

Laser Photochemistry and Transient Raman Spectroscopy of Silyl-Substituted Fischer-Type Carbene Complexes

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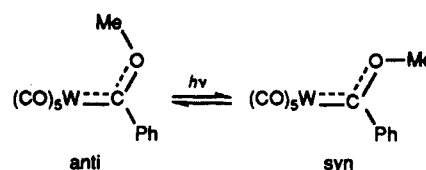
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Pulsed laser irradiation of the silyl-substituted carbene complexes $(\text{CO})_5\text{W}=\text{C}(\text{XR})\text{SiPh}_3$ ($\text{XR} = \text{NC}_4\text{H}_9$ (1); $= \text{OEt}$ (2)) in various solvents has been investigated using transient absorbance and time-resolved resonance Raman scattering as monitoring techniques. Irradiation of (1) in noncoordinating or weakly-coordinating solvents at 355 nm within the ligand field absorption band results in the rapid formation, within the laser pulse duration, of a permanent photoproduct. Saturation of the irradiated solution with CO results in regeneration of the starting complex 1. IR and Raman spectral data suggest that the photoproduct is the internally stabilized 16-electron species $(\text{CO})_4\text{W}=\text{C}(\text{NC}_4\text{H}_9)\text{SiPh}_3$. The observations are discussed in relation to the previously reported formation of the same 16-electron species by thermolysis of 1. When the irradiation is carried out in CH_3CN as solvent, UV-visible evidence suggests formation of the photosubstituted species $(\text{CO})_4(\text{CH}_3\text{CN})\text{W}=\text{C}(\text{NC}_4\text{H}_9)\text{SiPh}_3$. No photoactivity, either transient or permanent, is seen in any solvent when the irradiation is carried out at 416 nm, a wavelength which falls within the MLCT absorption region of 1. When the ethoxy-substituted carbene complex 2 is irradiated in either the LF or MLCT absorption regions a transient species forms rapidly, within the laser pulse duration, and decays on a time scale of several μs , with a lifetime dependent on solvent polarity but independent of CO concentration in solution. Time-resolved resonance Raman studies in which the sample is photolyzed at 355 nm and probed by means of a delayed pulse at 406 nm show the formation and decay of a transient consistent with the flash photolysis results. The data are interpreted in terms of photoinduced anti-syn isomerization of 2 about the $\text{C}_{\text{carbene}}-\text{O}$ bond.

Introduction

Organometallic photochemistry and spectroscopy including time-resolved studies are areas of considerable and growing interest, with metal carbonyls and mixed-ligand carbonyls receiving the most attention.¹ Metal-carbene complexes have also been studied, both in solution² and in low-temperature matrices³ and were the subject of the first reported⁴ application of time-resolved resonance Raman spectroscopy to the study of photogenerated transients in an organometallic complex. The Fischer carbene complex, $(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$, has absorption bands with maxima near 350 and 375 nm, attributable to ligand field and MLCT transitions, respectively. In a

matrix at 10 K the most significant primary process following irradiation³ into either the LF or MLCT bands is anti \rightleftharpoons syn isomerization about the carbene C-O bond.



Upon irradiation into the LF band alone, secondary photodissociation of CO is observed, in addition to isomerization. A closely related but much less widely studied group of carbene complexes are those with silyl substituents.⁵ The thermal reactivity of species of the type $(\text{CO})_5\text{WC}(\text{XR})\text{SiPh}_3$ has been investigated.^{5,6} When $\text{XR} = \text{NC}_4\text{H}_9$ (1), thermal dissociation of CO is observed^{6c} to give the 16-electron product, $(\text{CO})_4\text{WC}(\text{NC}_4\text{H}_9)\text{SiPh}_3$. This product is stabilized by a relatively minor change of conformation so that one of the phenyl rings of the SiPh_3 group can act as a screen for the vacant site at the tungsten center. In contrast, when $\text{XR} = \text{OC}_2\text{H}_5$ (2), no 16-electron products are observed upon thermolysis. Several major species are formed, among them HSiPh_3 , ethene, EtSiPh_3 , and $\text{Ph}_3\text{SiC}(\text{O})\text{Et}$. The photoreactivity of these systems has not previously been studied. The present paper reports

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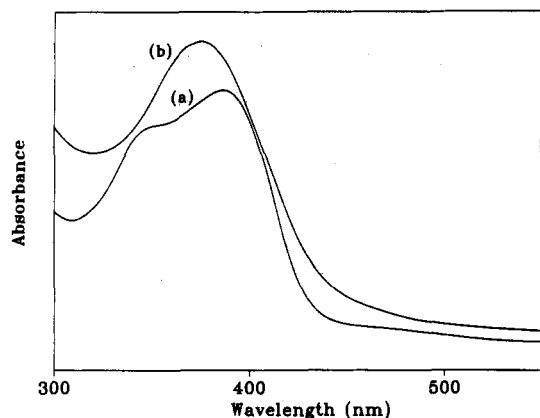


Figure 1. Spectral changes observed in $(\text{CO})_5\text{W}=\text{C}(\text{NC}_4\text{H}_8)\text{SiPh}_3$ upon irradiation in pentane solution at 354.7 nm. Trace a: spectrum prior to photolysis. Trace b: spectrum recorded after pulsed irradiation at 354.7 nm for 3 min (pulse energy ca. 5 mJ; rep rate 10 Hz). Spectra have been displaced vertically for convenience of presentation.

our findings from an investigation of 1 and 2 by laser flash photolysis coupled with time-resolved UV-visible and resonance Raman spectroscopy.

Experimental Section

Flash photolysis and transient resonance Raman (RR) studies were carried out using the apparatus described previously,⁷ based upon a pulsed Nd/YAG laser. Two-color time-resolved RR experiments were conducted at the Central Laser Facility, Rutherford Appleton Laboratory (RAL), using excimer and excimer-pumped dye lasers as pump and probe sources respectively.

Compounds were prepared as described elsewhere.⁶ For the flash photolysis experiments involving spectrophotometric monitoring in the UV-visible range degassed or argon-purged samples in 1-cm fluorimeter cells were used. For the time-resolved Raman measurements the argon-purged samples were circulated through a quartz capillary (ca. 1-mm i.d.) at a rate which ensured that each pump/probe pulse combination encountered a fresh volume of sample, thus minimizing sample decomposition in the laser beam.

Results

(a) Flash Photolysis. $(\text{CO})_5\text{WC}(\text{NC}_4\text{H}_8)\text{SiPh}_3$ (1). Complex 1 is a pale yellow solid with a ground-state electronic absorption spectrum exhibiting two bands located at 354 and 380 nm in dichloromethane solution. Excited-state absorption measurements, following pulsed excitation at 355 nm of a solution of 1 in pentane resulted in a rapid, instrument-response-time-limited change in the absorbance which was permanent over the range 350–500 nm. The observed spectral changes are shown in Figure 1. The ground-state MLCT absorption band of 1 undergoes a small blue shift while the adjacent LF band near 350 nm gradually decreases in intensity. When CO is bubbled through the solution the parent complex is regenerated and the original spectrum is restored. No detectable photoreaction occurred when the irradiation wavelength was altered to 416 nm.

When the 355-nm irradiation experiment was repeated in CH_3CN instead of pentane, a similar shift to the blue

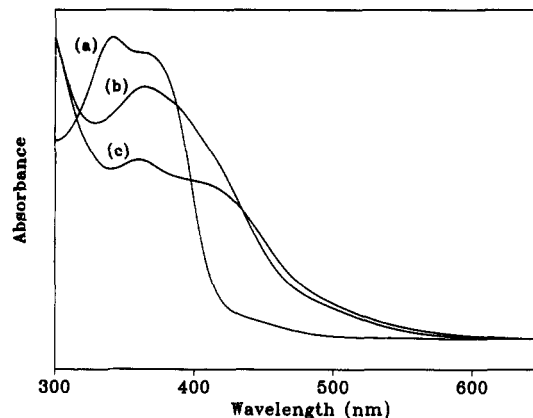


Figure 2. Spectral changes following pulsed irradiation at 354.7 nm of $(\text{CO})_5\text{W}=\text{C}(\text{NC}_4\text{H}_8)\text{SiPh}_3$ in Ar-purged CH_3CN solution: (a) before irradiation; (b) after 2 min of irradiation; (c) after 4 min of irradiation (ca. 5 mJ pulse energy, rep rate 10 Hz). Spectra have been displaced vertically for convenience of presentation.

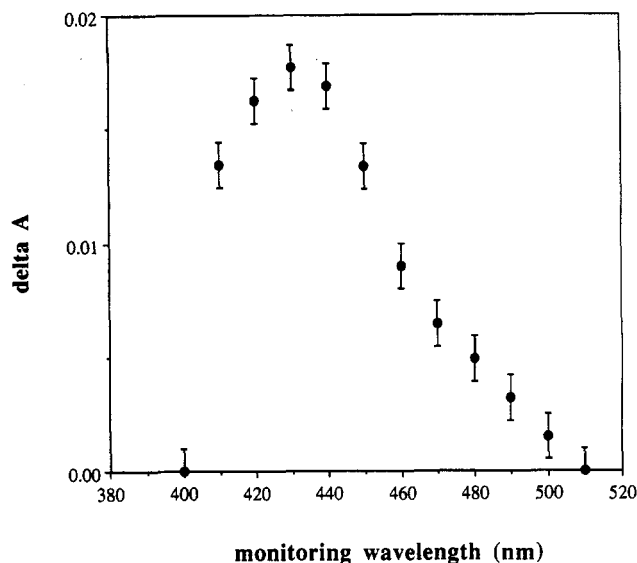


Figure 3. Transient absorbance difference spectrum recorded following flash photolysis of 2 at 354.7 nm in pentane solution (solution concentration ca. 10^{-3} mol dm^{-3} , pulse energy 10 mJ; error bars refer to an estimated 10% error).

Table I. Influence of Solvent on Lifetimes of Transients Generated by Flash Photolysis of $(\text{CO})_5\text{WC}(\text{OEt})\text{SiPh}_3$ at 355 nm

solvent	lifetime ^a /μs	solvent	lifetime ^a /μs
CH_2Cl_2	$7.0 \pm 0.2^{b,c}$	C_6H_{12}	2.5 ± 0.2
$n\text{-C}_5\text{H}_{12}$	2.3 ± 0.4	CHCl_3	$4.6 \pm 0.2^{b,d}$
CH_3CN	5.5 ± 0.5		

^a Ar-saturated solutions at 21 °C. ^b Values unchanged in CO-saturated solutions. ^c Lifetimes also measured in this solvent at the temperatures (K) indicated: 14.7 ± 0.5 (281), 20.9 ± 0.7 (276), 33.6 ± 3.0 (269). ^d Solution temp, 24 °C.

of the MLCT band was again observed, and in addition the growth of a new band occurred near 420 nm. The spectral changes are shown in Figure 2.

$(\text{CO})_5\text{WC}(\text{OEt})\text{SiPh}_3$ (2). Complex 2 is a dark red solid, the electronic absorption spectrum in dichloromethane exhibiting two bands at 358 and 398 nm. Markedly different flash photolysis behavior compared to 1 was observed for complex 2. Irradiation at 355 nm in pentane caused a rapid, instrument response-limited

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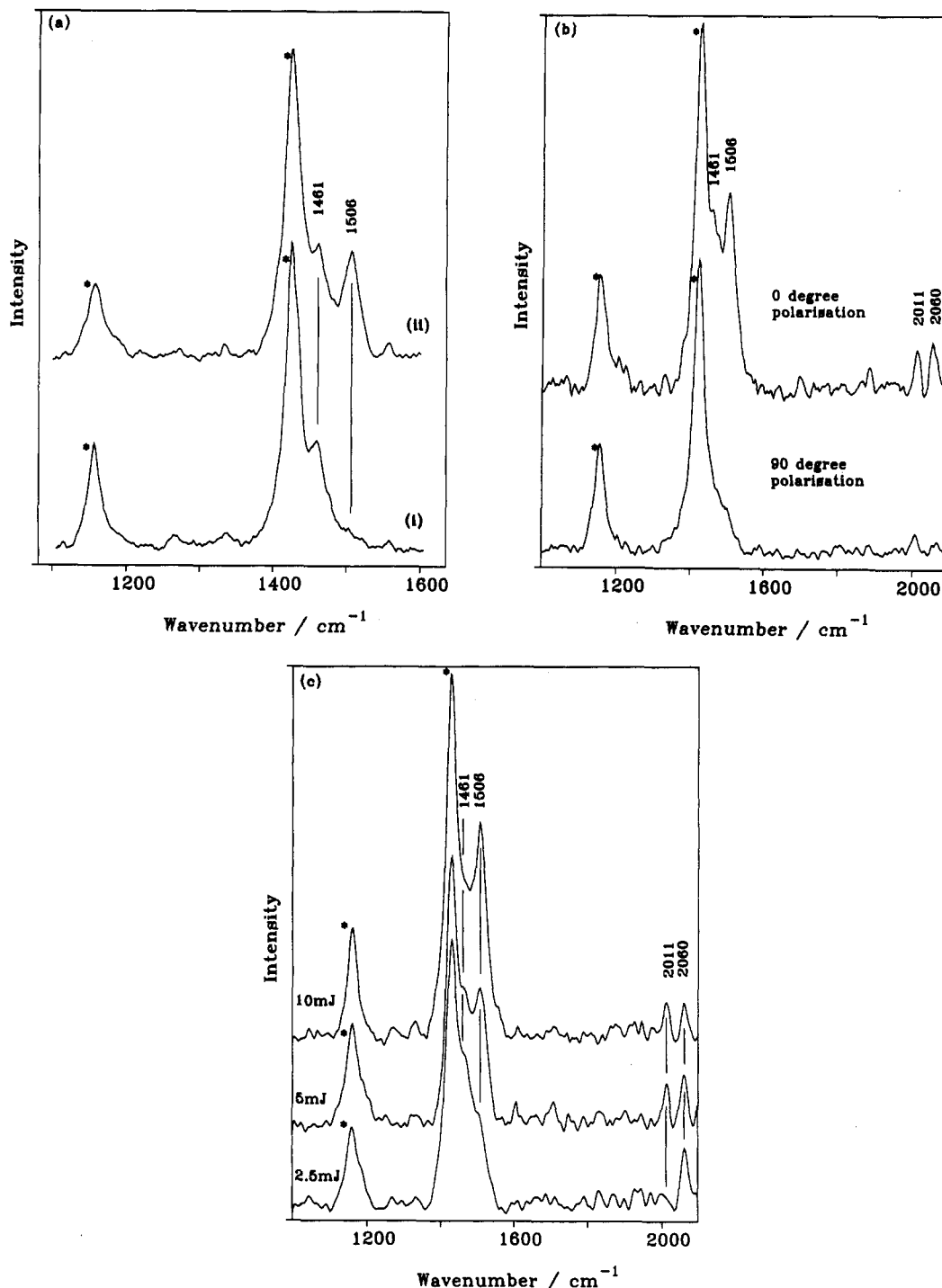


Figure 4. Changes in Raman spectra observed following pulsed irradiation of $(\text{CO})_5\text{W}=\text{C}(\text{NC}_4\text{H}_9)\text{SiPh}_3$ in CH_2Cl_2 (ca. 10^{-3} mol dm^{-3}). (a) Trace i: spectrum recorded at $\lambda_{\text{exc}} = 416$ nm (pulse energy ca. 4 mJ, spectra accumulated for 6 min). Trace ii: spectrum recorded at $\lambda_{\text{exc}} = 354.7$ nm (pulse energy ca. 4 mJ, spectra accumulated for 10 min). (b) Polarization study of a sample similar to that used to record trace ii above, $\lambda_{\text{exc}} = 354.7$ nm. (c) Influence of laser energy on grow-in of features at 1506 and 2011 cm^{-1} due to permanent photoproduct, $\lambda_{\text{exc}} = 354.7$ nm. Spectral accumulation time was 10 min on fresh sample at each energy (* = solvent features).

rise in absorbance monitored at several wavelengths in the range 340–500 nm, followed by exponential decay to the preflash absorbance level. The transient absorbance difference (ΔA) spectrum is shown in Figure 3 and exhibits a red shift from the absorption spectrum of the parent complex. Saturation of the solution with CO had no effect on the transient lifetime. However, the lifetime did vary with temperature and solvent, as shown by the data in Table I. In contrast to the situation with 1, no permanent photoproduct was observed following irradiation of 2 in pentane or CH_3CN at either 355 or 416 nm.

(b) Resonance Raman Spectroscopy. The resonance Raman spectrum of 1 in CH_2Cl_2 generated by pulsed excitation at 416 nm is shown in Figure 4a, trace i. At 416 nm no photoproduct is created and the Raman spectrum observed is that of the parent complex 1. The main spectral features are bands at 1461 cm^{-1} and in the carbonyl region near 2060 cm^{-1} . Attempts to generate the ground-state resonance Raman spectrum of 1 using $\lambda_{\text{exc}} = 354.7$ nm invariably resulted in a spectrum with new features (trace ii), at 1506 and 2011 cm^{-1} . Figure 4c shows the effect on solutions of 1 of varying the 354.7-nm excitation energy.

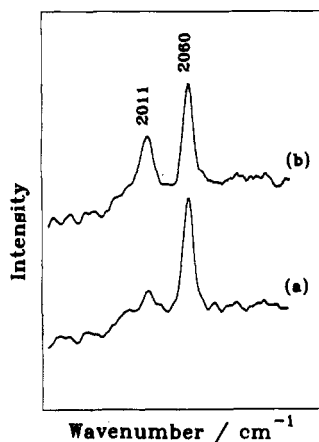


Figure 5. Influence of CW irradiation (Ar^+ laser) at 363.8 nm on solution of **1** in CH_2Cl_2 (ca. 10^{-3} mol dm^{-3}). Trace a: spectrum recorded without prior irradiation. Trace b: same sample irradiated for 20 min at 363.8 nm prior to recording Raman spectrum (laser power at sample ca. 20 mW).

Table II. Raman^a and IR^b Bands (cm^{-1}) for $(\text{CO})_5\text{WC}(\text{NC}_4\text{H}_9)\text{SiPh}_3$ and Photolysis and Thermolysis Products

	Raman	IR
$(\text{CO})_5\text{WC}(\text{NC}_4\text{H}_9)\text{SiPh}_3$ (1)	2060, 1461	2055, 1968, 1931, 1928, 1921
photoproduct from irradiation of 1 at 355 nm	2011, 1506	2015, 1923, 1909, 1856
product from thermolysis ^c of 1		2010, 1925, 1911, 1859

^a Recorded in dichloromethane. ^b Recorded in pentane. ^c Data taken from ref 6.

At higher light intensities, where photoproduct formation is more rapid, the 1506 and 2011 cm^{-1} bands are stronger. Fresh solutions of **1** were used to record each of the three spectra shown in Figure 4c. Both the 1506 and 2011 cm^{-1} features are polarized (Figure 4b). Although the spectrum excited at 416 nm (Figure 4a, trace i) showed only ground-state features, bands at 1506 and 2011 cm^{-1} did appear in the spectrum (not shown here) generated at this same λ_{exc} after the sample had been irradiated at 354.7 nm. The same frequency changes are seen at $\lambda_{\text{exc}} = 363.8$ nm (CW excitation using an Ar^+ laser) after the sample had been irradiated at this wavelength for several minutes prior to recording the Raman spectrum. The effect is demonstrated in Figure 5 which shows the influence of 363.8-nm irradiation on the Raman spectra in the carbonyl region. Trace a shows the spectrum recorded immediately upon exposure to 363.8-nm radiation, while for trace b, in which the 2011 cm^{-1} CO band is evident, the sample was irradiated for 20 min at 363.8 nm prior to recording the Raman spectrum.

The above findings are summarized in Table II which includes the IR spectra data for complex **1** recorded before and after irradiation at 363.8 nm. Also shown for comparison are the IR data^{6c} for the thermally generated 16-electron species, $(\text{CO})_4\text{W}=\text{C}(\text{NC}_4\text{H}_9)\text{SiPh}_3$.

The Raman spectra recorded for the OEt-substituted complex **2** are different from those which characterize **1**. The results are summarized in Figure 6. The spectral range from ca. 300 to 2100 cm^{-1} was scanned, but the main features which appear in the ground-state spectrum excited at 363.8 nm are two moderately intense bands at 798 and 875 cm^{-1} . A single color pump and probe study employing

pulsed excitation at 416 nm results in the appearance of an additional transient feature at 782 cm^{-1} as shown in trace b of Figure 6. In this experiment, the effective delay between pump and probe is the pulse duration, i.e., ca. 8 ns. A complete two-color time-resolved resonance Raman (TR³) study on **2** was also carried out, using a pump wavelength of 351 nm and a probe wavelength set at 406 nm. The results are shown in Figure 7. The 782 cm^{-1} feature is present at short pump-probe delays but decays over a time scale of a few μs . The findings parallel the flash photolysis studies referred to above on **2** in the same solvent (CH_2Cl_2) where a transient lifetime of 7 μs was recorded.

Discussion

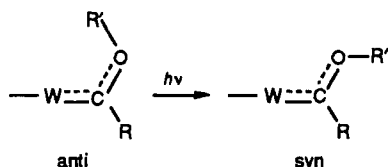
The shift in λ_{max} (in pentane) of the longest wavelength band in the ground electronic state absorption spectra, from 380 nm in **1** to 398 nm in **2**, suggests that the lowest excited state in these complexes is MLCT in nature since the shift is in line with the degree of stabilization of such a state in metal-carbene complexes which would be expected⁸ upon replacement of nitrogen (NC_4H_9 in **1**) by the less electron-donating oxygen atom (OEt in **2**). The bands at slightly higher energy (354 and 358 nm in **1** and **2**, respectively) are attributed to LF transitions.

The IR and Raman spectral data summarized in Table II indicate that the permanent photoproduct formed when complex **1** is irradiated at 355 nm is identical to the 16-electron CO-loss species generated by thermolysis of **1**. Hence, the results of the irradiation experiment is also consistent with the assignment of this band as LF in nature since excitation here would be expected to result in CO loss as observed. On the basis of the established X-ray structure reported^{6c} for the thermolysis product from the analogous complex, $(\text{CO})_5\text{WC}(\text{NC}_5\text{H}_{10})\text{SiPh}_3$, the permanent photoproduct from **1** is assigned to a 16-electron complex in which a phenyl ring of the SiPh_3 group screens the vacant site on the tungsten. The fact that **1** and the analogous complexes with $\text{NR}_2 = \text{NC}_5\text{H}_{10}$ and $\text{NR}_2 = \text{NEtMe}$ behave in identical fashion upon thermolysis^{6c} supports our assignment. It is significant that no photoproduct is formed when **1** is irradiated at 416 nm. This is in line with the band assignments proposed above since 416 nm lies within the MLCT transition whereas CO loss is associated with population of the higher energy LF state. The blue shift to 356 nm of the MLCT band at 386 nm and the growth of a new band at 420 nm when **1** is irradiated in CH_3CN indicate the formation of a photosubstitution product in which CH_3CN occupies the site vacated by CO. This is analogous to the behavior previously noted^{2j} for the Fischer carbene complex. The band at 2011 cm^{-1} characteristic of the 16-electron species appears both in the Raman and IR spectra. An equivalent band (ca. 2017 cm^{-1}) also appears^{2j} in the IR spectra of *cis*- $(\text{CO})_4\text{LW}=\text{C}(\text{OR})\text{R}$ where the ligand L is in a *cis* arrangement with respect to the $\text{W}-\text{C}_{\text{carbene}}$ bond. The band is assigned^{2j} to a ν_{CO} mode of species a_1 in the approximate local symmetry of C_{2v} assumed for the *cis* complex. The 16-electron product from thermolysis of $(\text{CO})_5\text{WC}(\text{NC}_5\text{H}_{10})\text{SiPh}_3$, the analogue of **1**, also shows^{6c} a *cis* arrangement of the $\text{W}-\text{C}_{\text{carbene}}$ bond with respect to the phenyl ring of the SiPh_3 group which screens the vacant site at the tungsten.

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The fact that the 2011 cm^{-1} band in the Raman spectrum of **1** (Figure 4b) is polarized is consistent with its assignment to a CO mode of species a_1 .

The behavior of complex **2** upon irradiation contrasts markedly with the above. No permanent photoproduct is formed upon irradiation at 355 nm in pentane, and the additional irradiation studies at this wavelength in acetonitrile exhibited no evidence for CO photosubstitution. This suggests that the quantum yield ϕ for CO loss in this complex at an irradiation wavelength of 355 nm is very low. The transient species which does form following irradiation at either 355 nm or 416 nm decays with a lifetime independent of [CO] in solution, a further indication that CO photodissociation is not involved. The dependence of transient lifetime on solvent is reminiscent of that observed⁴ for the Fischer complex $(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{Ph}$ for which it has recently been suggested³ on the basis of irradiation studies in an inert gas matrix that the major process following irradiation in either the MLCT or LF absorption region is photoinduced isomerization to the syn form from the anti configuration of the ground electronic state:



X-ray crystallographic studies⁹ of the Cr analogue of **2**, $(\text{CO})_5\text{CrC}(\text{OEt})\text{SiPh}_3$, show that it exists in the ground state largely as the anti-isomer. If we suppose that in **2** the anti isomer is likewise favored, as with the majority of carbene complexes of this type, then the transient formation and solvent-dependent decay observed when **2** is irradiated in the LF or MLCT absorption regions may be attributed to anti to syn photoisomerization by analogy with the Fischer complex. This conclusion is supported by the data in Table I showing the variation with temperature observed for the transient in CH_2Cl_2 solution. An Eyring plot of the data yields an approximate activation enthalpy of 42 kJ mol^{-1} , similar to that measured¹⁰ for the Fischer complex in the same solvent. The photophysical picture proposed³ in the latter case envisages the isomerization to take place via the lowest lying triplet MLCT state, and it seems reasonable to conclude that the photoisomerization in **2** is also mediated by the corresponding lowest lying triplet state. If it is assumed that electric dipole transitions from either the anti or the higher energy syn isomers of **2** take place to equienergetic Franck-Condon levels of this MLCT state, the red shift observed in the ΔA spectrum of the syn isomer (Figure 3) can be accounted for, and this in turn would be internally consistent with the attribution of the transient absorbance changes to the photoisomerization. A similar red shift noted¹¹ in the ΔA spectrum associated with the corresponding anti to syn isomerization of the carbene complex $(\text{CO})_5\text{WC}(\text{OMe})\text{Me}$ (**3**) may be explained in a like manner.

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(10) Rooney, A. D. Ph.D. Thesis, Queen's University, Belfast, 1991.

(11) This simple picture in which the MLCT state is represented by a symmetrical PE "curve" is evidently not applicable in the case of the Fischer complex, $(\text{CO})_5\text{WC}(\text{OMe})\text{Ph}$, where a blue shift¹⁰ is observed in the ΔA spectrum associated with photoisomerization. This point will be taken up elsewhere.

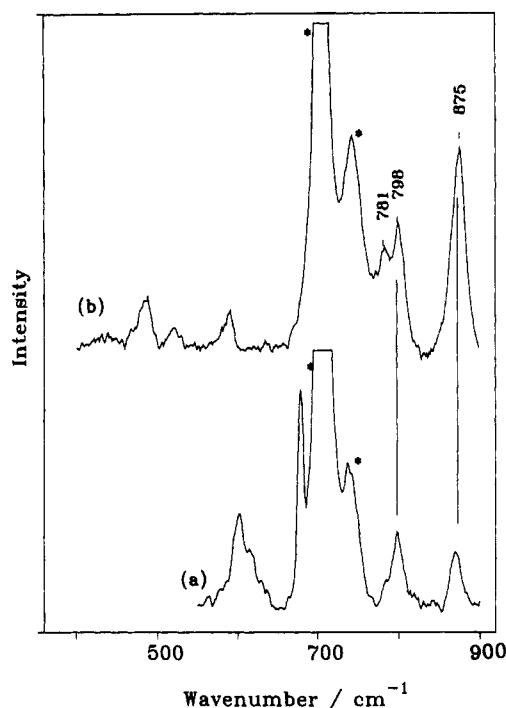


Figure 6. Raman spectra of $(\text{CO})_5\text{W}=\text{C}(\text{OEt})\text{SiPh}_3$ recorded in CH_2Cl_2 : (a) CW excitation with Ar^+ laser, $\lambda_{\text{exc}} = 363.8 \text{ nm}$; (b) pulsed excitation at $\lambda_{\text{exc}} = 416 \text{ nm}$ (single color pump and probe experiment with effective pump-probe delay of ca. 8 ns) (* = solvent features).

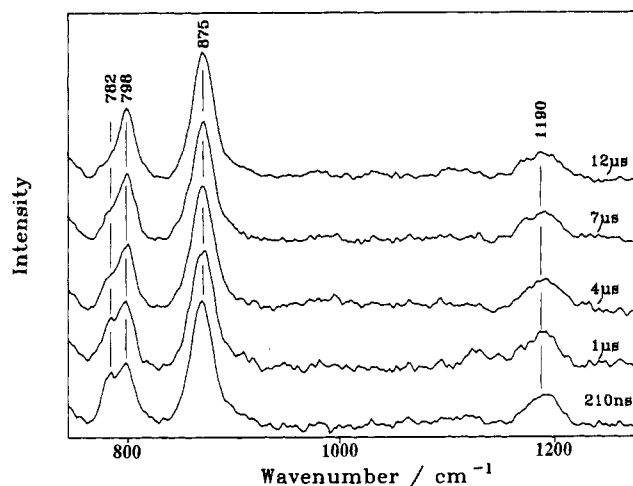


Figure 7. Two-color time-resolved resonance Raman study of $(\text{CO})_5\text{W}=\text{C}(\text{OEt})\text{SiPh}_3$ in CH_2Cl_2 (ca. $10^{-3} \text{ mol dm}^{-3}$): Pump λ 351 nm; probe λ 406 nm (probe pulse energy ca. 0.4 mJ).

However, the transient ΔA decay time (in effect the lifetime of the syn isomer) measured in this case¹⁰ is at least 2 orders of magnitude longer than for complex **2** under investigation here. This may be largely a reflection of a greater degree of steric interaction between the OEt and bulky SiPh_3 groups in **2** compared to that between the OMe and Me groups of **3**.

The results of the TR³ studies displayed in Figure 7 show that the feature at 782 cm^{-1} decays on the μs time scale. This provides strong evidence that this feature is associated with the transient observed in the flash photolysis experiments and assigned to the syn isomer. The 782 cm^{-1} band is thus a convenient Raman signature for this isomer. No species have been detected in the transient Raman studies which could be attributed to CO

loss, suggesting that ϕ for this process is very low, as already suggested by the flash photolysis studies. In the case of complex 1 CO loss does occur and a permanent CO loss photoproduct is readily detectable.

The two systems therefore provide an interesting contrast in photochemical behavior. With 1, photoactivity in the form of CO photodissociation occurs only upon irradiation within the LF band. Irradiation within the MLCT region produces no detectable effect. In the case of complex 2 irradiation at wavelengths within either LF or MLCT absorption regions produces a transient species with μs lifetime assigned to the syn isomer generated by photoisomerization of 2 about the $\text{C}_{\text{carbene}}\text{-O}$ bond followed by decay to the favored anti form of the ground state of the complex. The fact that photoisomerization also occurs upon irradiation in the LF region suggests efficient communication between the initially populated LF state and the lower lying MLCT state. Anti and syn isomers are not defined in complex 1 because of the symmetry of the NC_4H_8 group. In this context a complex such as $(\text{CO})_5\text{-}$

$\text{WC}(\text{NMeEt})(\text{SiPh}_3)$ is worthy of investigation. It is already known⁵ to form a 16-electron CO loss species upon thermolysis, and it would therefore be interesting to see whether it can undergo both types of photoreaction, namely CO loss through population of a LF state and photoisomerization about the $\text{C}_{\text{carbene}}\text{-NMeEt}$ bond via the lowest MLCT state.

This preliminary study of the flash photolysis of silyl carbene complexes provides some illustration of the value of complementing conventional spectrophotometric detection with time-resolved resonance Raman spectroscopy in probing the photoreactions of these systems.

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