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Low-Temperature Infrared Spectral Study of the Photochemical Reaction of $(CO)_5Cr{=}C(OMe)Ph$ with Solvent and Alkynes

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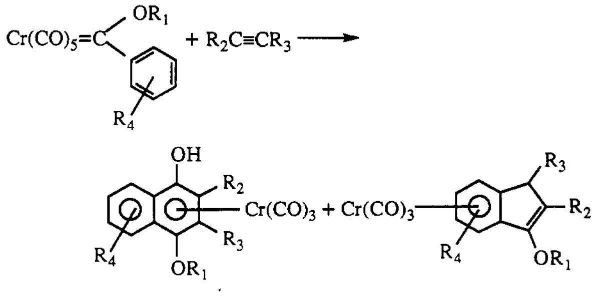
The photochemical behavior of the Fisher carbene $(CO)_5Cr{=}C(OMe)Ph$ (1) under a variety of low-temperature conditions is studied. Photolysis of 1 with low-pressure mercury lamps at 95 K in a 3-methylpentane (3MP) glass is followed by FTIR observation during programmed warmup in the range from 95 K to 295 K. Photolysis of 1 in 3MP glass results in loss of CO with low quantum yield and formation of a *cis*-solvento species. Recombination with CO occurs in the temperature range to 140 K. When THF is present in low concentration, photolysis results in formation of *cis*-$(CO)_4(THF)Cr{=}C(OMe)Ph$. In the temperature interval 95–160 K this species undergoes changes of uncertain origins, before reverting to 1 upon THF loss and recombination with CO, at temperatures above 165 K. In the presence of dilute *p*-$CF_3C_6H_4$-CCH, photolysis at 95 K results in formation of a single intermediate which remains unchanged upon warming until, in the temperature range 200–235 K, it converts to the final phenol annulation product. When THF is present in addition to the alkyne, the *cis*-THF complex is formed at low temperature and then converts to the same alkyne intermediate as THF dissociates from the complex. The results of these experiments are discussed in terms of the various intermediates previously proposed for the reactions of 1 with alkynes.

Fischer carbene complexes are of considerably utility in synthetic organic chemistry. One of the more important applications is the reaction of phenylalkoxychromium carbenes, $(CO)_5Cr{=}C(OMe)Ph$ (1), with alkynes, to form annulated products, principally the two shown in eq 1.[1] This, the so-called Dötz reaction, has been developed extensively as a powerful synthetic tool for regioselective construction of highly functionalized aromatic rings.[1b,2,3]



(1)

The overall reaction is the result of a rather complex set of carbon–carbon bond formations, and the detailed pathway is by no means clear. At the same time, a wealth of information exists regarding the effects of solvent, reagent concentrations, temperature, and other variables on product yields and distributions.[3] A kinetic study of the thermal reaction of $(CO)_5Cr{=}C(OMe)Ph$ with PhCCPh and related alkynes, in dibutyl ether at temperatures in the range 45–73 °C, revealed that the initial and rate-limiting step is loss of CO.[4] Many lines of evidence point to a key role for solvent in the reaction.[1b,3] In general, stronger donor solvents lead to higher proportions of indene vs phenol products.[3] Substituents in the *o*-positions of the phenyl ring in the starting carbene that have the ability to coordinate to the metal (e.g., OMe) similarly shift the product distribution toward indenes.

The proposed mechanisms for the reaction involve a series of intermediates formed following CO loss. The species that appear at present to be most likely to play a role in formation of the phenol product are shown in Scheme 1. (In the scheme, the possibilities for initial solvent coordination following CO loss are not shown; this aspect of the process is discussed later.)

There is no unambiguous evidence for the independent existence of an η^2-coordinated alkyne. That mode of binding may obtain in the product of the low-temperature photolysis of $(CO)_5W{=}C(OMe)Ph$ with PhCCPh,[5] but it was not possible to distinguish between η^2-coordination of the alkyne and formation of a metallacyclobutene or vinylcarbene. The vinylcarbene, **vc**, which is best considered as an η^3-vinylcarbene, as opposed to a more or less planar chromacyclobutene,[6] is postulated as the successor species. Geoffroy and co-workers have generated a reactive alkylidene species at low temperature through protonation of $Cp(CO)_2W{\equiv}CTol$[7] and observed its reaction with

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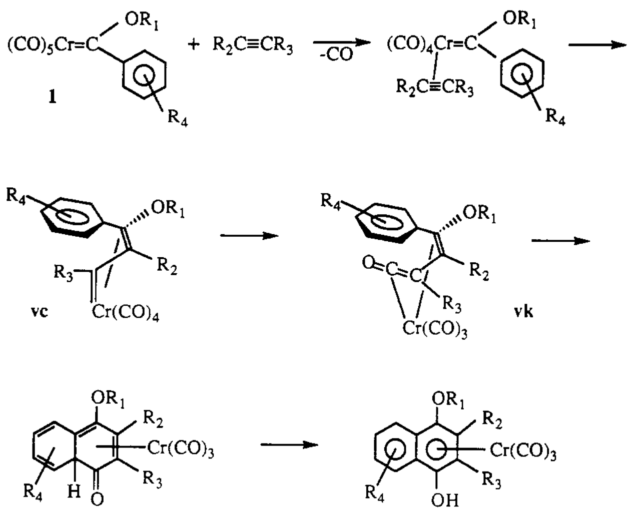
Scheme 1



PhCCPh. They were able to isolate and characterize crystallographically a vinylcarbene derivative.

The product of CO insertion, the η^4-vinylketene, **vk**, was first proposed as an intermediate by Dötz and coworkers.[8] A vinylketene has been isolated from heating the amino carbene, $(CO)_5Cr{=}C[N(CH_2)_4](CH_2)_3C{\equiv}CMe$, and characterized by an x-ray structure determination.[9]

Photochemical approaches offer possibilities for mechanistic inquiry that are not available through study of the thermal reaction. The electronic absorption spectra of $(CO)_5M$(alkylidene) complexes generally exhibit an absorbance in the 400-nm region attributable to a M → carbene MLCT transition, inactive toward CO or carbene dissociation.[10] The LF transitions that lead to CO dissociation lie at shorter wavelength. Internal conversion from the active LF states to the inactive MLCT state appears to be rapid; thus, the quantum yields for CO loss upon irradiation in the 300-nm region are low, on the order of 0.01.

Irradiation of the carbene complexes at −10 °C in hexane in the presence of tertiary phosphines leads to initial formation of *cis*-$M(CO)_4PR_3$(alkylidene), which may subsequently isomerize to the *trans* product.[11]

In carbene complexes of the form $(CO)_5M{=}C(OR)Ph$, the OR group may exist in *syn* or *anti* configuration with respect to the phenyl group.[12,13] The *syn*:*anti* ratio in solution depends on the metal, the R group, solvent, and temperature. The *anti* configuration is favored when the metal–carbon distance is long and the R group is not sufficiently large to destabilize the *anti* form. For $(CO)_5Cr{=}C(OMe)Ph$, nearly equal amounts of the two forms are present at room temperature. Photochemical irradiation produces a photostationary state heavily shifted toward the *syn* isomer.[13] In the analysis of solution spectra following irradiation, it is necessary to take the shift in *syn*:*anti* ratio, and the subsequent return to a thermal equilibrium, into account.

Photochemical irradiation or flash photolysis of organometallic substrates in a glass at low temperature has proven a valuable tool in identification of intermediates which are otherwise impossible to observe and characterize.[14] Programmed warming of irradiated glasses provides the opportunity to observe a progression of reaction steps. We report here the results of irradiation of 1 in 3-methylpentane (3MP) glasses at about 90 K, with subsequent programmed warming to room temperature. We have studied the effects of added bases, such as THF or pyridine, and have observed the interactions of the photochemical products with the alkyne $4\text{-}CF_3C_6H_4CCH$. This alkyne was chosen because it affords almost pure phenol product under the various conditions employed, a chemoselectivity characteristic of terminal alkynes.[3] Our results clarify the role of solvent in the reactions with alkyne and provide evidence that there exist very few observable intermediates along the reaction pathway.

Experimental Section

3-Methylpentane (3MP), 99+%, Aldrich, was distilled over liquid Na/K alloy under Ar and stored over 4A molecular sieve. The solvent was degassed by three freeze–pump–thaw cycles and then covered with Ar. Tetrahydrofuran, THF, was distilled over CaH_2 under Ar and then stored over 4A molecular sieve. Before use as solvent, it was degassed by three freeze–pump–thaw cycles and then covered with Ar. Pyridine was distilled over potassium hydroxide under Ar and then stored over 4A molecular sieve. Before use as solvent, it was degassed by three freeze–pump–thaw cycles and then covered with Ar. Triphenylphosphine was used as received from Aldrich. 4-Ethynyl(trifluoromethyl)-benzene was prepared according to a published literature procedure,[15] and its purity was established via standard analytical methods. 4-Ethynyltoluene and phenylacetylene were used as received from Aldrich.

$(CO)_5Cr{=}(OMe)Ph$ (1) was prepared by modification of literature procedures.[3,16] The modification consisted chiefly in the purification. The crude product was purified by chromatography on silica gel, using 90:10 hexane/ether as eluent. The resulting product was determined to be analytically pure by standard spectroscopic methods.

Variable-Temperature IR Spectroscopy. All IR spectra were obtained using a Perkin-Elmer Model 1710 FTIR spectrophotometer. The digitized spectra were transferred to a 386- or 486-type computer for subsequent manipulation and analysis using ASYST routines.

A sample solution was prepared by combining carbene, solvent, and any other reagents in a flame-dried Schlenk tube under Ar and degassing by three freeze–pump–thaw cycles. A sample of the degassed solution was transferred into an IR cell under Ar using a syringe. The cell was loaded into a SPECAC P/N 21500 variable-temperature apparatus and cooled under vacuum to 95 K. IR spectra were obtained at 2-min intervals while the same was warmed without coolant. Initially the rate of warming was determined by the rate of heat exchange of the cell assembly with the surroundings. However, for temperatures in the range of 190 K to room temperature, the sample temperature was ramped linearly at 1.5–2 K/min, using a heater and programmable temperature controller. The preirradiation spectra obtained in this way furnish the background spectra.

Upon cooling of the sample once again to 95 K, it was irradiated for 10 min, generally with a bank of 8-W mercury vapor lamps

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Table 1. IR Data for Photochemical Intermediates Following Irradiation at 97 K of $(CO)_5Cr{=}C(OMe)Ph$ in 3MP with Added THF or Pyridine (cm^{-1})

	species						
	4	**5**	**5′**	**4**	**4′**	**6**	**1/2**
(a) [**1**] = 0.64 mM, [THF] = 4.9 mM							
TR[a] (K)	97–120	97–150		120–185		150–185	165→295
IR	2011	2010		2012		2012?[b]	2063
		(1925)				(1930)[c]	1986
	1903	1898		1905		1894	1962
	1859	1840		1859		1816	1952
							1940
(b) [**1**] = 0.64 mM, [THF] = 64 mM							
TR (K)	97–120	97–155		120–190		150–185	165→295
IR	2008	2010		2011		2011?	2063
	(1923)[c]	(1925)[c]		1905		(1930)[c]	1986
	1898	1897		1859		1895	1962
	1853	1844				1817	1952
							1940
(c) [**1**] = 0.32 mM, [THF] = 0.61 M							
TR (K)		115–170		170–210			170→295
IR		2008		2010			as above
		1897		1903			
		1845		1855			
(d) [**1**] = 0.64 mM, [py] = 4.9 mM							
TR (K)			95–205		150–298		205→295
IR			2003		2008		as above
			1888		1902		
			1844		1868		

[a] Indicates the temperature range in which the species is seen during warmup, using the temperature programming described in the Experimental Section. [b] The question mark indicates that the band overlaps with those for other species but is identified on the basis of the relative changes in absorbance at this wavenumber as compared with those in cases where no overlap exists. [c] Bands that are in the range of those associated with **1** and **2** are difficult to discern, because the small changes in their absorbances are commingled with those arising from *syn* → *anti* equilibration and recovery of **1**/**2** via recombination with CO.

providing mainly 254-nm light, in a Rayonet RMR-600 minireactor. The irradiation was sufficient to effect photochemical conversion of about 20–25% of the starting carbene complex. IR spectra were then obtained as the sample was warmed, as described above. Difference spectra were obtained by subtracting the spectra obtained after irradiation from those obtained at the same temperature before irradiation.

Results and Discussion

Photolysis in 3MP or in 3MP and THF. Photolysis of $(CO)_5Cr{=}C(OMe)Ph$ in 3MP results in *anti* → *syn* conversion and loss of CO. The latter is followed by formation of the solvento form, in analogy to the behavior exhibited by other metal carbonyl compounds upon photochemical CO dissociation at low temperature in hydrocarbon solvents.[14b,17] Observation of the difference between pre- and postphotolysis spectra as the sample is warmed in the range 95–140 K reveals loss of bands at 2033, 1944, 1902, and 1882 cm^{-1}, ascribed to the solvento species, **3**, with formation of *syn*-$(CO)_5Cr{=}C(OMe)Ph$, which we label **2**. The *syn* → *anti* conversion back to thermal equilibrium is observed to occur in the temperature interval 153–167 K with the temperature programming employed.

In the presence of 4.9 or 61 mM THF, there is no evidence of the solvento species following irradiation at 97 K. Aside from difference spectral bands attributable to photochemical *anti* → *syn* conversion, additional absorbances appear at 2011, 1903, and 1859 cm^{-1}. Table 1 lists the absorption maxima discerned in these and other experiments to be described. A band in the 1920–1930-cm^{-1} region is evident for the sample containing 61 mM THF, but the strong absorbances due to **1** and **2** obscure this interval and make it difficult to determine the frequency of band maximum with precision. The four new band maxima are ascribed to formation of the THF complex *cis*-$(CO)_4(THF)Cr{=}C(OMe)Ph$ (**4**).

At 97 K, 3MP forms a glass with very high macroscopic viscosity. Nevertheless, small molecules, such as CO and, to a lesser extent, THF, are capable of migrating through the glass, particularly in those regions surrounding molecules which have dissipated excess energy into the surrounding medium following electronic excitation. Upon warming of the glasses containing THF in either concentration in the temperature range 97–120 K, the bands ascribed to **4** change shape or partially disappear, concurrent with the appearance of new absorbances at 2010, (1925), 1897, and 1844 cm^{-1}, ascribed to a new species, **5**, as shown in Figure 1. (The parentheses around 1925 in Table 1 indicate that the band maximum cannot be determined with accuracy because of the strong absorbances due to **1** and **2** in this region). The assignment of bands at 2010 and 1897 cm^{-1} to **5** follows from the comparative magnitudes of the absorbance changes at these frequencies; it is clear from the comparative losses in absorbances that there are underlying absorbances of lower intensity growing in as those due to **4** are lost.

Remarkably, at still higher temperatures, in the range 120–150 K, the reverse process occurs; **5** disappears, with reappearance of additional **4**, albeit with slightly shifted absorbance maxima, as shown in Figure 2. At this higher temperature, the presence of absorptions at both 1898 and 1905 cm^{-1} is evident. In the presence of a much higher concentration of THF, 0.61 M, substantially more **5** is

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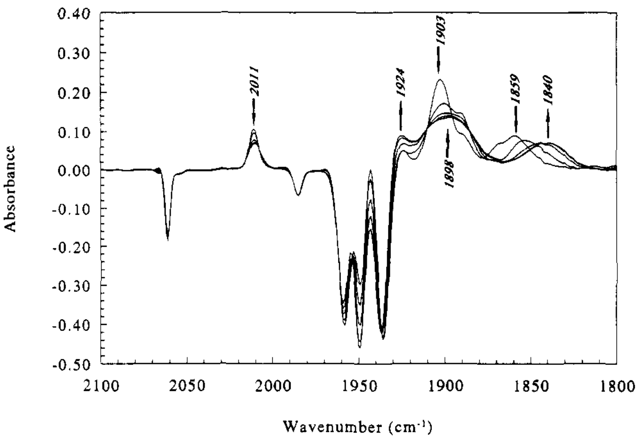

Figure 1. Difference spectra between the spectrum taken before irradiation of 1 in 3MP, 0.64 mM, in the presence of 4.9 mM THF, at 97 K and at temperatures ranging from 97 to 120 K during programmed warmup following irradiation. The negative absorptions are the result of loss of starting material; some small positive absorptions result from *anti* → *syn* conversion.

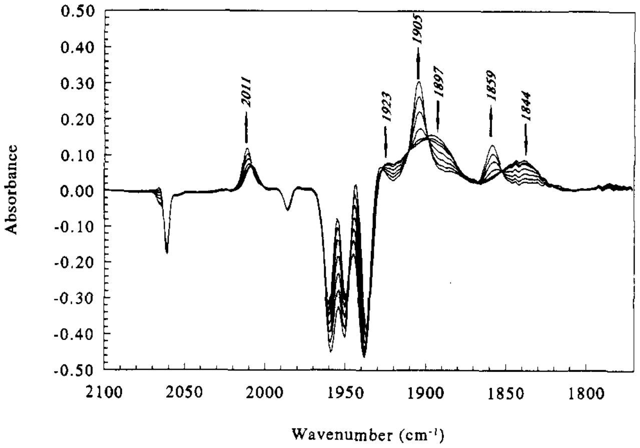

Figure 2. Difference spectra between the spectrum taken before irradiation of 1 in 3MP, 0.64 mM, in the presence of 64 mM THF, at 97 K and at temperatures ranging from 120 to 150 K during programmed warmup following the irradiation. The growth and slight frequency shift in absorbance at 2010–2012 cm^{-1} along with those at 1905 and 1859 cm^{-1} indicates that 5 has an absorption at about 2010 cm^{-1}.

seen following irradiation at 97 K. As with lower concentrations of THF, however, 5 reverts to 4 as the sample is warmed in the interval 120–150 K.

The conversion of 4 to 5 at low temperature, and the reversion of 5 to 4 as the temperature is increased, is reflected in IR band shifts of fairly small magnitude. This fact and their ready interconvertability suggest that 4 and 5 are not greatly different. One possibility is that they represent different conformations of the coordinated THF relative to the carbene group. Another is that they are related to weak, reversible binding of THF to the carbene ligand. Fischer and co-workers have shown that phosphines and nitrogen ligands are capable of reversible addition to the carbene carbon to form phosphorus or nitrogen ylides.[18] They demonstrated that the addition–dissociation equilibrium is strongly temperature-dependent. Thus, for example, the equilibrium constant for addition of diethylphenylphosphine to 1 is 28 L/mol at −29 °C and only 0.28 L/mol at 8 °C.[18a]

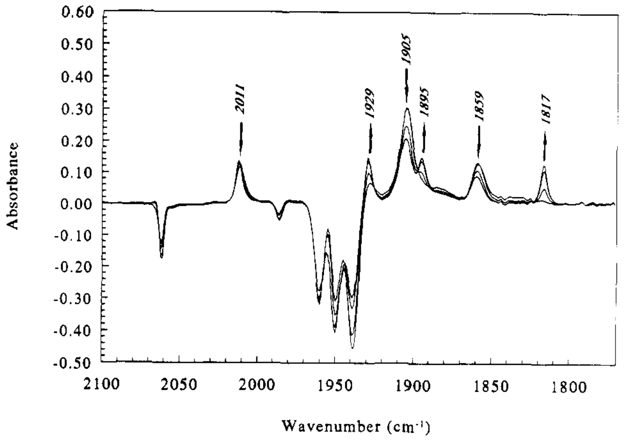

Figure 3. Difference spectra of the solution described in Figure 2 caption, in the temperature interval from 154 to 163 K.

It is reasonable to expect that at sufficiently low temperature a weak base such as THF will bind to the carbene carbon, analogously to tertiary amines. The result of such binding would be to shift the IR CO stretching frequencies to generally lower values, since addition of the base to the carbene carbon converts the carbene ligand from a moderately strong π acceptor to a purely σ donor. In keeping with formation of a weak complex, the major IR stretching bands of 1 at 95 K are shifted toward lower frequencies, and there is some change in the band pattern, in the presence of 4.9 mM THF, as compared with the absence of THF. Larger shifts are evident at higher concentrations of THF. The shift in CO stretching frequencies between 4 and 5 is considerably smaller than is noted upon addition of 1,4-diazabicyclo[2.2.2]octane to $(CO)_5Cr{=}C(OMe)Ph$,[18d] but in the direction of lower values, as consistent with a rather weak interaction. The weakness of the interaction is evident also in the fact that the process is reversible in a low-temperature regime. Further test of the conjecture that 5 arises from formation of a weak THF adduct due to binding at the carbene carbon will require additional experiments. The fact that extended irradiation is required to effect sufficient extent of reaction using the present setup beclouds the issue, because such irrradiation doubtless produces local heating in the glass due to dissipation of energy associated with absorption into the MLCT band.

As the solutions containing 4.9 and 61 mM THF are warmed beyond 150 K, at which point no 5 is present, 4 is observed to convert in part to a new species, 6. New absorptions are observed at 1930, 1895, and 1817 cm^{-1} (Figure 3). The absence of significant change in the difference spectral absorbance at 2011 cm^{-1} suggests that 6 also has an absorbance at this frequency, of intensity comparable to that of the band due to 4. No evidence for 6 was observed in the solution containing 0.61 M THF. As the temperature is increased beyond 165 K, both 4 and 6 disappear, as shown in the difference spectra in Figure 4. At 190 K all evidence of 6 is gone; thus, this species persists only over a narrow temperature range. The THF adduct, 4 disappears more gradually, as THF is replaced by CO, forming 1. Consistent with the formulation for 4, it persists to higher temperatures in the solutions containing higher concentrations of THF.

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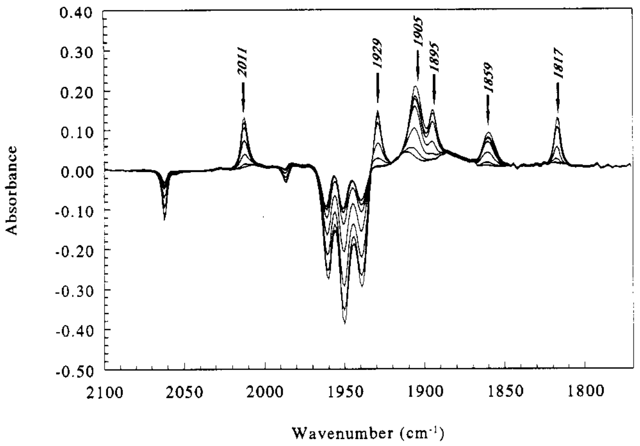

Figure 4. Difference spectra of the solution described in Figure 2 caption, in the temperature interval from 163 to 190 K. Bands ascribed to both **4** and **6** disappear in this temperature interval; concurrently, the negative absorptions due to initial loss of **1** disappear, as **1** is formed via recombination with CO.

The origin of **6** is not clear. One possibility is that it is associated with the *syn* → *anti* conversion, which might be expected to occur in this temperature range, as indicated above for the experiments with **1** in the absence of base. However, the frequency shifts associated with the **4** → **6** process are much larger than would be expected to arise from the *syn* → *anti* process. A *cis* → *trans* isomerism of the THF complex is another possibility, but the number and frequencies of the resulting IR bands are not consistent with such a process. For example, the lowest CO stretching band for *trans*-$(CO)_4PR_3Cr{=}C(OMe)Ph$ complexes, and the only band of significant intensity, occurs in the vicinity of 1890 cm^{-1}.[11a] A third possibility is that **6** is an intermediate following THF dissociation that is stabilized by an agostic interaction with C–H of the methoxy methyl groups, a form suggested for the tungsten analog of **1**.[13] Thus, for the present, we are unsure of the nature of **6**.

In summary, the experiments involving irradiation of **1** in 3MP alone and in the presence of THF reveal the existence of a solvento species formed at 97 K following CO loss and formation of *cis*-$(CO)_4(THF)Cr{=}C(OMe)Ph$ when THF is present. The low-temperature spectra show also that upon warming there is an additional interaction of THF with the THF-complexed molecule, which we ascribe to weak, reversible binding of THF to the carbene carbon. At higher temperature, THF is replaced by CO, forming the starting material, **1**. These and additional, and more tentative, conclusions are summarized in Scheme 2.

Additional evidence in support of the proposed interaction of THF with the carbene carbon was obtained by carrying out the photolysis of **1** in 3MP in the presence of 4.9 mM pyridine. The initially-formed product exhibits bands at 2003, 1888, and 1844 cm^{-1}. Upon warming, in the temperature range 157–207 K, the initially-formed species disappears, to be replaced by an intermediate with bands at 2008, 1902, and 1868 cm^{-1}. This intermediate in turn reverts to **1** as the solution is warmed beyond 207 K. We ascribe the initially-formed photoproduct to the *cis*-substituted pyridine adduct, in which a pyridine is bound to the carbene carbon, *cis*-$(CO)_4(py)CrC(OMe)(py)Ph$. As the sample is warmed, pyridine dissociates from the carbene carbon, resulting in *cis*-$(CO)_4(py)Cr{=}C(OMe)Ph$, which has generally higher CO stretching frequencies. Upon still further warming, the pyridine is replaced by CO. The CO stretching frequencies for the py compounds are closely similar to those for the corresponding THF analogs, as is to be expected. There is no evidence for an analog of **6** in the py experiments.

Scheme 2

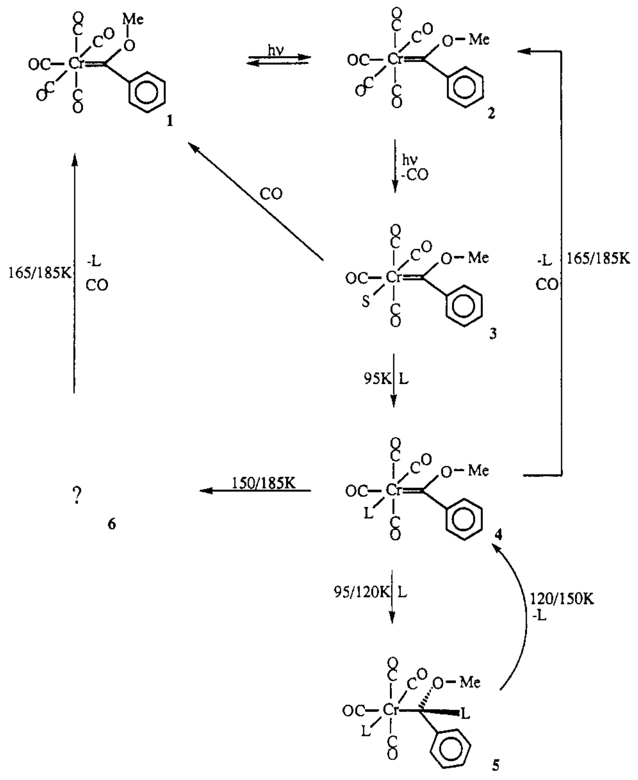

Table 2. IR Data for Photochemical Intermediates Following Irradiation at 95 K of $(CO)_5Cr{=}C(OMe)Ph$ (1, 2) in the Presence of 4-$CF_3C_6H_4CCH$ (7) (cm^{-1})

	species		
	8	9	10
	(a) [1] = 0.51 mM, [7] = 0.68 mM		
TR (K)	95–223		200→295
IR	2040		1967
	1987		1904
	1970		1891
	1908		
	(b) [1] = 0.70 mM, [7] = 0.68 mM, [THF] = 2.5 mM		
TR (K)[a]	155–220	200–295	230→295
	2040	1960	1968
	1987	1895	1906
	1970	1873	1892
	1908		

[a] The spectra in the range from 95 to 155 K exhibit bands due to **4–6**, just as in the absence of **7** (Table 1).

Photolysis in the Presence of 4-$CF_3C_6H_4CCH$. When **1**, 0.51 mM in 3MP, is photolyzed in the presence of 0.68 mM 4-$CF_3C_6H_4CCH$ (**7**) at 95 K, the sole product observed, other than *anti* → *syn* conversion, in the shortest time in which an IR spectrum can be obtained, about 2 min, exhibits bands at 2040, 1987, 1970, and 1908 cm^{-1}. On warmup, this product, **8**, is relatively persistent; it converts in the temperature range 200–235 K (Figure 5) to a new species, **10**, with absorptions at 1967, 1904, and 1891 cm^{-1}, bands characteristic of the phenol annulation product[1a,4,19] (Scheme 1, $R_1 = CH_3$, $R_2 = p\text{-}CF_3C_6H_4$, $R_3 = H$, $R_4 = H$).

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(19) Dötz, K. H.; Mühlemeier, J.; Schubert, U.; Orama, O. *J. Organomet. Chem.* **1983**, *247*, 187–201.

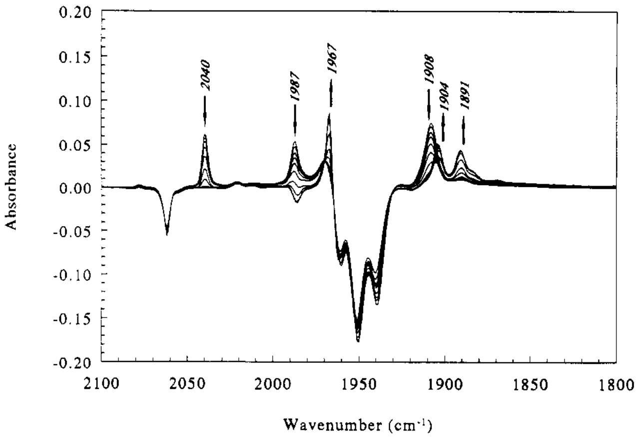

Figure 5. Difference spectra between the spectrum taken before irradiation of a 0.51 mM solution of **1** in 3MP, with 0.68 mM **7**, and following irradiation, in the temperature interval from 195 to 235 K. As in earlier figures, the negative absorbances correspond to loss of **1** upon irradiation.

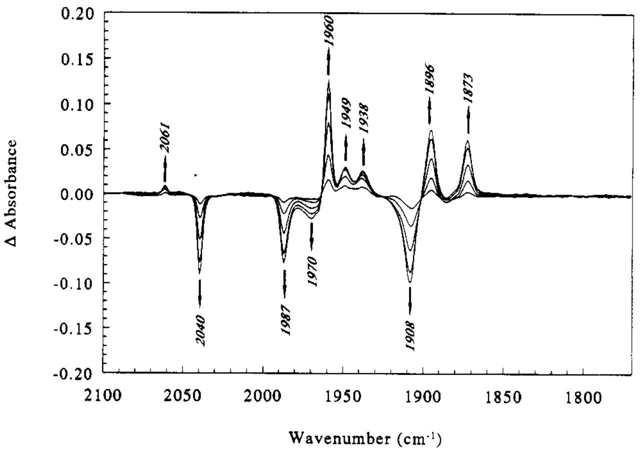

Figure 6. Difference spectra for a 0.70 mM solution of **1**, with 0.68 mM **7** and 2.5 mM THF in 3MP, irradiated at 97 K, upon programmed warmup. The spectra represent the difference between the spectrum at 198 K and successive spectra to 220 K. The major positive bands correspond to the growth in **9**. The lesser positive bands correspond to recovery of small amounts of starting materials, **1**/**2**, through reaction of CO with residual **4** or **6**. The negative absorptions correspond to loss of **8** as it converts to **9**.

Comparable IR bands are observed at 1965, 1900, and 1886 cm^{-1} for $R_1 = CH_3$, $R_2 = C_6H_5$, $R_3 = CH_3$, and $R_4 = H$.[4] These results suggest that in the absence of a competing base, the alkyne binds to the coordinative vacancy at Cr following CO loss and that only a single stable intermediate exists in the pathway toward final product. We defer for the moment a discussion of what this intermediate might be.

When 0.70 mM **1** is similarly photolyzed at 95 K in the presence of 0.68 mM alkyne and 2.5 mM THF, the initial product observed is **4**. Upon warmup, the behavior of the system is entirely analogous to that seen when only THF is present: **4** converts to **5**, which at higher temperature reverts to **4**, and **6** is observed to appear in the temperature interval 155–180 K. Beginning at about 155 K, however, **4** and **6** are observed to convert to **8**, the sole alkyne product observed in the absence of THF. As **8** disappears in the temperature range of 220 K upon continued warmup, a new product, **9**, with bands at 1960, 1895, and 1873 cm^{-1}, is observed (Figure 6). This new intermediate in turn disappears in the temperature range 230–295 K, forming **10**.

The spectral changes observed when both alkyne and THF are present clearly indicate that THF competes effectively for binding at the site of coordinative vacancy at Cr following CO loss. Furthermore, the changes that occur upon warming, that are seen when only THF is present, also occur in the presence of dilute alkyne. Not until the temperature regime is reached at which THF dissociation occurs, as measured by recombination with CO in the absence of an alternative nucleophile, does reaction with alkyne occur to yield the same product as seen in the absence of THF. From this, one can infer that, in THF as solvent, the solvent binds initially to Cr following CO loss in the thermal reaction. Nevertheless, the observed kinetics[4] lead to the conclusion that the rate at which alkyne achieves access to the metal is sufficiently high so, that the reaction rate is determined by the rate of CO loss rather than by alkyne concentration.

In the photolysis experiments in the presence of alkyne and absence of THF, it was necessary to irradiate over an extended period to time, 10 min, to produce sufficient photoproduct for IR analysis. It could therefore be the case that **8** is a secondary photochemical product, resulting from rapid photochemical conversion of an initially-formed product. Thus, it is significant that, in the experiments just described, **8** is the first observable product resulting from a *thermal* reaction of the alkyne with the complex.

The alkyne-containing intermediate **8** is observed to decay at the same temperature whether or not THF is present. This suggests that the transformation of **8** is not promoted by base attack. On the other hand, at some stage in the process leading from **8** to the annulation product, an intermediate must arise that can interact with THF, leading to the observed intermediate **9**.

Scheme 3 illustrates several possibilities for the identities of intermediates **8** and **9**. While an η^2-coordinated alkyne is at least a possibility for **8**, this seems unlikely on several grounds. It seems unlikely that alkyne could compete effectively with THF as ligand at higher temperature if it were not able to do so at the lower temperature. At the temperature of irradiation, the alkyne is likely incapable of diffusion through the solvent glass. However, as the glass warms, diffusional mobility should set in at lower temperature than that at which **8** makes its appearance. Secondly, the CO stretching frequencies observed for **8** are considerably higher than observed for the analogous solvento species **3** or the THF adduct **4**.

The alternative structures for **8** include the vinylcarbene and the frequently-mentioned vinylketene, which is presumed to exist following CO insertion on the pathway to the phenol annulation product, eq 1.[1b,3,8] The vinylketene is rendered less likely as the origin of **8** by the fact that there is no evidence for a coordinated ketene functionality in the region around 1775–1700 cm^{-1}, where an absorption of moderate intensity is seen in vinylketenes.[9,20]

Assuming that species **8** is the vinylcarbene, four alternatives drawn from among previously proposed intermediates suggest themselves as the structure of **9**, as shown in Scheme 3. The carbonyl stretching modes are shifted to lower frequencies for **9** as compared with **8**. This

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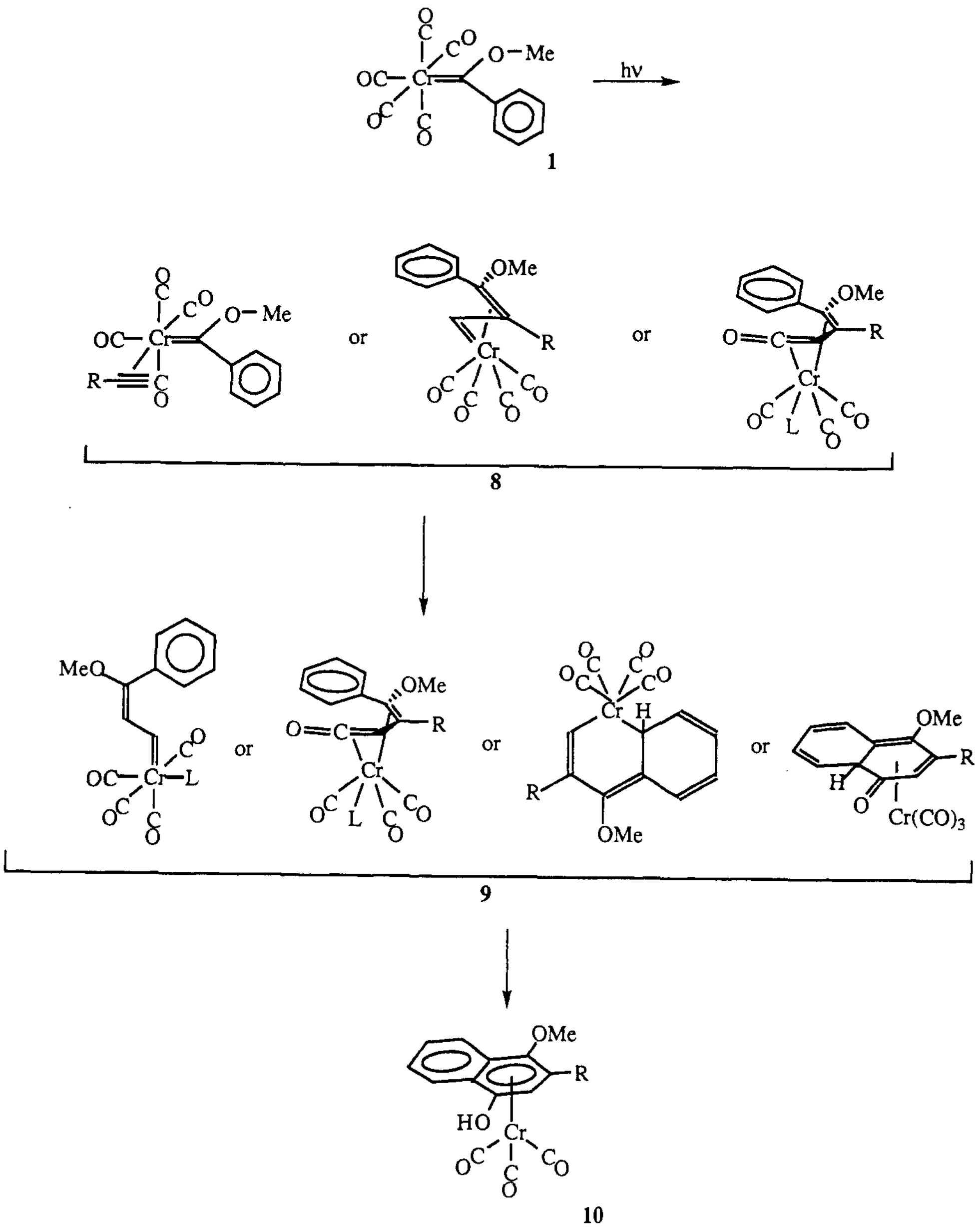
[20] (a) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 8617–8618. (b) Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, T.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368–378.

Scheme 3



is not to be expected for the η^1-carbene, on the basis of comparisons with the IR data for 4 or 5, or other substituted carbenes reported in the literature. Similarly, the IR bands for reported metallacyclic analogs[21] lie at much higher frequencies than observed for **9**.

If **9** is indeed the vinylketene, a band associated with the ketene function should be seen in the vicinity of 1725 cm^{-1}, whereas we see no evidence of absorption there. Even though ketene absorptions are lower in intensity than the carbonyl stretching modes, it seems unlikely that they would not be observable under the conditions giving rise to the spectra shown in Figure 6.

A fourth possibility is that **9** is the immediate product of the ring closure process, before hydrogen atom transfer. An interaction with THF at the metal center could stabilize this form as compared with hydrocarbon solution. In additional support for this possibility, it is noteworthy that only three CO stretch modes are seen for **9**, and the pattern is not much different from that seen for the final product, **10**.

Summary

The experimental approach taken in this work does not in itself provide more than indirect evidence regarding the structures of intermediates formed in the course of complex processes in which several intermediates might be formed. At the same time, the IR bands observed are quite sensitive to structural changes; thus they do provide useful pointers to what the coordination environment around the metal center must be. Of equal importance, the use of low-temperature irradiation with subsequent warmup provides conditions under which the number and variety of intermediates can most readily be discerned.

In the absence of a competing nucleophilic solvent, reaction of a prototypical terminal alkyne, **7**, with **1** under photochemical conditions leads to formation of just one observable intermediate, **8**, which proceeds directly to product. Given that the warmup procedure begins at a

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[21] (a) Lindner, E.; Schass, E.; Hiller, W.; Fawzi, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 711. (b) Bird, C. W.; Briggs, E. M. *J. Chem. Soc. C* **1967**, 1862. (c) Grevels, F. W.; Buchkremer, J.; Koerner von Gustorf, E. A. *J. Organomet. Chem.* **1976**, *111*, 235. (d) Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1977**, *128*, 399.

comparatively low temperature of 95 K and that 8 persists to relatively high temperature, on the order of 200–225 K, it seems unlikely that any other intermediates along the reaction pathway possess substantial energy minima, at any rate with the particular alkyne employed.

The results obtained when 1 is irradiated in the presence of both alkyne and THF point to the existence of a second intermediate, which might contain solvent, formed along the reaction pathway just before formation of the phenol product. Under other reaction conditions, with higher concentrations of alkyne, the alkyne might serve in the role of nucleophile in stabilizing such an intermediate.

There is no evidence in our results for the intermediacy of a vinylketene along the reaction pathway. Such a species might very well form, but if it does, the barrier to its further reaction is sufficiently low so that it does not accumulate to a significant extent.

We have observed no evidence for a direct interaction of a second molecule of alkyne with the metal complex at any stage, as postulated by Wulff and co-workers in their proposal for an "allochemical" mechanism.[3] The interaction with a second molecule of alkyne is proposed to result in an increased proportion of phenol vs indene product. Inasmuch as the alkyne chosen for the present study leads predominantly to the phenol product, some evidence of the proposed interaction might have been anticipated. However, the conditions of our experiments, particularly the low concentration of alkyne, are probably inappropriate for probing this issue. We plan on extending our studies to a wider range of reaction conditions and to other alkynes.

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