C(OMe)(Ph)]$ and $(CO)_5W[C(OMe)(Me)]$ indicated that they did not undergo photoinduced loss of the carbene ligand to any significant extent.[16]

Time-resolved and low-temperature IR and matrix isolation spectroscopy studies have been carried out previously on the complexes $(CO)_5W[C(OMe)(Ph)]$, $(CO)_5Cr[C(OMe)(Ph)]$, and $(CO)_5W[C(OMe)(Me)]$.[17−19] These experiments showed that the major product upon excitation into the MLCT band was the *syn* isomer (eq 3), while CO loss products were observed upon excitation into the higher energy LF band of *syn*-$(CO)_5M[C(OMe)(Ph)]$ (M = Cr, W). There was no evidence for photoinduced carbene loss from any of these complexes in low-temperature matrices or as an observable transient in the solution studies. Since both of the known photoinduced transient species have previously been well-characterized by IR and UV−vis spectroscopy, it should be easy to distinguish these from a ketene complex. Here we report the results of a series of solution and matrix isolation studies on the complexes $(CO)_5Cr[C(OMe)(Me)]$, $(CO)_5W[C(OMe)(Me)]$, and $(CO)_5Cr[C(OMe)(biphenyl)]$.



(3)

Experimental Section

General Methods and Materials. The organometallic complexes and 1,3-dimethyl-3-methoxy-4-phenyl-2-azetidinone were synthesized using literature procedures.[4,20,21] The complexes were manipulated under nitrogen using standard Schlenk and high-vacuum techniques. The solvents were dried by refluxing over sodium/benzophenone and distilled under a nitrogen atmosphere. The gases used for the matrices were as follows; argon (99.999% purity) supplied by BOC, nitrogen (99.9% purity) and carbon monoxide (99.97% purity) supplied by Linde Gas, and ammonia (99.99% purity) supplied by Aldrich. Chromium hexacarbonyl, tungsten hexacarbonyl, trimethyloxonium tetrafluoroborate, methyllithium, phenyllithium, *tert*-butyllithium, *N*-benzylidenemethylamine, and 2-bromobiphenyl were obtained from Aldrich. THF-d_8 was purchased from Goss Scientific Instruments Ltd. and stored under vacuum in the presence of 4 Å molecular sieves, and chloroform-*d* was purchased from Aldrich and stored under nitrogen.

Irradiation in the matrix experiments was carried out using a Philips HPK 125 W medium-pressure mercury lamp or a 1000 W Oriel xenon arc lamp (Model 66023). Excess heat was removed with a water filter; wavelengths were selected with cutoff filters. The irradiation for the synthetic experiments was carried out using four 25 W Philips low-energy fluorescent light bulbs arranged around the Schlenk tube.

---

(8) Hegedus, L. S.; Montgomery, J.; Narukawa, Y.; Snustad, D. C. *J. Am. Chem. Soc.* **1991**, *113*, 5784.

(9) McGuire, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 5538.

(10) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

(11) Köbbing, S.; Mattay, J. *Tetrahedron Lett.* **1992**, *33*, 927.

(12) Köbbing, S.; Mattay, J.; Raabe, G. *Chem. Ber.* **1993**, *126*, 1849.

(13) Fong, L. K.; Cooper, N. J. *J. Am. Chem. Soc.*, **1984**, *106*, 2595.

(14) Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657.

(15) Edwards, B. H.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *210*, 91.

(16) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*, 3154.

(17) (a) Bell, S. E. J.; Gordon, K. C.; McGarvey, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 3107. (b) Rooney, A. D.; McGarvey, J. J.; Gordon, K. C. *Organometallics* **1995**, *14*, 107.

(18) Knorr, J. R.; Brown, T. L. *Organometallics* **1994**, *13*, 2178.

(19) Servaas, P. C.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* **1990**, *390*, 61.

(20) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954.

(21) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M. *Org. Synth.* **1987**, *65*, 140.

Spectroscopy. The NMR spectra were recorded with a Bruker MSL300 or a Bruker 80AC. The ^{1}H NMR chemical shifts were referenced to TMS (0 ppm) or residual protiated solvent as follows: chloroform-*d*, δ 7.27 ppm; THF-d_8, δ 3.74 ppm. The ^{13}C NMR chemical shifts were referenced to TMS (0 ppm) or to the solvent signals as follows: chloroform-*d*, δ 77 ppm; THF-d_8, δ 67.4 ppm. The ^{13}C NMR spectra were recorded with proton broad-band decoupling.

The IR spectra were recorded on either a Mattson Research Series or a Nicolet Magna 550 FTIR spectrometer. Both spectrometers were continuously purged with CO_2-free dry air. The spectra were recorded as the average of 128 scans with 1 cm^{-1} resolution. The UV−vis spectra were recorded on a Perkin-Elmer Lambda 7G spectrometer.

The matrix isolation apparatus at York has been described in detail elsewhere.[22] The apparatus at Maynooth is similar to the one at York; it contains a CsI window onto which the matrix sample is condensed. Either the complex is sublimed slowly from a right-angled tube onto the CsI window concurrent with the matrix gas, which enters the vacuum shroud from a separate inlet, or alternatively, if the sample is sufficiently volatile, the sample is mixed with the matrix gas in the gas handling line before condensation. The shroud is evacuated using an Edwards E02K oil vapor diffusion pump with a liquid-nitrogen cold trap which is backed by an Edwards E0M2 mechanical pump. The CsI window is cooled to a temperature of 12 K using an APD Cryogenics CSW202 displex closed-cycle refrigeration system. The pressure in the matrix shroud is 1×10^{-6} mbar at room temperature and goes down to 1×10^{-7} mbar at 12 K. There are three windows in the shroud; two of these are on opposite faces and are made of CsI, through which IR spectra can be recorded, and the third is made of quartz, through which the matrix can be irradiated. On the fourth face of the shroud there is a blank flange, or a flange with a high-vacuum Swagelok metal-to-glass fitting onto which the right-angled glass tubes containing the complex can be fitted. The CsI cold window can be turned through 180°, depending on whether the matrix is being deposited or irradiated or if an IR spectrum is being recorded. The gas handling system is evacuated using a Balzer TPU180H turbo molecular pump, and the pressure in the gas handling system is standardly 1×10^{-7} mbar. Upon addition of the gas to the handling line the pressure is recorded by two Tylan General Baratron capacitance manometers, Model No. CDLD 31 and CDLG 11, spanning the pressure ranges 0−10 and 0−1000 Torr, respectively.

Results

(a) Solution Results. (i) Photochemical Reaction of $(CO)_5CrC[(OMe)(Me)]$ and $(CO)_5W[C(OMe)(Me)]$ with *N*-Benzylidenemethylamine. The photochemical reaction of $(CO)_5Cr[C(OMe)(Me)]$ with *N*-benzylidenemethylamine ($CH_3NC(Ph)H$) to form the β-lactam (1,3-dimethyl-3-methoxy-4-phenyl-2-azetidinone) has been carried out previously.[21] Under the experimental procedure used here the β-lactam was formed in 50% yield. The reaction was repeated under identical conditions using an equimolar amount of $(CO)_5W[C(OMe)(Me)]$. No β-lactam was observed in the ^{1}H NMR and the main species formed was identified as a thermal product.[2,23] A solution of imine and $(CO)_5W[C(OMe)(Me)]$ in hexane was irradiated for 18 h at $\lambda > 320$ nm using a 1000 W Xe lamp. Again no bands which could be assigned to the β-lactam were observed in the ^{1}H NMR or the IR spectrum of the product mixture.

(ii) Irradiation of $(CO)_5Cr[C(OMe)(Me)]$ and $(CO)_5W[C(OMe)(Me)]$ under an Atmosphere of CO. This study was carried out in order to investigate the relative ability of these complexes to undergo photoinduced loss of the carbene ligand. A previous photochemical study by Dahlgren and Zink on $(CO)_5W[C(OMe)(Me)]$ using the 405 nm line from a 1000 W Hg lamp did not result in carbene substitution by CO after several hours of irradiation and put an upper limit to the quantum yield (ϕ) for this reaction at 0.01.[16] In the experiment carried out here, equimolar amounts of $(CO)_5Cr[C(OMe)(Me)]$ and $(CO)_5W[C(OMe)(Me)]$ (0.1 mol) were dissolved in hexane (30 cm^3) in two ampules, each under 1 atm of CO. The solutions were irradiated for 3 h at $\lambda > 400$ nm, after which time IR spectra of both solutions were recorded. The IR spectrum of the solution of $(CO)_5W[C(OMe)(Me)]$ showed a *ca.* 4% depletion in the intensity of the starting material bands and the formation of a small band at 1983 cm^{-1} assigned to $W(CO)_6$. The IR spectrum of the solution of $(CO)_5Cr[C(OMe)(Me)]$ indicated that this complex was significantly more reactive: it showed complete depletion of the starting material and the formation of an intense band at 1986 cm^{-1}, which was assigned to $Cr(CO)_6$.

(iii) Photochemical Formation of $(CO)_5Cr$(pyridine) from $(CO)_5Cr[C(OMe)(Me)]$. The $Cr(CO)_6$ discussed in the previous section could have been produced by the dissociation of the carbene ligand, or it could have resulted from decomposition of the proposed chromium−ketene transient. In order to attempt to distinguish between these two mechanisms, we carried out an experiment to see if it was possible to form $(CO)_5Cr$(pyridine) photochemically from $(CO)_5Cr[C(OMe)(Me)]$. Loss of a ketene ligand should leave a tetracarbonylchromium species which will not form $(CO)_5Cr$(pyridine). $(CO)_5Cr[C(OMe)(Me)]$ (25 mg) was dissolved in THF (30 cm^3) under an atmosphere of nitrogen and irradiated for 3 h at $\lambda > 400$ nm. During the course of the reaction the solution was evacuated every 30 min and then put back under an atmosphere of N_2 in order to remove any CO if it had possibly dissociated. After 3 h of irradiation an excess of pyridine was added to the solution, upon which the solution immediately became paler in color. The solution was stirred overnight. $(CO)_5Cr$(pyridine) (20 mg, 74% yield) was isolated, purified by sublimation, and identified by IR spectroscopy.[24] Thus, it would appear that $(CO)_5Cr[C(OMe)(Me)]$ is photochemically labile to loss of the carbene ligand. Studies are ongoing to chemically trap the methylmethoxycarbene. This study indicates that if a ketene complex is formed, it does not decompose by loss of the ketene ligand.

(b) Photoproduct Studies in Cryogenic Solid Matrices. (i) $(CO)_5Cr[C(OMe)(Me)]$ in an Ar Matrix. The first notable feature is that the absorption spectrum of this complex exhibits only one band in the near-UV−visible region (Figure 1a). This indicates that the MLCT band and the 2 LF bands in this complex are overlaid, unlike the UV−vis spectrum of the tungsten analogue, in which the MLCT band and the higher energy LF band can be identified (Figure 1b). Upon deposition into an argon matrix $(CO)_5Cr[C(OMe)(Me)]$ exhibits bands in the IR spectrum due to the *anti* isomer (Figure 2a).[19] A summary of the major bands observed in the IR and UV−vis spectra for the different matrix

---

[22] Haddleton, D. M.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 1810.

[23] (a) Knauss, L.; Fischer, E. O. *Chem. Ber.* **1970**, *103*, 3744. (b) Knauss, L.; Fischer, E. O. *J. Organomet. Chem.* **1971**, *31*, C68.

[24] Kolodziej, R. M.; Lees, A. J. *Organometallics* **1986**, *5*, 450.

Table 1. Principal Features of the IR and UV–Vis Spectra of Carbene Complexes in Low-Temperature Matrices[a]

complex	ν(CO), cm^{-1}	ν(C$_{carbene}$–O), cm^{-1}	ν(N$_2$), cm^{-1}	λ_{max} of lowest energy band, nm
	Ar Matrix			
anti-(CO)$_5$Cr[C(OMe)(Me)]	2071 m, 1991 w, 1967 br, 1950 br	1254 m		369
syn-(CO)$_5$Cr[C(OMe)(Me)]	2072 m, 1996 w, 1970 br, 1951 br	1248 m		377
(CO)$_4$Cr[C(OMe)(Me)][b]	2047 m,[b] 2041 w,[b] 1906 m	1332 m,[b] 1241 sh[b]		
anti-(CO)$_5$W[C(OMe)(Me)][c]	2075 m, 1985 w, 1950 br	1255 m		368
syn-(CO)$_5$W[C(OMe)(Me)][c]	2075 m, 1985 w, 1950 br	1250 m		375
(CO)$_4$W[C(OMe)(Me)][b]	2053 m, 1900 m	1320 vw, 1243 sh		
anti-(CO)$_5$Cr[C(OMe)(biphenyl)]	2067 m, 1955 m	1238 m		394
syn-(CO)$_5$Cr[C(OMe)(biphenyl)]	2070 m, 1959 m	1274 m, 1253 m		405
(CO)$_4$Cr[C(OMe)(biphenyl)]	2037 m[d]	1258 m		492
(CO)$_4$Cr[(η^2-C$_6$H$_5$)C$_6$H$_4$C(OMe)]	2022 s, 1928 vw, 1890 s	1232 m		
	N$_2$ Matrix			
(CO)$_4$(N$_2$)Cr[C(OMe)(Me)][e]	2034 m, 1940 vs, 1915 s, 1877 s	1320 m, 1225 w	2230 m, 2202 s	
(CO)$_4$(N$_2$)W[C(OMe)(Me)]	2038 w, 1933 s	1228 m	2196 s	
	2% NH$_3$/98% Ar Matrix			
(CO)$_5$(NH$_3$)[CrC(OMe)(Me)]	2012 w, 1904 s	1217 m		434

[a] The list of data is not comprehensive, as (1) not all the ν(CO) bands of the products are included, since they overlap with the starting material band, and (2) we do not include bands due to secondary photoproducts. [b] The presence of two sets of bands indicates that two isomers of (CO)$_4$M[C(OMe)(Me)] are formed, and we propose that these are due to either the *cis* and *trans* isomers or an *agostic* (CO)$_4$M[C(OMe)(Me)] in which the site is blocked by the methoxy group. [c] Taken from ref 17b. [d] Other ν(CO) bands obscured by bands due to (CO)$_4$Cr[(η^2-C$_6$H$_5$)C$_6$H$_4$C(OMe)]. [e] The presence of four reasonably intense bands in the ν(CO) region of the IR spectrum suggests trapping of *cis*-(CO)$_4$(N$_2$)Cr[C(OMe)(Me)]. ν(CO) bands due to the *trans* isomer are likely to be coincident with those of the *cis* species.

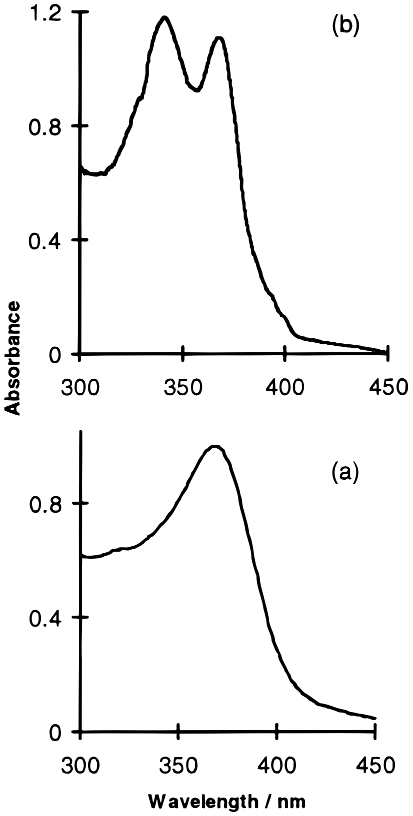


Figure 1. UV–vis spectra of (a) (CO)$_5$Cr[C(OMe)(Me)] and (b) (CO)$_5$W[C(OMe)(Me)] upon deposition in an argon matrix at 12 K.

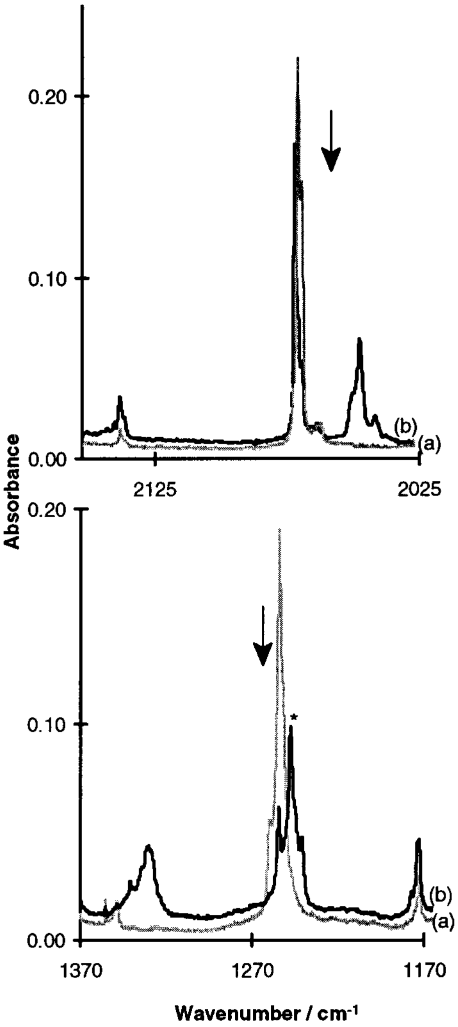


Figure 2. IR spectra of (CO)$_5$Cr[C(OMe)(Me)] in an argon matrix at 12 K: (a) upon deposition; (b) after 0.5 h of irradiation at λ > 320 nm. The asterisk denotes a band due to *syn*-(CO)$_5$Cr[C(OMe)(Me)].

experiments is given in Table 1.[25] After irradiation into the lower energy side of the absorption band for 7.5 h at λ > 385 nm bands were observed in the IR and the UV–vis spectrum which were assigned to the *syn* isomer; no bands in the IR spectrum recorded could be assigned to a chromium–ketene complex. The ν(CCO) bands of free ketenes generally occur in the range of

---

[25] It should be noted that our studies center on the high-energy ν(CO) bands of the starting materials and photoproducts. This is because, as the ν_e(CO) band of the starting material is very intense and subject to severe matrix splittings, it is difficult to distinguish the photoproduct bands which lie close in frequency.

2100–2200 cm^{-1} and those of (η^2-ketene)metal complexes in the range 1600–1800 cm^{-1}.[26] However, there was a *ca.* 30% depletion in the intensity of the bands arising from *syn*- and *anti*-(CO)$_5$Cr[C(OMe)(Me)] and an increase in the intensity of a band at 2140 cm^{-1}, which is assigned to ν(CO) of uncoordinated CO, and of two bands at 2047 and 2041 cm^{-1}. These bands do lie in the expected range for ν(CCO) of a η^1-ketenyl metal complex, but they are most likely to arise from ν(CO) of isomers of (CO)$_4$Cr[C(OMe)(Me)] by comparison with literature values.[19] That these bands were associated with CO-loss products was confirmed by irradiation of the sample into the LF band (0.5 h, λ > 320 nm). The IR spectrum (Figure 2b) showed that the amount of free CO in the matrix increased substantially, along with a concurrent increase in the intensity of the bands at 2047 and 2041 cm^{-1}. Even when (CO)$_5$Cr[C(OMe)(Me)] in an argon matrix was irradiated into the very edge of the low-energy side of the MLCT band at λ > 400 nm for 0.5 h some CO dissociation was observed. CO dissociation is not associated with MLCT excitation of metal carbene complexes and its observation here indicates that at this irradiation wavelength range population of one of the higher energy LF excited states is occurring.

(ii) (CO)$_5$Cr[C(OMe)(Me)] in a 2% NH$_3$/98% Ar Matrix. This experiment was carried out to test whether the presence of a reactive species in the matrix was needed to promote the formation of a ketene complex. It is known that amines react photochemically with the chromium carbenes, and again a metal–ketene complex had been proposed as the reactive intermediate.[5] The matrix was irradiated for 5.5 h at λ > 395 nm, and the IR spectrum recorded showed bands arising from the *syn* isomer and an increase in the amount of free CO in the matrix. Again no bands were observed which could be assigned to the ν(CCO) of a ketene transient. The IR spectrum recorded after irradiation into the LF band for 3.5 h at λ > 315 nm showed bands at 2044 and 2012 cm^{-1}, which we assign as arising from (CO)$_4$Cr[C(OMe)(Me)] and (CO)$_4$(NH$_3$)Cr[C(OMe)(Me)] (Table 1).

(iii) (CO)$_5$Cr[C(OMe)(Me)] in a N$_2$ Matrix. The IR spectrum of (CO)$_5$Cr[C(OMe)(Me)] upon deposition into a N$_2$ matrix is shown in Figure 3a. When this matrix was irradiated for 75 min at λ > 320 nm, the IR spectrum recorded (Figure 3b) showed that the starting material band at 2069 cm^{-1} had decreased in intensity by 80%. There was a substantial increase in the intensity of the bands at 2140, 2045, 2034, 2013, 1940, 1915, and 1877 cm^{-1}. IR bands were observed in the ν(N$_2$) region of the spectrum at 2230, 2202, and 2192 cm^{-1}. This indicated that more than one nitrogen adduct was being formed under matrix isolation conditions. The possibility of carbene dissociation and the formation of (CO)$_5$Cr(N$_2$) was discounted, as the IR bands for this species are well-documented and do not correspond with bands observed in the spectrum.[27] Several isomers of a(CO)$_4$(N$_2$)Cr[C(OMe)(Me)] species are possible; the N$_2$ ligand could be in a *cis* or *trans* site on the chromium, and the carbene ligand could be *syn* or *anti* with respect to the chromium. Upon prolonged irradiation (4 h, λ > 320 nm) the band at 2230 cm^{-1} decreases in intensity and the band at 2202 cm^{-1} becomes sharper. Concurrent with these changes, the ν(CO) band at 2034 cm^{-1} associated with the (CO)$_4$(N$_2$)Cr[C(OMe)(Me)] species decreases in intensity and the band position moves upward slightly in wavenumber. These observations would be consistent with a selective depletion of certain isomers. The ν(N$_2$) band at 2192 cm^{-1} only becomes clearly visible after 0.5 h irradiation at λ > 320 nm, suggesting that it might arise as a secondary photoproduct. Clearly the ν(CO) band at 2013 cm^{-1} can also be assigned as arising from a secondary photoproduct, as after 4 h irradiation at λ > 320 nm this band increases in intensity while the bands due to (CO)$_4$(N$_2$)Cr[C(OMe)(Me)] decrease. No band was observed in this region when a similar concentration of (CO)$_5$Cr[C(OMe)(Me)] was irradiated in an argon matrix (λ > 320 nm, 4 h).

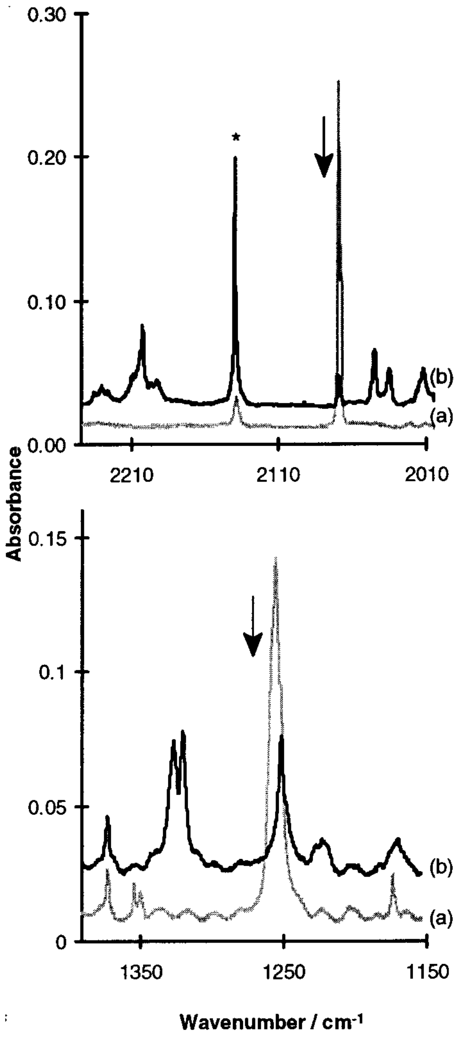


Figure 3. IR spectra of (CO)$_5$Cr[C(OMe)(Me)] in a nitrogen matrix at 12 K: (a) upon deposition; (b) after 75 min of irradiation at λ > 320 nm. The asterisk denotes a band due to uncoordinated CO.

(iv) (CO)$_5$Cr[C(OMe)Me] in a CO Matrix. Although photoinduced carbene loss from this complex had been observed in solution, it was not observed in the previous matrix experiments. This is to be expected, as "in cage" recombination of the carbene with (CO)$_5$Cr will be highly favored since it is difficult for the relatively large [(OMe)(Me)C] group to escape from the matrix cage. In order to attempt to trap the carbene loss species, we carried out a matrix experiment using

---

[26] Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1.

[27] Burdett, J. K.; Downs, A. J.; Gaskill, G. P.; Graham, M. A.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 523.

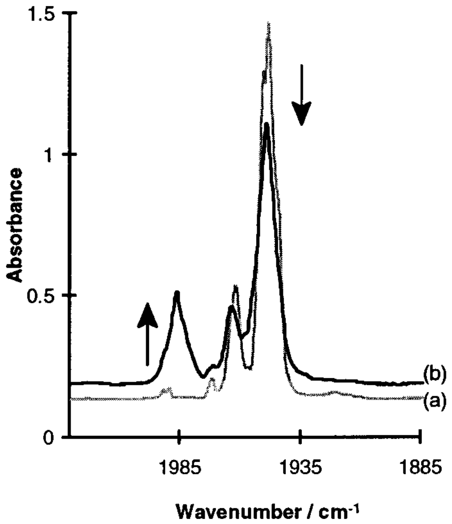


Figure 4. IR spectra of $(CO)_5Cr[C(OMe)(Me)]$ in a carbon monoxide matrix at 12 K: (a) upon deposition; (b) after 3 h of irradiation at $\lambda > 320$ nm.

CO as the matrix gas. The IR spectrum of $(CO)_5Cr[C(OMe)(Me)]$ deposited in a CO matrix is given in Figure 4a. After 3 h of irradiation at $\lambda > 320$ nm the IR spectrum recorded (Figure 4b) showed a *ca.* 30% decrease in the intensity of the bands due to $(CO)_5Cr[C(OMe)(Me)]$ and an increase in a band at 1986 cm^{-1}, assigned as the ν(CO) mode of $Cr(CO)_6$. There were no new bands in the IR spectrum which could be unambiguously assigned to the methylmethoxycarbene. This transient has been isolated in a nitrogen matrix previously.[28] However, this study showed that the methylmethoxycarbene was itself photosensitive and is destroyed upon irradiation at 335 nm (for the *trans* isomer) and at 435 nm (for the *cis* isomer). Therefore, it is probable that the carbene underwent photodecomposition in the experiment carried out here.

(v) $(CO)_5W[C(OMe)(Me)]$ in an Ar Matrix. The MLCT photochemistry of $(CO)_5W[C(OMe)(Me)]$ has been studied previously using matrix isolation.[17b] This study found that irradiation of the complex in an argon matrix (0.5 h, $\lambda = 397$ nm; 1 h, $\lambda = 367$ nm) resulted solely in the *syn* isomer (Table 1). However, no study on its LF photochemistry or any direct comparison of its photochemical products with those of $(CO)_5Cr[C(OMe)(Me)]$ has been carried out. The IR spectrum of $(CO)_5W[C(OMe)(Me)]$ upon deposition in an argon matrix is given in Figure 5a. Upon irradiation into the LF band (45 min, $\lambda > 320$ nm) the IR spectrum recorded (Figure 5b) showed bands at 2140 and 2053 cm^{-1}, indicating that CO loss had occurred.

(vi) $(CO)_5W[C(OMe)(Me)]$ in a N_2 Matrix. The IR spectrum of $(CO)_5W[C(OMe)(Me)]$ upon deposition in a N_2 matrix is given in Figure 6a. Irradiation of $(CO)_5W[C(OMe)(Me)]$ (4 h, $\lambda > 320$ nm) in a nitrogen matrix (Figure 6b) showed photoproducts different from those observed upon LF irradiation of $(CO)_5Cr[C(OMe)(Me)]$ in a nitrogen matrix. Only one band assigned to $\nu(N_2)$ (2196 cm^{-1}) was observed, compared to the three seen in the experiment with $(CO)_5Cr[C(OMe)(Me)]$. Small bands were also observed at 2050, 2038, and 2007 cm^{-1}; these are assigned as arising from $(CO)_4W[C(OMe)(Me)]$, $(CO)_4(N_2)W[C(OMe)(Me)]$, and the secondary photoproduct, respectively.

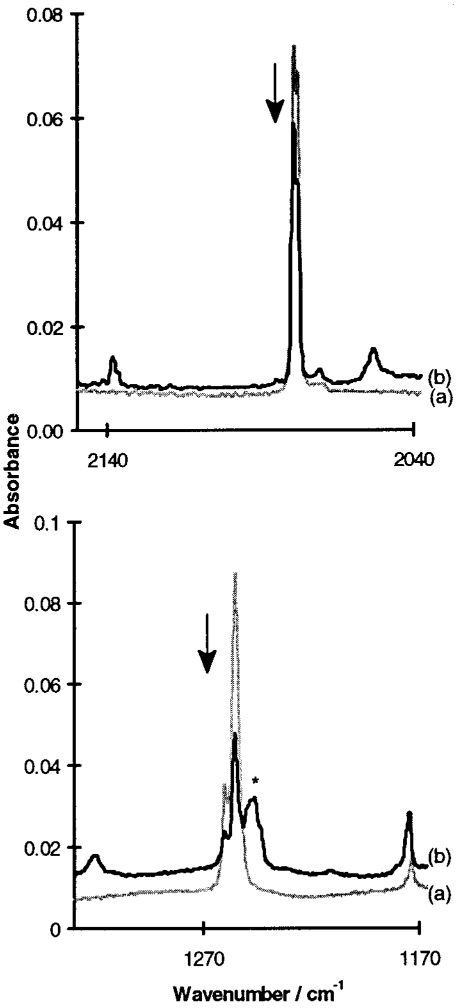


Figure 5. IR spectra of $(CO)_5W[C(OMe)(Me)]$ in an argon matrix at 12 K: (a) upon deposition; (b) after 30 min of irradiation at $\lambda > 400$ nm and 45 min at $\lambda > 320$ nm. The asterisk denotes a band due to *syn*-$(CO)_5W[C(OMe)(Me)]$.

(vii) $(CO)_5W[C(OMe)(Me)]$ in a CO Matrix. When $(CO)_5W[C(OMe)(Me)]$ was irradiated in a CO matrix for 4 h at $\lambda > 320$ nm, there was a *ca.* 10% decrease in the intensity of the IR bands due to $(CO)_5W[C(OMe)(Me)]$, but only a small band due to ν(CO) of $W(CO)_6$ was observed at 1983 cm^{-1}. This band was approximately 20 times less intense than the analogous band for $Cr(CO)_6$ which was recorded upon irradiation of $(CO)_5Cr[C(OMe)(Me)]$ in a CO matrix (Results, section b(iv)).

(viii) Comparative Study on the Amount of CO Loss from $(CO)_5Cr[C(OMe)(Me)]$ and $(CO)_5W[C(OMe)(Me)]$. A striking observation from the results obtained upon excitation into the higher energy LF state of the two complexes in the different matrix experiments was that $(CO)_5Cr[C(OMe)(Me)]$ underwent CO loss more readily than its tungsten analogue. A series of experiments was carried out in which similar amounts and concentrations of each compound were put into argon and nitrogen matrices and all samples were irradiated using a reproducible setup for 0.5 h at $\lambda > 320$ nm. From the intensity of the IR bands it was observed that, over this irradiation time, $(CO)_5Cr[C(OMe)(Me)]$ was depleted by *ca.* 70% and 40% whereas $(CO)_5W[C(OMe)(Me)]$

---

[28] Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Wlostowski, M.; Kesselmayer, M. A.; Subramanian, R.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1988**, *110*, 7563.

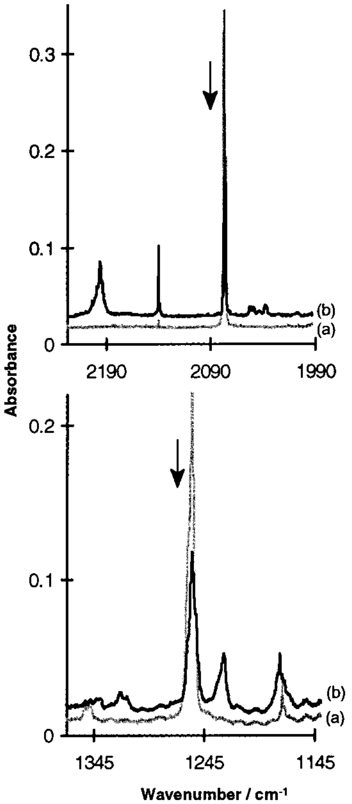


Figure 6. IR spectra of $(CO)_5W[C(OMe)(Me)]$ in a nitrogen matrix at 12 K: (a) upon deposition; (b) after 4 h of irradiation at $\lambda > 320$ nm.

was only depleted by *ca.* 20% and 10% in nitrogen and argon matrices, respectively. Also, it was observed that for the same matrix gas *ca.* 3.5 times more free CO was formed from the irradiation of the chromium compared to the tungsten complex.

(ix) $(CO)_5Cr[(OMe)(biphenyl)]$ in an Ar Matrix. This complex undergoes a photoinduced intramolecular benzannulation reaction in solution, which is proposed to occur via a chromium−ketene intermediate.[4] It was hoped that using matrix isolation spectroscopy intermediates of the solution photoproducts would be trapped. An IR spectrum of $(CO)_5Cr[C(OMe)(biphenyl)]$ deposited in argon showed bands which are assigned as arising from the *anti* isomer (Figure 7a).[29] Again, only one clear band in the UV−vis spectrum ($\lambda_{max} = 394$ nm) was observed due to overlap in the LF and MLCT absorption bands. After irradiation into the MLCT band (4 h at $\lambda > 435$ nm, 9 h at $\lambda > 420$ nm), the IR (Figure 7b) and UV−vis spectra were recorded. The changes in the spectra are consistent with an *anti* to *syn* isomerization for a carbene complex in which there is an aromatic group on the carbene carbon (Table 1).[19] Again no bands were observed which could be assigned to a ketene complex. After irradiation for 1 h at $\lambda > 315$ nm, both IR (Figure 7c) and UV−vis spectra were recorded, and it was determined from the decrease in the bands in the IR spectrum compared to those in the deposition spectrum that there was approximately 70% depletion of the starting material. There was also an increase in the amount of free CO observed in the matrix. New bands at 2037, 2022, 1928, 1890, and 1850 cm^{-1} were observed in the IR spectrum. The band at 2037 cm^{-1} is probably due to ν(CO) of a coordinatively unsaturated $(CO)_4Cr[C(OMe)(biphenyl)]$ species. Comparison with literature values for *cis*- and *trans*-substituted carbene complexes indicates that the bands at 2022, 1928, and 1890 cm^{-1} are most likely due to ν(CO) of a species in which the biphenyl group fills the site left on the metal by the loss of a CO.[10,14]

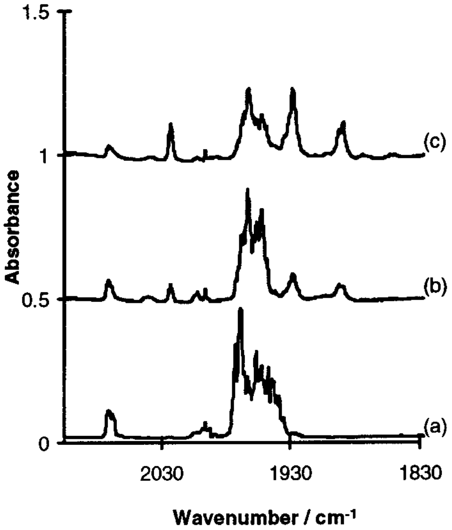


Figure 7. IR spectra of $(CO)_5Cr[C(OMe)(biphenyl)]$ in an argon matrix at 12 K: (a) upon deposition; (b) after 4 h of irradiation at $\lambda > 435$ nm and 9 h of irradiation at $\lambda > 420$ nm; (c) after a further 1 h of irradiation at $\lambda > 315$ nm.

(x) $(CO)_5Cr[C(OMe)(biphenyl)]$ in a N_2 Matrix. After irradiation for 15 min at $\lambda > 320$ nm the IR spectrum recorded showed new bands at 2022, 1929, and 1890 cm^{-1}, which we have assigned as arising from a $(CO)_4Cr[(\eta^2\text{-}C_6H_5)C_6H_4C(OMe)]$ species. There was also a band at 2037 cm^{-1} associated with a $(CO)_4(N_2)$-$Cr[C(OMe)(biphenyl)]$ species and two bands in the $\nu(N_2)$ region at 2204 and 2227 cm^{-1}, indicating that two nitrogen adducts were formed.

Discussion

(a) Solution Studies. The studies on $(CO)_5M[C(OMe)(Me)]$ (M = Cr, W) showed two differences in their photochemical behavior. These were as follows.

(1) $(CO)_5Cr[C(OMe)(Me)]$ reacted with the imine to form a β-lactam, whereas the tungsten analogue did not, even upon irradiation with UV light ($\lambda > 320$ nm).

(2) Upon irradiation at $\lambda > 400$ nm of equimolar amounts of the two complexes in hexane solution under a CO atmosphere, $(CO)_5Cr[C(OMe)(Me)]$ was completely converted to $Cr(CO)_6$, while there was only 4% depletion of $(CO)_5W[C(OMe)(Me)]$. That the hexacarbonyl complexes were formed as a result of loss of solely the carbene ligand was confirmed, as $(CO)_5Cr(pyridine)$ was formed from $(CO)_5Cr[C(OMe)(Me)]$ using the same irradiation wavelength range. If more than one ligand had been lost from $(CO)_5Cr[C(OMe)(Me)]$, we would not expect a pentacarbonyl fragment to be trapped by the pyridine. It is proposed that this carbene loss occurs due to population of the lower energy LF excited state.

(b) Matrix Studies. (i) MLCT Excitation. A comparison between the solution photochemistry of

---

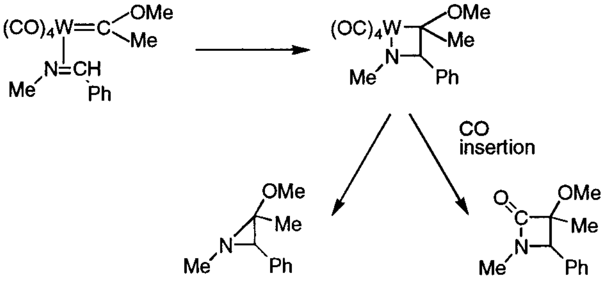
[29] There were also bands of low intensity at 2022, 1890, and 1874 cm^{-1} observed, in addition to an appreciable amount of uncoordinated CO in the matrix. The complex $(CO)_5Cr[(OMe)(biphenyl)]$ is substantially less volatile than the other carbenes studied and needed to be heated to 60 °C to sublime it into the matrix. It is likely that the small bands observed are due to a CO-loss thermal product.

$(CO)_5Cr[C(OMe)(Me)]$ and $(CO)_5W[C(OMe)(Me)]$ demonstrated that under the same conditions the tungsten carbene did not react with an imine to form a β-lactam. A comparison of the matrix photochemistry of all the complexes studied showed that upon MLCT excitation the same product, the *syn* isomer, was formed. The changes observed in the IR-active modes and UV–vis spectra for such an isomerization are slight but are characteristic. These include a shift downward in frequency of the IR band assigned to ν(COMe) and a shift to longer wavelength of the λ_{max} value of the MLCT band in the UV–vis spectrum. A minor product is observed along with the *syn* isomer, and this is assigned as a CO-loss species with the amount of these species observed depending on the complex and matrix gas. No bands were observed that could be assigned to the proposed coordinated ketene species. This transient would be expected to exhibit significant changes in the ν(CO) modes in comparison to those of the starting material.

There are two reasons the ketene species may occur in solution but was not observed upon MLCT excitation in a matrix. First, the ketene complex may be an excited-state species and therefore cannot be trapped by matrix isolation techniques. However, this is an unlikely explanation, considering that the reaction to form a β-lactam is bimolecular and that time-resolved spectroscopic studies on chromium and tungsten carbene complexes put an upper limit of 10 ns for the lifetime of their MLCT excited states.[17,30] Alternatively, the ketene complex might not be observed if the migration of the CO from the metal onto the carbene carbon in the excited state resulted from a thermally activated process, as only thermal processes which require less energy than 5 kJ mol^{-1} can occur in a matrix at 10 K.

(ii) Excitation into the Higher Energy LF State. (1) Relative Ease of CO Loss from $(CO)_5W[C(OMe)(Me)]$ and $(CO)_5Cr[C(OMe)(Me)]$. One difference in the matrix photochemistry of $(CO)_5Cr[C(OMe)(Me)]$ and $(CO)_5W[C(OMe)(Me)]$ was that upon irradiation into the higher energy LF band the chromium complex loses CO more readily. We discount the possibility that the lower ability of $(CO)_5W[C(OMe)(Me)]$ compared to $(CO)_5Cr[C(OMe)(Me)]$ to undergo photoinduced CO loss is due to differences in the degree of interconversion between the higher energy LF and MLCT excited states. The UV–vis spectra of the two complexes indicate that if the efficiency of intersystem crossing between the higher energy LF and MLCT states does differ for the two complexes, it would actually be favored for $(CO)_5Cr[C(OMe)(Me)]$, in which the two states lie closer in energy. The possibility that in the case of $(CO)_5Cr[C(OMe)(Me)]$ the LF band is lower in energy than the MLCT band can be discounted, as LF photochemistry only predominates upon excitation with higher energy light. The difference in the amounts of CO loss which occur during irradiation of the complexes could arise for several reasons. One explanation is that "in cage" recombination of the CO trapped in the matrix cage is favored for the $(CO)_4W[C(OMe)(Me)]$ species. This is likely to arise, as the W–CO bond strength is higher than that of the Cr–CO bond (for $(CO)_5M[C(OMe)(Ph)]$ $\Delta H^{\ddagger}_{W-CO} = 178$ kJ mol^{-1} and $\Delta H^{\ddagger}_{Cr-CO} = 108$ kJ mol^{-1}).[1a] Therefore, the photoejected CO from the chromium complex will probably contain more vibrational energy, which must be dissipated before it can recombine with the metal. Another possibility is that there is a difference in the rates of nonradiative decay from the higher energy LF state for the two complexes. A third possiblity is that the lower energy LF state is active toward CO loss for $(CO)_5Cr[C(OMe)(Me)]$ but not for $(CO)_5W[C(OMe)(Me)]$. UV irradiation would lead to CO loss from two excited states for the chromium complex but only from one for its tungsten analogue. Our current matrix studies cannot distinguish whether one or more of these pathways is important in determining the differing efficiencies in CO loss from the two complexes.

Scheme 2. Possible Products Formed from a CO-Loss Reaction Mechanism for the Reaction of $(CO)_5W[C(OMe)(Me)]$ and *N*-Benzylidenemethylamine



Although $(CO)_5Cr[C(OMe)(Me)]$ undergoes photochemical loss of a CO ligand more readily than $(CO)_5W[C(OMe)(Me)]$, we are in agreement with the proposal given by Hegedus and co-workers that this is not an important step in the reaction of the chromium complex with imines to form β-lactams.[5] Even upon irradiation into the LF band from which CO loss is known to occur, $(CO)_5W[C(OMe)(Me)]$ does not react with *N*-benzylidenemethylamine to form either a β-lactam (1,3-dimethyl-3-methoxy-4-phenyl-2-azetidinone) or the three-membered ring 2-methoxy-1,2-dimethyl-3-phenylazirane (Scheme 2).

(2) Assignment of CO Loss Species Formed in Nitrogen and Argon Matrices. There were other differences observed in the products formed upon LF excitation of $(CO)_5Cr[C(OMe)(Me)]$ and $(CO)_5W[C(OMe)(Me)]$, but these are difficult to interpret due to the number of possible different isomers of the CO-loss species formed and the fact that many of the IR bands are overlapping. However, the number of $\nu(N_2)$ bands in the IR spectra would indicate that $(CO)_5Cr[C(OMe)(Me)]$ and $(CO)_5Cr[C(OMe)(biphenyl)]$ each form two nitrogen complexes upon CO loss, whereas $(CO)_5W[C(OMe)(Me)]$ forms only one. Studies have shown that CO loss should occur from a *cis* position upon population of the higher energy LF band and from the *trans* position upon population of the lower energy LF band. Nevertheless, in most solution photochemical studies of CO substitution in carbene complexes of this type only the *cis* isomer is formed.[10,13,14,18] However, it may be possible to trap both isomers in a low-temperature matrix, and we suggest that the two nitrogen adducts arise from *cis*- and *trans*-$(CO)_4(N_2)Cr[C(OMe)(R)]$ (R = Me, biphenyl).

There is some evidence from the IR spectra of $(CO)_5M[C(OMe)(Me)]$ that a species is formed in which the vacant site is blocked by a group on the carbene ligand. The band at 2040 cm^{-1} formed upon LF irradia-

---

[30] Rooney A. D. Ph.D. Thesis, QUB Belfast, 1991.

tion of $(CO)_5Cr[C(OMe)(Me)]$ is little changed on altering the matrix gas from argon to nitrogen, whereas this mode is quite sensitive to the nature of L for *cis*- and *trans*-$(CO)_4LCr[C(OMe)Me)]$ (L = phosphine).[14] Moreover, upon LF irradiation of $(CO)_5W[C(OMe)(Me)]$ in a nitrogen matrix only one $\nu(N_2)$ signal is observed, but the bands in the CO stretching region would indicate that more than one CO-loss species has been formed.

Certain differences were observed in the photochemical activity of the complexes studied here in comparison to what was found during previous studies on the $(CO)_5M[C(OMe)(Ph)]$ (M = Cr, W) analogues.[19] For these complexes CO loss was observed as a secondary photochemical process from the *syn* isomer and only occurred upon irradiation with UV light ($\lambda = 366$ nm). In the case of the $(CO)_5M[C(OMe)(Me)]$ complexes photoinduced CO loss appeared to occur from both isomers and for $(CO)_5Cr[C(OMe)(Me)]$ it occurs to some extent even upon excitation into the lower energy side of the MLCT absorption band ($\lambda > 400$ nm).

(iii) Excitation into the Lower Energy LF Band. Solution studies showed that carbene loss is significantly more favored for $(CO)_5Cr[C(OMe)(Me)]$ than for $(CO)_5W[C(OMe)(Me)]$. This finding was supported by the studies carried out on the two complexes in CO matrices, in which significantly more $Cr(CO)_6$ than $W(CO)_6$ was formed. It is most likely that carbene loss occurs upon population of the lower energy LF excited state. The photochemistry of this excited state has generally been overlooked because its associated absorption band is completely masked by the more intense MLCT band for most carbene complexes of this type. Moreover, the studies on $(CO)_5W[C(OMe)(R)]$ (R = Ph, Me) indicated that this excited state was not very active for these complexes.[16] Our findings would suggest that this is not the case for the chromium analogues.

(c) Proposed Mechanism for the Formation of a Ketene Transient upon Irradiation of Chromium Carbenes. Our findings support the proposal that a pathway involving CO loss and the formation of a metallacycle is not involved in the photochemical reaction of chromium carbenes with imines, even though CO loss does occur for $(CO)_5Cr[C(OMe)(Me)]$ upon irradiation with visible light ($\lambda > 400$ nm). Although the matrix isolation studies did not trap a metal−ketene transient, this does appear to be a likely intermediate in chromium−carbene solution photochemistry. Our findings do show that there is a significant difference in the reactivities of the lower energy LF excited states for $(CO)_5W[C(OMe)(Me)]$ and $(CO)_5Cr[C(OMe)(Me)]$, and we would propose that it is possible that this ketene complex forms by population not of the MLCT of the carbene complexes but of this lower energy LF excited state. Upon excitation into the lower energy LF band the metal−carbene σ-bond is broken. The carbene ligand is still attached to the metal through the π-bond, and it is possible that, in competition with complete dissociation, the carbene can undergo an intramolecular nucleophilic attack on a *cis* metal carbonyl to form the metal−ketene complex. Intramolecular carbene attack of this type has been observed previously in the thermal reaction of $(CO)_5M[C(Ph)_2]$ (M = Cr, W) to form the uncoordinated ketene Ph_2CCO, and it was observed that the chromium complex was more reactive.[31] Also, studies on the uncoordinated methylmethoxycarbene have shown that it has a very high nucleophilic selectivity.[28] It is possible that the ketene transient is not observed in the cryogenic matrix experiments because recombination of the carbene is favored under low-temperature conditions.

Conclusions

1. The matrix isolation experiments give no evidence for the formation of a ketene transient upon longer wavelength irradiation. The major product formed in all cases is the *syn* isomer. However, this does not preclude that such a transient requires thermal activation and that it does occur in room-temperature solution studies.
2. The studies showed that $(CO)_5Cr[C(OMe)(Me)]$ loses CO more readily than $(CO)_5W[C(OMe)(Me)]$ when irradiated under similar conditions for similar time periods, both in cryogenic matrices. However, there appears to be no link between these differences in CO-loss behavior and the difference in their solution photochemistry with respect to the formation of β-lactam.
3. Two $\nu(N_2)$ bands were observed in the IR spectra upon UV irradiation of $(CO)_5Cr[C(OMe)(R)]$ (R = Me, biphenyl) in nitrogen matrices. We suggest these bands arise from *cis*- and *trans*-$(CO)_4(N_2)Cr[C(OMe)(R)]$.
4. The studies showed that $(CO)_5Cr[(C(OMe)(Me)]$ undergoes loss of the carbene ligand more readily than $(CO)_5W[C(OMe)(Me)]$ both in solution and in a CO matrix. It is likely that the carbene ligand is lost due to population of the lower energy LF excited state, and we suggest that it may be this state instead of the MLCT excited state which is involved in the formation of a metal−ketene transient upon irradiation of chromium−carbene complexes.
5. $(CO)_5Cr[C(OMe)(biphenyl)]$ undergoes loss of CO readily upon irradiation at $\lambda > 320$ nm in both nitrogen and argon matrices. It is likely that some of the benzannulation product formed upon irradiation of this complex in solution using a similar wavelength range does result from CO loss as the primary step. However, a photochemical pathway to this product involving a metal−ketene transient may be occurring concurrently.

Acknowledgment. We are sincerely grateful to Prof. R. N. Perutz for the use of the equipment at York and for useful discussions. We are also grateful to Dr. C. M. Gordon for showing us unpublished results and to Dr. J. McCaffrey and Dr. V. Bracken, who built the matrix rig at Maynooth. We thank Donegal County Council and the Irish American Partnership for a grant to M.L.G. and the British Council and Forbairt for a travel grant to A.D.R.

OM970495+

---

[31] Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 874.