

A kinetic and spectroscopic study of the interaction between a $M(\text{CO})_5$ ($M = \text{Cr}, \text{W}$) fragment and ethyl diazoacetate

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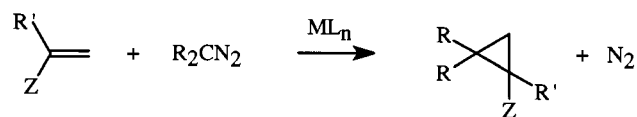
Abstract

The reaction between $\text{Cr}(\text{CO})_5[\text{C}_6\text{H}_6]$ and ethyl diazoacetate (EDA) has been studied using the technique of laser flash photolysis. Results indicate that the $\text{Cr}(\text{CO})_5$ fragment reacts very rapidly with the EDA ligand. Low temperature spectroscopic studies suggest that in the case of $\text{W}(\text{CO})_5$, and by analogy also in the case of $\text{Cr}(\text{CO})_5$, the initial adduct between the pentacarbonyl fragment and EDA is one where the oxygen atom of the diazocarbonyl ligand is bound to the metal center. This kinetic product is then converted to a thermodynamically favored complex which is tentatively assigned as the nitrogen bound $\text{W}(\text{CO})_5$ -EDA complex that appears to be stable at r.t. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Laser flash photolysis; Ligand; Pentacarbonyl fragment

1. Introduction

Diazoalkanes have been used to promote the cyclopropanation of alkenes in the presence of transition metal containing catalysts [1].



While the most common transition metals employed for such transformations are Pd and Cu, other organometallic complexes have also been used [2–4]. For example, $\text{Mo}(\text{CO})_6$ has been used to promote the cyclopropanation of α,β -unsaturated carboxylate esters and nitriles in the presence of ethyl diazoacetate ($\text{N}_2\text{CHCO}_2\text{Et}$) [3,4]. Both $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ also act as catalysts in cyclopropanation reactions although neither is as effective as $\text{Mo}(\text{CO})_6$ [2,3]. It is likely that the active intermediate in most cases is the metal pentacarbonyl fragment generated by the thermal loss of a

carbonyl ligand [3]. Mechanistic studies have suggested that in some cases a diazo carbon bound metal complex is generated which subsequently loses N_2 to generate a metal carbene complex which is the active catalyst [1,2]. However, direct evidence for the presence of a diazo carbon bound adduct has not been obtained. In an effort to better understand the role of the Group 6 transition metal hexacarbonyls in promoting cyclopropanation reactions, and to determine the nature of the interaction between the transition metal center and the diazoalkane, we decided to study the reaction between the photolytically generated $\text{Cr}(\text{CO})_5$ fragment and ethyl diazoacetate (EDA).

The coordinatively unsaturated Group 6 metal pentacarbonyls are very unstable fragments that react rapidly with a wide variety of ligands including noble gases [5–8]. Therefore, traditional kinetic methods cannot be employed to study the reactions of these fragments. We have used the technique of laser flash photolysis to perform a kinetic and mechanistic study of the reaction between $\text{Cr}(\text{CO})_5$ and EDA. Spectroscopic studies were also carried out at low temperatures to try to determine the mode of bonding between the

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metal center and the EDA ligand. Ethyl diazoacetate can bind to a metal center through a variety of donor atoms including nitrogen, carbon, and oxygen. Our results appear to indicate that the intermediate formed immediately after the reaction between the metal pentacarbonyl and EDA is one where the oxygen atom of the carbonyl group of EDA acts as the donor atom.

2. Experimental

Benzene and hexane (Aldrich) were freshly distilled from CaH_2 under N_2 prior to use. Piperidine (99%+, Aldrich) was used as received. Ethyl diazoacetate (Aldrich) was pumped on for a few minutes before use to remove residual methylene chloride which was present as a trace contaminant (<10%). The EDA sample was then analyzed by GC/MS to ensure complete removal of CH_2Cl_2 . Acetone (Aldrich) was pre-dried over anhydrous CaSO_4 and then distilled under N_2 . Chromium hexacarbonyl (Atomeergic) and tungsten hexacarbonyl (Aldrich) were used as received.

The laser flash photolysis apparatus employed a Lambda Physik EMG 102 XeCl excimer laser (308 nm, 5 mJ pulse⁻¹) operating at 1–2 Hz as the photolysis source. The monitoring system, arranged in a cross-beam configuration, consisted of a 150 Watt Xe arc lamp (Xenon Corporation), a monochromator (Jobin-Yvon Spex HD-20, 8 nm bandpass), and a high gain 5 MHz Si photodiode. Signal from the detector was captured by a LeCroy 5310 digital storage oscilloscope. The data were stored on the oscilloscope, converted to ASCII format and analyzed using the program KaleidaGraph (Synergy Software). A 360 nm long wave pass UV filter was placed in front of the lamp to prevent photolysis of the solution by the probe beam. The photolysis solutions were prepared under a N_2 atmosphere and were placed in a 1 cm pathlength quartz fluorescence cuvette and capped to prevent exposure to air. Purging the solutions with argon prior to photolysis had no measurable effect on the results. Typical concentration of $\text{Cr}(\text{CO})_6$ was $1\text{--}3 \times 10^{-3}$ M. Kinetic runs were done under pseudo-first order conditions with the concentration of the ligand at least ten times that of the hexacarbonyl. All kinetic runs were carried out under ambient temperature conditions ($20 \pm 1^\circ\text{C}$).

Low temperature photolysis experiments were conducted using 308 nm light from the XeCl excimer laser (5 mJ pulse⁻¹). The solutions were exposed to approximately 60 shots of the laser light prior to obtaining the low temperature IR spectra. Low temperature IR spectra were obtained at 2 cm^{-1} resolution using a Nicolet 510M FTIR spectrometer. Room temperature spectra were acquired at 0.5 cm^{-1} resolution using a Nicolet 750 Magna FTIR spectrometer. All IR spectra were

obtained using a 0.5 mm pathlength variable temperature cell with CaF_2 windows.

3. Results and discussion

3.1. Kinetic studies

Photolysis of a solution of $\text{Cr}(\text{CO})_6$ in benzene (C_6H_6) generates a transient absorption with a $\lambda_{\text{max}} = 460$ nm which is attributed to the solvated pentacarbonyl species $\text{Cr}(\text{CO})_5[\text{C}_6\text{H}_6]$ that has been observed previously at the same wavelength [9,10]. In the absence of added ligand this species decays on the several millisecond time scale ($k_{\text{obs}} \approx 200\text{ s}^{-1}$). As shown in Fig. 1, in the presence of EDA, $\text{Cr}(\text{CO})_5[\text{C}_6\text{H}_6]$ exhibits a first order exponential decay and concurrent with the decay of the solvated pentacarbonyl, a new species grows in with a $\lambda_{\text{max}} = 430$ nm. We assign the 430 nm product absorption to the $\text{Cr}(\text{CO})_5[\text{EDA}]$ adduct. Because the bands of the product and reactant overlapped, decay of the solvated $\text{Cr}(\text{CO})_5[\text{C}_6\text{H}_6]$ complex was monitored at 530 nm.

While EDA is a photosensitive molecule readily losing N_2 upon photolysis, its UV absorption spectrum shows that it does not absorb at 308 nm, the wavelength employed in these experiments. Further evidence that EDA is not photolyzed by 308 nm light is provided by the photolysis of EDA in methanol. Previous studies have shown that methanol is an effective trap for the photoproducts that are generated when EDA is photolyzed [11]. When 308 nm light was used the IR

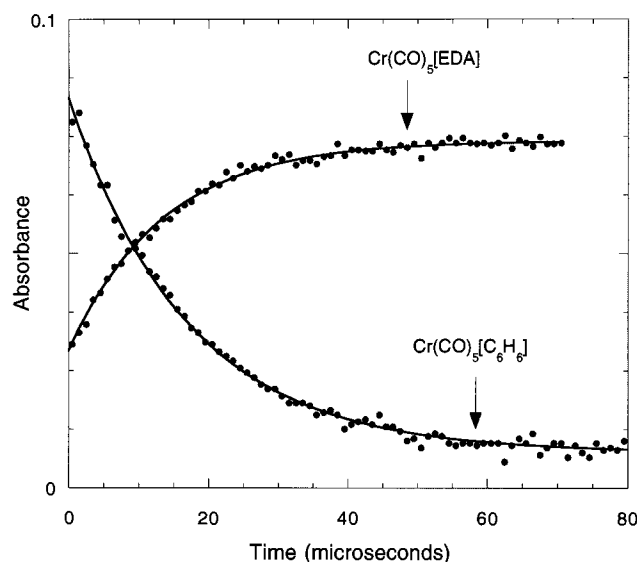


Fig. 1. Decay of the $\text{Cr}(\text{CO})_5[\text{C}_6\text{H}_6]$ complex monitored at 530 nm and growth of the $\text{Cr}(\text{CO})_5[\text{EDA}]$ complex observed at 410 nm. Solid lines represent first order exponential fits to the data. Absorbance of the $\text{Cr}(\text{CO})_5[\text{EDA}]$ complex is non-zero at time zero due to overlap with the absorbance of the $\text{Cr}(\text{CO})_5[\text{C}_6\text{H}_6]$ species.

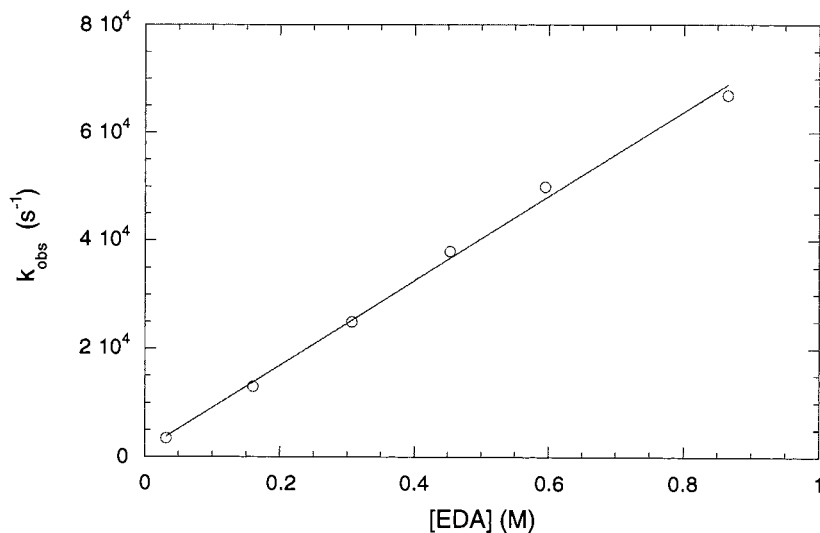


Fig. 2. A plot of k_{obs} vs. [EDA] at 20°C. Observed rate constants were determined by following the disappearance of $\text{Cr}(\text{CO})_5[\text{C}_6\text{H}_6]$ at 530 nm.

spectrum of EDA in methanol remained unchanged before and after photolysis. However, when the mixture was photolyzed with UV light from the Xe arc lamp (without any filters), bands appeared in the carbonyl stretching region of the IR spectrum indicating the formation of new species. We therefore conclude that in these experiments the pentacarbonyl fragment is reacting only with EDA and not with a photoproduct of the diazocarbonyl compound.

As shown in Fig. 2, the observed rate constant, k_{obs} , varies linearly with EDA concentration. The linear dependence of k_{obs} on [EDA] is consistent with both a dissociative and associative mechanism of benzene displacement from the Cr center (Scheme 1). Assuming a steady state concentration of $\text{Cr}(\text{CO})_5$, the dependence of k_{obs} on [L] can be derived.

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{L}]}{k_{-1} [\text{C}_6\text{H}_6]} + k_3 [\text{L}]$$

The first term in the above equation represents the dissociative component while the second term arises due to the associative component of the reaction. Derivation of this expression assumes that $k_2 [\text{L}] \ll k_{-1} [\text{C}_6\text{H}_6]$ [12]. The solvated $\text{Cr}(\text{CO})_5$ complex is known to react with a variety of ligands through a dissociative mechanism, $k_3 = 0$ [9,13]. However, $\text{M}(\text{CO})_5[\text{solvent}]$ ($\text{M} = \text{Cr}, \text{W}$) can also react with some ligands through a competing associative pathway, $k_3 \neq 0$ [9,14–16].

A plot of k_{obs} vs. [L] yields a slope of;

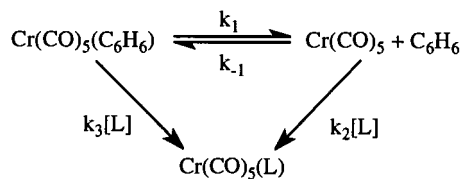
$$\frac{k_1 k_2}{k_{-1} [\text{C}_6\text{H}_6]} + k_3$$

Again, the first term in the above expression is due to the dissociative component and the second term is due to the associative component of the reaction. A value for k_1 (the rate constant for the dissociation of the

benzene ligand from the $\text{Cr}(\text{CO})_5$ fragment) has been determined previously by studying the reaction of $\text{Cr}(\text{CO})_5[\text{C}_6\text{H}_6]$ with various ligands [9]. Furthermore, Dobson has determined that the ratio $k_2/k_{-1} \approx 2-3$ for two electron donor ligands such as piperidine and pyridine. If these values are used in the above equation then the relative contributions of the associative and dissociative steps in the reaction of the pentacarbonyl fragment with EDA can be estimated. Using an extrapolated value of $2.2 \times 10^5 \text{ s}^{-1}$ for k_1 at 20°C [17], a value of 3 for k_2/k_{-1} , and $[\text{C}_6\text{H}_6] \approx 11 \text{ M}$, the magnitude of the dissociative component is calculated to be $6 \times 10^4 \text{ s}^{-1}$. Since the slope of a plot of k_{obs} vs. [EDA] yields a value of $7.8 \pm 0.3 \times 10^4 \text{ s}^{-1}$ which is the sum of the dissociative and associative components, it is estimated that the dissociative pathway may contribute as much as 80% to the overall rate of displacement of benzene by EDA. A complete mechanistic study of the reaction will have to await determination of activation parameters which are useful in distinguishing between the two possible pathways [9].

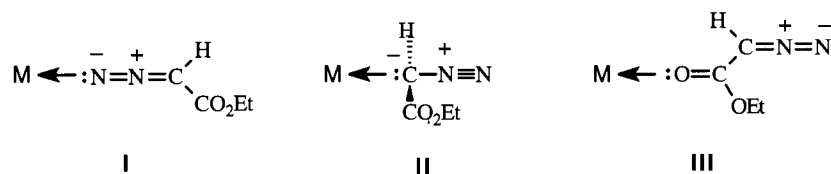
3.2. Low temperature spectroscopic studies

The EDA molecule has several sites that can be used to coordinate to a metal center. The terminal nitrogen atom, the diazocarbon, and the carbonyl oxygen can act as donor atoms in a metal-eda adduct. Therefore,



Scheme 1.

the three most likely structures for a metal-EDA adduct are,



With diazoalkanes other than EDA, complexes of type **I** are known and have been studied in connection with nitrogen activation [18–26]. Complexes where the nitrogen is coordinated to one metal center in both an end-on and side-on fashion have been synthesized. There is only one report in the literature that presents spectroscopic evidence for the existence of structure **II** at low temperature [27]. Some authors have argued for the intermediacy of complexes like **II** but conclusive evidence has not yet been obtained [18]. To our knowledge, there is no evidence for the existence of complexes with structure **III**.

3.2.1. $\text{Cr}(\text{CO})_6$

The product of the reaction between $\text{Cr}(\text{CO})_5$ and EDA is not stable at r.t. While useful for monitoring the kinetics of the reaction, the presence of an absorption at 430 nm due to the product does not provide any structural information about the $\text{Cr}(\text{CO})_5$ /EDA complex. Therefore, we decided to obtain an IR spectrum of the product by generating it at low temperature, assuming that the adduct would be stabilized at the lower temperature. When a solution of $\text{Cr}(\text{CO})_6$ in hexane was photolyzed at -78°C in the presence of EDA, four new peaks appeared in the IR spectrum at 2074, 1941/1935, 1903 and 1637 cm^{-1} . While the peaks in the $2100\text{--}1900\text{ cm}^{-1}$ region are close in frequency to those observed for the $\text{Cr}(\text{CO})_5\text{-H}_2\text{O}$ adduct [28], as

discussed below in the case of $\text{W}(\text{CO})_5$, they are not due to water contamination. When a solution of $\text{Cr}(\text{CO})_6$ in hexane with added water was photolyzed intense peaks were observed due to the $\text{Cr}(\text{CO})_5\text{N}_2$ adduct [28,29] and only weak peaks were observed at 2074, 1944, and 1913 cm^{-1} which are assigned to the previously observed $\text{Cr}(\text{CO})_5\text{-H}_2\text{O}$ adduct [30]. As discussed below, the $\text{Cr}(\text{CO})_5$ -EDA adduct formed at -78°C has a type **III** structure where the oxygen atom of the carbonyl group on the EDA ligand is bonded to the metal center.

3.2.2. $\text{W}(\text{CO})_6$

When a solution of $\text{W}(\text{CO})_6$ in hexane with 60 mM EDA was photolyzed at -78°C four new bands appeared at 2075, 1932/1928 (shoulder), 1902, 1622 cm^{-1} (Fig. 3). By analogy with other $\text{W}(\text{CO})_5\text{L}$ complexes, and based on their position and relative intensities, the first three bands are assigned to the metal CO stretching frequencies of the pentacarbonyl fragment [7,28,31,32]. For a $\text{M}(\text{CO})_5\text{L}$ species where L is a symmetrical ligand, three CO stretching bands are expected to be IR active, two bands with A_1 symmetry and one band with E symmetry. In the case of the $\text{W}(\text{CO})_5$ -EDA adduct the shoulder on the E symmetry absorption at 1932 cm^{-1} shows evidence that this band comprises two peaks as expected for a $\text{M}(\text{CO})_5\text{L}$ complex with an asymmetric ligand such as EDA [28].

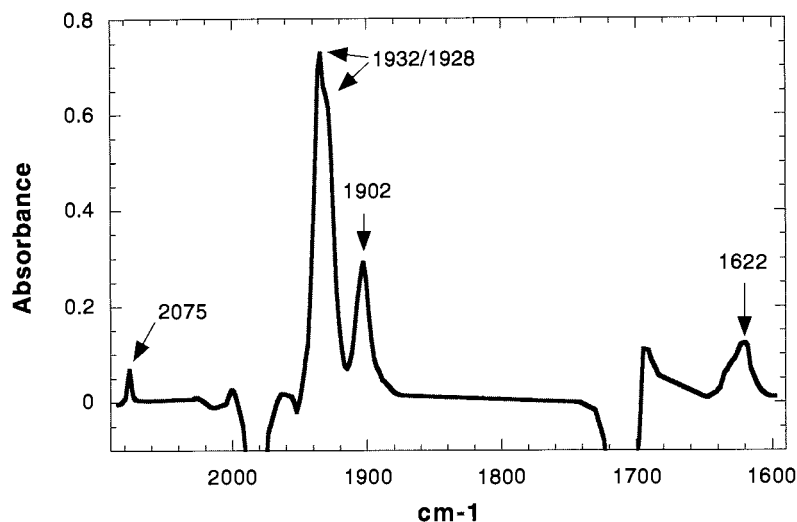


Fig. 3. Difference IR spectrum obtained upon photolysis of $\text{W}(\text{CO})_6$ in hexane in the presence of ethyl diazoacetate at -78°C .

The three metal CO stretches are close in frequency to the literature values of the CO bands in the $W(CO)_5[H_2O]$ and $W(CO)_5[O=C(CH_3)_2]$ complexes [31,32]. Water, perhaps present as a trace contaminant, was ruled out as the source of the bands we observe by conducting a control experiment where water was added to a solution of $W(CO)_6$ in hexane and then photolyzed at $-78^\circ C$. Consistent with previous work, three new peaks appeared at 2077, 1938, and 1912 cm^{-1} [32]. Since the shift in the position of the parent hexacarbonyl peak is negligible when experiments are conducted with added water or EDA, the difference in the CO stretching frequencies of the $W(CO)_5[EDA]$ and $W(CO)_5[H_2O]$ complexes appear to be real. Furthermore, as shown in Fig. 4, the absorption bands of the CO stretching modes in the $W(CO)_5[H_2O]$ and $W(CO)_5[EDA]$ complexes have different shapes. In the case of the EDA complex, the most intense *E* symmetry band has a clear shoulder while in the water complex the analogous band does not. We therefore conclude that the O stretching bands observed in the presence of EDA, while close in frequency to those of the $W(CO)_5[H_2O]$ complex, are not due to water contamination.

When the experiment was done with added acetone, three peaks assigned to the metal CO stretches of the $W(CO)_5[O=C(CH_3)_2]$ adduct were observed at 2076, 1934, and 1908 cm^{-1} . As shown in Fig. 4, the similarity of the IR bands observed for the $W(CO)_5[EDA]$ adduct and the $W(CO)_5[H_2O]$ and $W(CO)_5[O=C(CH_3)_2]$ complexes, leads us to conclude that the IR data are consistent with the formation of an oxygen bound $W(CO)_5$ -EDA complex (type III). As shown in Table 1, previous studies [31,32] have also shown that when a ligand binds to the pentacarbonyl fragment through an oxygen atom, the CO stretching frequencies of the pentacarbonyl fragment are very similar and are in the range observed for the $W(CO)_5$ -EDA complex. Consequently, the 1622 cm^{-1} band observed for the

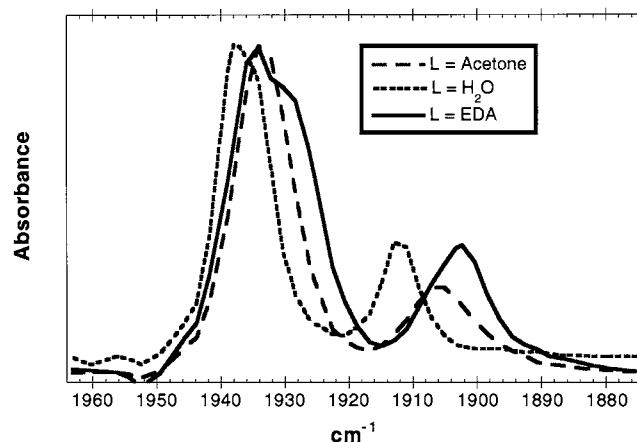


Fig. 4. Difference IR spectra obtained when $W(CO)_6$ is photolyzed in the presence of ligand L at $-78^\circ C$.

Table 1

Metal CO stretching frequencies in $W(CO)_5L$ complexes where L is bound to the metal center through an oxygen atom.

L	ν_{CO} (cm^{-1})		
	A_1	E	A_1
H_2O	2077	1938 (1944)	1912 (1912)
$(CH_3)_2CO$	2076	1934 (1942)	1908 (1914)
N_2CHCO_2Et	2075	1932/1928	1902
CH_3OH	—	(1942)	(1916)

Values in parenthesis are from Ref. [32] at r.t. in cyclohexane solvent.

$W(CO)_5[EDA]$ adduct is assigned to the carbonyl stretch of the complexed diazocarbonyl molecule [33]. The shift in the carbonyl stretching frequency of EDA upon complexation is 90 cm^{-1} .

While an oxygen bound metal-EDA adduct has not been observed before, formation of such an adduct is consistent with several studies which indicate that the Group 6 metal pentacarbonyls are exceptionally reactive towards oxygen containing molecules like water, diethylether, acetone, tetrahydrofuran, and methanol [31,32,34,35]. As evidenced by the similarity of the IR spectra for the $W(CO)_5$ -EDA and $Cr(CO)_5$ -EDA complexes, it appears likely that the EDA ligand also binds to the $Cr(CO)_5$ fragment via the carbonyl oxygen of the diazocarbonyl molecule.

3.3. Room temperature spectroscopic studies

When the photolysis of $W(CO)_6$ in the presence of EDA is conducted at $-25^\circ C$, the peaks due to the oxygen bound $W(CO)_5$ -EDA adduct decay over a period of several minutes and a new absorbance appears at 2000 cm^{-1} which persists even at r.t.. As shown in Fig. 5, when a solution of $W(CO)_6$ in hexane with EDA was photolyzed at room temperature, a strong absorption was observed at 2000 cm^{-1} , and shoulders at 1981, 1979, and 1972 cm^{-1} were observed on either side of the $W(CO)_6$ parent absorption at 1983 cm^{-1} . In addition a peak was also detected at 2098 cm^{-1} . The presence of these absorptions indicate that the initial oxygen bound $W(CO)_5$ -EDA adduct is converted to a more stable complex with a different structure.

A reliable assignment of a structure for this r.t. adduct cannot be made solely on the basis of the observed IR spectrum. However, it should be noted that the 2098, 1979, and 1971 cm^{-1} absorptions are close in frequency to the CO stretching bands observed in the IR spectra of the $M(CO)_5N_2$ complexes that have been detected in matrices and liquified noble gases [7,28,36]. Consequently, it is possible that the metal-EDA adduct observed at r.t. is a nitrogen bound $W(CO)_5$ -EDA complex with a type I structure. Since the highest occupied sigma orbital of a N_2 ligand and a

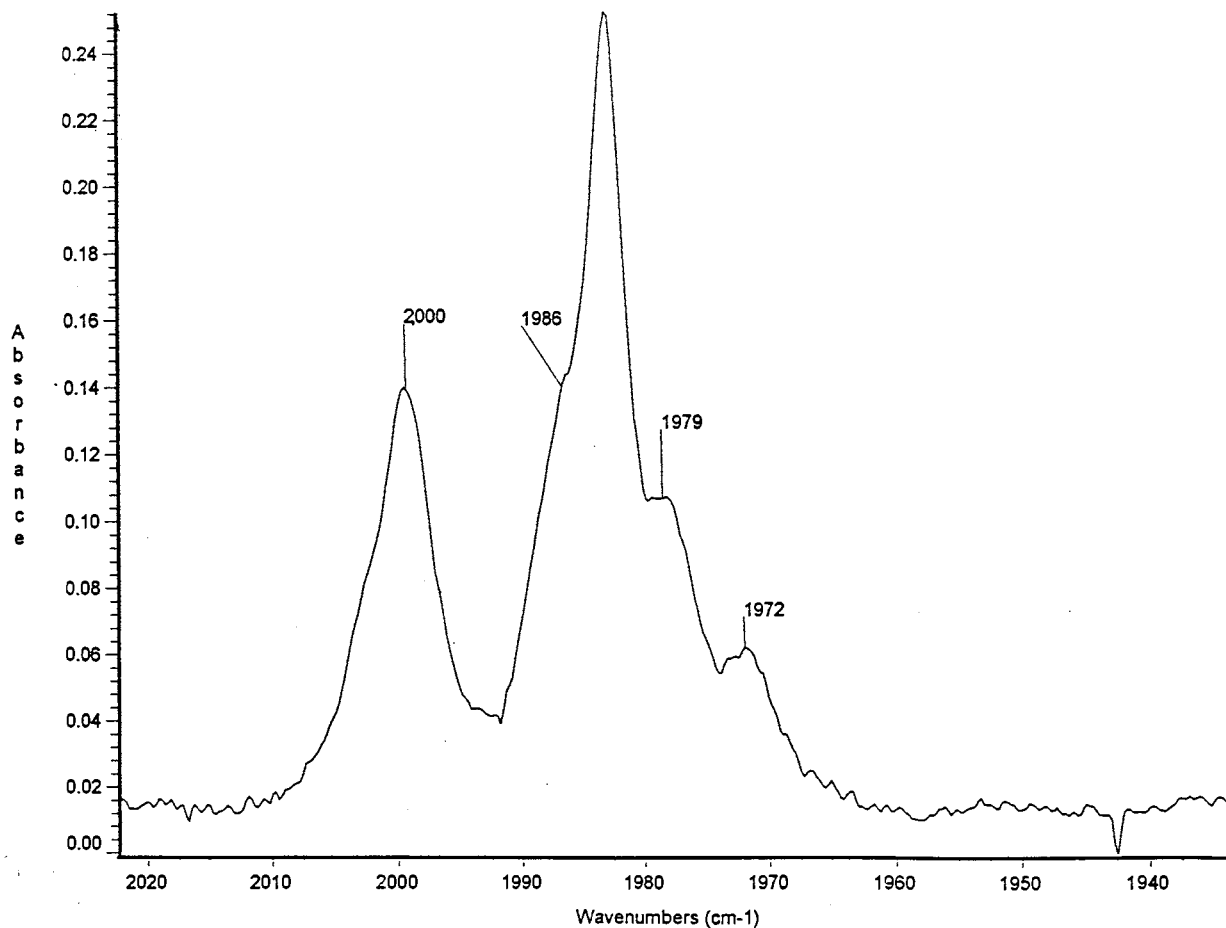


Fig. 5. IR spectra obtained upon photolysis of $W(CO)_6$ in the presence of EDA at room temperature. The most intense peak is due to residual $W(CO)_6$.

diazo compound closely resemble one another, [19] the nature of the W–N bond, and hence the CO stretching frequencies for the two complexes are expected to be similar. The 2000 cm^{-1} absorption may then be assigned to the CN_2 stretching mode of the complexed diazo group. This frequency is similar to the 1911 cm^{-1} band observed for the CN_2 stretch in the end-on nitrogen bound $(C_5H_5)Mn(CO)_2[N_2C(CO_2Et)_2]$ complex [26]. The 110 cm^{-1} shift in the CN_2 stretching frequency upon complexation of the diazo ligand is consistent with the 100 cm^{-1} shift observed in the N–N stretching frequency when N_2 binds to a pentacarbonyl fragment [28]. While the IR frequencies are consistent with a type I structure for this adduct, conclusive evidence must await more definitive structural studies.

Finally, it should be noted that flash photolysis experiments using $W(CO)_6$ as the organometallic complex should be interesting since it may be possible to monitor the conversion of the initial oxygen bound $W(CO)_5$ -EDA complex to the postulated nitrogen bound complex. However, this study was not undertaken since the $W(CO)_5[EDA]$ complex appeared to absorb in a region ($\lambda < 410\text{ nm}$) where the Si photodiode detector

used in the present study has low sensitivity and the signal strength was insufficient to yield good data.

4. Conclusion

The results of the present study indicate that EDA reacts very rapidly with $Cr(CO)_5$ to generate an oxygen bound $Cr(CO)_5$ -EDA adduct. This adduct is extremely unstable and decomposes to yield an unidentified species. Similarly, in the case of $W(CO)_5$ the EDA molecule binds to the metal center through the carbonyl oxygen of the diazocarbonyl to yield the kinetic product. However, unlike the chromium compound, this adduct decays to form the nitrogen bound $W(CO)_5$ -EDA complex that appears to be the thermodynamically favored molecule and is stable at room temperature. In previous work where the Fisher carbene $(CO)_5W=C(OMe)(Ph)$ in the presence of EDA was used to cyclopropanate alkenes, it was suggested that the active cyclopropanation agent was the unstable $(CO)_5W=CHCO_2Et$ complex [37]. This complex was thought to have been generated by the reaction between

W(CO)₅ and EDA resulting in the formation of a diazocarbon bound adduct which subsequently underwent thermal loss of N₂. While the results of the present study do not argue against the above mechanism, our data do suggest that generation of the (CO)₅W=CHCO₂Et complex is most likely preceded by the formation of an extremely unstable (CO)₅W–O=C(OEt)(CHN₂) complex. Further work is underway to probe the nature of the interaction between a number of other organometallic complexes and the EDA molecule.

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