

# Time-Resolved Raman Spectroscopy and Matrix Isolation Studies of *Anti*–*Syn* Photoisomerization in Metal Carbonyl Carbenes

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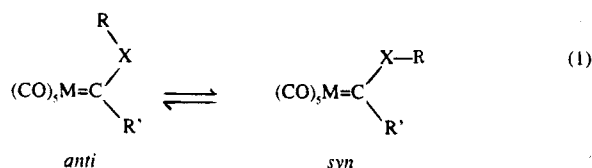
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Photoinduced *anti*–*syn* isomerization in tungsten carbonyl carbenes,  $(\text{CO})_5\text{W}=\text{C}(\text{OR})\text{R}'$ , [**1** with  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Me}$ ; **2** with  $\text{R} = \text{Me}$ ,  $\text{R}' = p\text{-Tolyl}$ ; **3** with  $\text{R} = \text{Et}$ ,  $\text{R}' = \text{Ph}$ ] brought about by irradiation in the MLCT absorption region has been investigated by laser flash photolysis coupled with transient absorbance and time-resolved resonance Raman spectroscopy (TR<sup>3</sup>S). The studies, carried out in solution in solvents of varying polarity, have been supplemented by matrix isolation studies using UV-vis and IR detection. Pulsed irradiation in the MLCT absorption region of **1**–**3** results in the formation within the pulse risetime of the *syn* isomer from the ground state (*anti*) form, followed by thermal relaxation/isomerization back to the ground state. In all three complexes the transient lifetimes increase with increasing solvent polarity falling in the range 120  $\mu\text{s}$ –3 ms for **1** and 1–2 orders of magnitude shorter for **2** and **3**. Growth and decay of the *syn* isomer were also monitored by TR<sup>3</sup>S. For **1**, bands in the Raman attributable to modes of the carbene group showed little change in frequency between the *anti* and *syn* isomers. In the case of the *anti* forms of **2** and **3**, a band near 1235  $\text{cm}^{-1}$  attributable to  $\nu(\text{C}_{\text{carbene}}-\text{OR})$  shifts to *ca.* 1270  $\text{cm}^{-1}$  in the spectra of the *syn* isomer. The differences between **1**, **2** and **3** in respect of both vibrational spectra and rates of isomerization are discussed in relation to the possible influence on electronic stabilization of reorientation of the  $\text{R}'$  group which accompanies *anti*–*syn* transformation. Comparison of the *anti*–*syn* photoisomerization of **1** in an argon matrix with that of **4** ( $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Ph}$ ) shows that the process is photoreversible only in the case of **1**.

## Introduction

The existence of *anti* and *syn* isomers (eq 1) in solution for metal carbenes of the type  $[\text{M}]-\text{C}(\text{XR})(\text{R}')$ ,  $\text{X}=\text{O}, \text{N}$ ,



**S**, has been established since the NMR studies carried out on chromium pentacarbonyl carbenes.<sup>1</sup> The isomers arise as a result of inhibited rotation about the C–X bond in which the partial double bond character is due to the  $\pi$  interaction between the lone pair of electrons on the heteroatom and the carbene carbon  $2p_z$  orbital. The energy difference  $E_{\text{syn}} - E_{\text{anti}}$  between the two isomers is very dependent on the heteroatom ( $\text{N} > \text{O} > \text{S}$ ), the  $\pi$  donating ability of  $\text{R}'$ , steric interactions and the solvent environment. Which isomer is energetically the more favored will depend on the steric demands of the complex. However, in complexes of the type  $(\text{CO})_5\text{WC}(\text{OR})(\text{R}')$ , which are studied here, the *anti* isomer predominates.<sup>2</sup>

The electronic absorption spectra of  $(\text{CO})_5\text{WC}(\text{OR})-\text{R}'$  generally exhibit two bands, a higher energy LF transition, assigned in one-electron terms as  $(b_2^2) \rightarrow (2a_1^1, b_2^1)$  in the assumed<sup>3</sup> local  $C_{2v}$  symmetry of the carbene group, and a lower energy MLCT transition, assigned as  $(b_2^2) \rightarrow (3a_1^1, b_2^1)$ . The latter transition formally promotes electron density into the carbene carbon  $2p_z$  orbital. The photochemistry associated with the LF transition involves CO dissociation.<sup>3</sup> Until recently photoexcitation within the MLCT region has been less extensively investigated.<sup>4</sup>

Previous work from this laboratory on the photochemistry of  $(\text{CO})_5\text{WC}(\text{OMe})(\text{Ph})$ , the first time-resolved resonance Raman (TR<sub>3</sub>) study on an organometallic complex,<sup>5</sup> noted that LF excitation resulted in the formation of a transient with a lifetime in the  $\mu\text{s}$  range. Originally it was believed that this was a 16-electron species arising from CO loss. Subsequent work on this same complex in a matrix by Stufkens et al. demonstrated that irradiation into the MLCT band of the complex resulted in *anti* to *syn* photoisomerization,<sup>2</sup> according to eq 1. Furthermore, these workers showed that irradiation into the higher energy LF band also resulted in the same photoisomerization, apparently

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arising as a result of efficient radiationless decay from the initially populated LF state into the lower lying MLCT state. The transient species originally reported<sup>5</sup> in the TR<sub>3</sub> studies in solution was identified<sup>2</sup> as the *syn* isomer of (CO)<sub>5</sub>WC(OMe)(Ph) as observed in the matrix experiments. More recently we have reported the observation of a photogenerated transient *syn* isomer in the related carbene complex (CO)<sub>5</sub>WC(OEt)(SiPh<sub>3</sub>).<sup>6</sup>

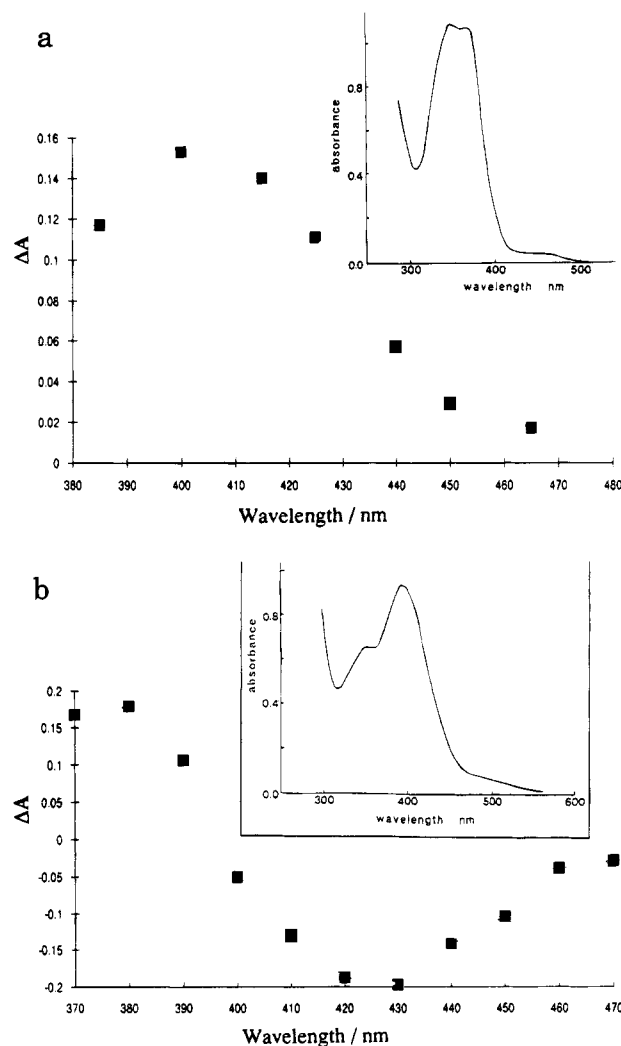
The primary aim of the present work has been to carry out a comparative study of the photoisomerization of (CO)<sub>5</sub>WC(OR)(R') complexes in solution, using the methods of flash photolysis and TR<sub>3</sub> spectroscopy, and in an argon matrix, using IR and UV/vis spectroscopic detection. The following complexes, containing both aryl and alkyl substituents have been investigated: (CO)<sub>5</sub>WC(OMe)(Me), **1**, (CO)<sub>5</sub>WC(OMe)(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), **2**, and (CO)<sub>5</sub>WC(OEt)(Ph), **3**. The results are considered in relation to the earlier studies<sup>5</sup> of the Fischer carbene, (CO)<sub>5</sub>WC(OMe)(Ph), **4**.

### Experimental Section

Flash photolysis experiments were carried out using either a Nd/YAG laser (355 nm, 10 ns pulse width, *ca.* 10–30 mJ pulse<sup>-1</sup>) or a XeCl excimer laser (308 nm, 30 ns pulse width, up to 40 mJ pulse<sup>-1</sup>). Both systems have previously been described in detail.<sup>7,8</sup> For resonance Raman studies the Nd/YAG laser coupled with a Raman shifter was used for recording the transient spectra and an argon ion laser for the ground state spectra.<sup>5,9</sup> Two-color TR<sub>3</sub> experiments were carried out at the Central Laser Facility, Rutherford Appleton Laboratory (RAL), using excimer and excimer-pumped dye lasers as pump and probe sources respectively. The matrix isolation experiments were carried out at the University of York and the apparatus has been described in detail elsewhere.<sup>10</sup> The samples were deposited on a BaF<sub>2</sub> window which was cooled to 12–20 K by an Air Products CS202 closed-cycle Displex refrigerator. The complexes were sublimed onto the window from a tube, concurrent with the gas stream that entered the vacuum shroud from a separate inlet.

Matrices were photolysed using a 300W Xe arc (ILC, model 302UV) with appropriate filters. The IR spectra were recorded on either a Mattson Sirius FTIR or Mattson Research Series FTIR spectrometer with a PbS detector and a KBr beam splitter (4000–450 cm<sup>-1</sup>) or a CsI beam splitter (4000–200 cm<sup>-1</sup>). The spectrometer was continuously purged with CO<sub>2</sub>-free dry air. The spectra were recorded as the average of 128 scans with 1 cm<sup>-1</sup> resolution (25K data points). The UV/vis spectra were recorded on a Perkin-Elmer Lambda 7G spectrometer. The complexes and their deuteriated analogs were synthesized by standard literature procedures.<sup>11</sup>

For the flash photolysis experiments the samples were dissolved in the appropriate solvent in a 1 cm path length quartz cuvette. The absorbances of the solutions were in the range 0.5–1.0 at the excitation wavelength. The solutions were either purged with argon or degassed by several freeze-pump thaw cycles to 10<sup>-4</sup> mbar before back filling to 1 atm of argon. For the transient resonance Raman spectra the argon-purged samples were circulated through a quartz capillary (*ca.*



**Figure 1.** Transient absorbance difference ( $\Delta A$ ) spectra recorded following flash photolysis at 354.7 nm of (a) (CO)<sub>5</sub>W=C(OCH<sub>3</sub>)CH<sub>3</sub> and (b) (CO)<sub>5</sub>W=C(OCH<sub>2</sub>CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>. Solution concentrations were *ca.* 10<sup>-3</sup> mol dm<sup>-3</sup> in CH<sub>2</sub>Cl<sub>2</sub> in both cases. Insets: corresponding ground electronic absorption spectra.

1 mm i.d.) at a rate which ensured that each laser pulse irradiated a fresh volume of solution, thus minimizing sample decomposition in the laser beam.

### Results

**(a) Flash Photolysis.** Complex **1** exhibits two absorption bands at 350 nm (LF) and 370 nm (MLCT) in cyclohexane solution. Irradiation of a solution of **1** in dichloromethane at 355 nm resulted in a rise in absorption in the range 390–460 nm occurring within the time resolution of the apparatus (*ca.* 10 ns) and followed by an exponential decay to the preflash absorbance level. The maximum in the  $\Delta A$  spectrum measured in CH<sub>2</sub>Cl<sub>2</sub> (Figure 1a) exhibited a red shift of *ca.* 15 nm from the ground state absorption maximum (365 nm). Little change was observed in the  $\Delta A$  maximum with solvent. The transient lifetime however was markedly solvent-dependent (Table 1) and varied with temperature, yielding an activation enthalpy of 51 ± 2 kJ mol<sup>-1</sup> in cyclohexane from an Eyring plot over the range (283–328) K.

Complex **2**, with absorption bands at 354 nm (LF) and 410 nm (MLCT) in cyclohexane displayed similar tran-

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**Table 1. Lifetimes ( $\mu\text{s}$ ) of *Syn* Isomers of Tungsten Carbenes in Solution<sup>a</sup>**

solvent	(CO) <sub>5</sub> WC-(OMe)Me	(CO) <sub>5</sub> WC-(OEt)Ph	(CO) <sub>5</sub> WC-(OMe)p-tol
hexane	126 ± 4	4.65 ± 0.10	1.1 ± 0.05
cyclohexane	294 ± 15	5.0 ± 0.2	1.62 ± 0.05
dichloromethane	1200 ± 100	14.3 ± 0.3	3.70 ± 0.15
methanol	2642 ± 211	20.7 ± 0.4	6.6 ± 0.3
acetonitrile	3356 ± 300	23 ± 2	7.1 ± 0.3

<sup>a</sup> Measurements at 20 °C, *ca.* 10<sup>-3</sup> mol dm<sup>-3</sup>.

**Table 2. Principal Bands (cm<sup>-1</sup>) in CW and Pulsed (Single Color) RR Spectra of Carbene Complexes**

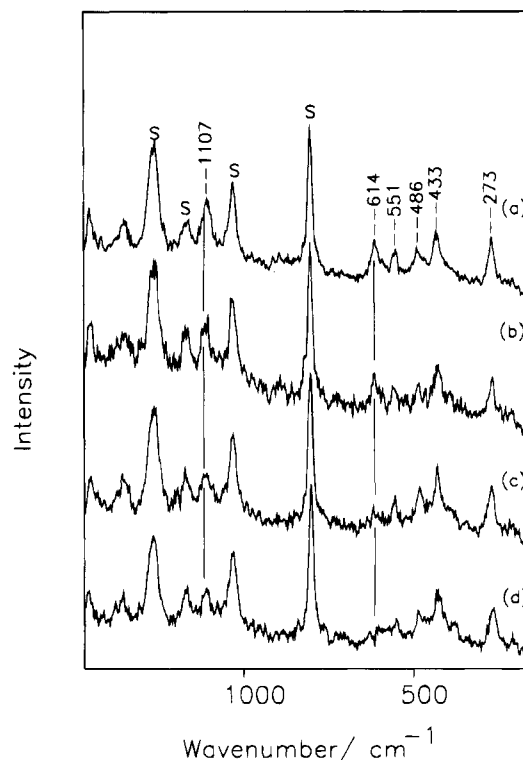
complex	$\lambda_{\text{exc}}/\text{nm}$	Raman bands/cm <sup>-1</sup>							
(CO) <sub>5</sub> WC(OMe)Me	363.8 (CW)	273	433	486	557	1107	1170	1264	
	354.7 (pulsed)				<i>a</i>	1107	1170	1264	
	396 (pulsed)	273	430	486	557	614	<i>b</i>		
(CO) <sub>5</sub> WC(OMe)p-tol	363.8 (CW)			878	990	1181	1210	1235	
	354.7 (pulsed)			878	920	1181	1235	1270	
	363.8 (CW)			903		1181	1233		
(CO) <sub>5</sub> WC(OEt)Ph	363.8 (CW)			903	935	1181			
	354.7 (pulsed)			903	935	1181		1266	

<sup>a</sup> Frequency range <1000 cm<sup>-1</sup> not probed. <sup>b</sup> Frequency range >1000 cm<sup>-1</sup> not probed.

sient behavior, again showing a rise in <10 ns (the response time of the experiment) in the absorbance between 370 and 390 nm and in this case a ground state depletion in the range 400–450 nm. The first order transient decay was temperature- and solvent-dependent as for **1** but the lifetime was some two orders of magnitude shorter.

Irradiation at 355 nm of the EtO-substituted analogue, **3**, which has absorption bands at 356 nm (LF) and 403 nm (MLCT) also resulted in formation of a transient within the laser pulse risetime and with a very similar  $\Delta A$  spectrum to that observed for **2**, positive over the range 370–390 nm and showing depletion between 400 and 460 nm (Figure 1b). The transient decayed exponentially as a function of temperature and solvent with a lifetime slightly longer than that of the phenyl analogue, **2**. In general, the behavior of **3** was very similar to the Fischer carbene, (CO)<sub>5</sub>WC(OMe)(Ph) **4**, reported in an earlier paper.<sup>5</sup> The latter investigation has been extended in the present work by investigating the temperature dependence of the thermal isomerization of the *syn* back to the *anti* form following photogeneration by flash photolysis at 308 nm. Measurements over the temperature range (283–328) K in cyclohexane solution, yielded an activation enthalpy from the Eyring plot of 37 ± 3 kJ mol<sup>-1</sup> for the thermal relaxation to the *anti* ground state.

**(b) Resonance Raman spectroscopy.** Principal features in the resonance Raman (RR) spectra recorded under CW- and pulsed-excitation for complexes **1–3** are summarized in Table 2. For complex **1**, spectra generated at either  $\lambda_{\text{exc}} = 363.8$  nm (CW) or 355 nm (pulsed) in CH<sub>2</sub>Cl<sub>2</sub> solution showed features at 1107, 1170 and 1264 cm<sup>-1</sup>. In the lower frequency region of the RR spectrum, generated at 363.8 nm in cyclohexane as solvent, bands appeared at 277, 430, 486, 557 and 594 cm<sup>-1</sup>. With pulsed excitation at 396 nm a new band grew in at 614 cm<sup>-1</sup>. The results of a two-color time-resolved experiment carried out on the same sample are shown in Figure 2. The spectra were recorded using a pump wavelength of 351 nm and a probe wavelength of 406 nm at a series of pump-probe delays over the time range 120 ns–600  $\mu\text{s}$ . The rate of decay which can be

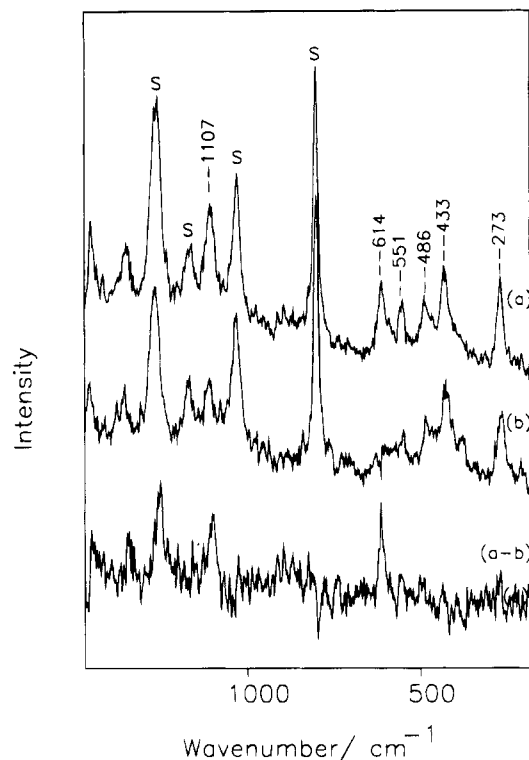


**Figure 2.** Two-color time-resolved resonance Raman study of (CO)<sub>5</sub>W=C(OCH<sub>3</sub>)CH<sub>3</sub> in C<sub>6</sub>H<sub>12</sub> (*ca.* 10<sup>-3</sup> mol dm<sup>-3</sup>); Pump  $\lambda$  351 nm; probe  $\lambda$  406 nm. Pump-probe time delays: (a) 120 ns; (b) 100  $\mu\text{s}$ ; (c) 300  $\mu\text{s}$ ; (d) 600  $\mu\text{s}$ .

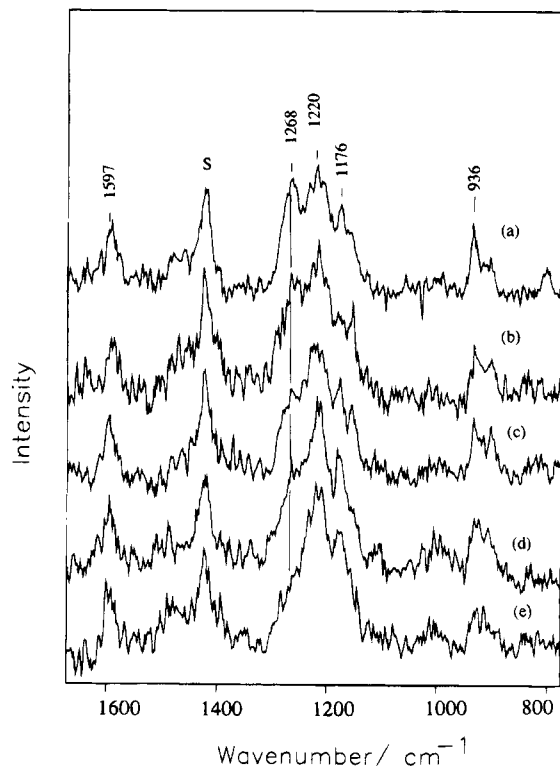
estimated from the gradual disappearance with increasing pump-probe delay of the 614 cm<sup>-1</sup> feature in Figure 2 is consistent with the 300  $\mu\text{s}$  lifetime recorded in the flash photolysis experiments in the same solvent (Table 1). CO saturation of the solution had no measurable effect on the rate of transient decay.

The intensity of the 1107 cm<sup>-1</sup> band relative to the solvent peak at 1028 cm<sup>-1</sup> also changes with pump-probe delay confirming it as a transient feature, unshifted from the ground state position. This is also the case for the band near 1264 cm<sup>-1</sup> although the variation of band intensity is not immediately evident from Figure 2 because of an overlapping solvent feature at 1266 cm<sup>-1</sup>. However a careful comparison of the spectra from Figure 2, recorded at the shortest and longest pump-probe delays brings out the point. The two spectra are replotted in Figure 3, along with the corresponding difference spectrum, from which the enhanced intensity of the 1264 cm<sup>-1</sup> band at the shortest delay is evident. The decrease in intensity of both this band and that at 1107 cm<sup>-1</sup> for the transient compared to the ground state is what would be expected from resonance enhancement considerations. The monitoring beam at 406 nm is more in resonance with the MLCT absorption of the transient (Figure 1a) than that of the ground state ( $\lambda_{\text{max}}$  370 nm). The observed changes in intensity confirm that the bands observed at the short time delays are transient features, unshifted in frequency from the ground state.

In the case of complex **2** several bands also appear at the same frequencies in CW- (363.8 nm) and pulsed- (355 nm) generated spectra but additional, transient bands were observed at 920 cm<sup>-1</sup> and 1270 cm<sup>-1</sup> in the pulse-generated spectra. The pattern for complex **3** was very similar, with several features common to the CW-

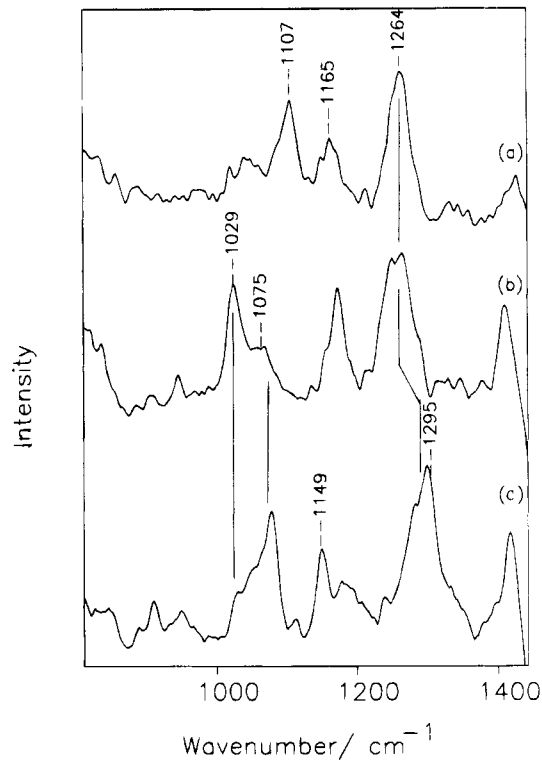


**Figure 3.** Two-color RR spectra from Figure 2 at shortest (120 ns, trace a) and longest (600  $\mu$ s, trace b) pump-probe delays, showing the increased intensity of the 1264  $\text{cm}^{-1}$  band at the shortest delay.



**Figure 4.** Two-color time-resolved resonance Raman study of  $(\text{CO})_5\text{W}=\text{C}(\text{OCH}_2\text{CH}_3)\text{C}_6\text{H}_5$  in  $\text{CH}_2\text{Cl}_2$  (*ca.*  $10^{-3}$  mol  $\text{dm}^{-3}$ ): Pump  $\lambda$  351 nm; probe  $\lambda$  420 nm. Pump-probe time delays: (a) 100 ns; (b) 500 ns; (c) 1  $\mu$ s; (d) 10  $\mu$ s; (e) 50  $\mu$ s.

and pulse-excited spectra as well as additional bands at 935  $\text{cm}^{-1}$  and 1266  $\text{cm}^{-1}$  in the spectra recorded under pulsed excitation at 355 nm. Figure 4 shows two color TR<sub>3</sub> spectra recorded for complex **3** in  $\text{CH}_2\text{Cl}_2$  using



**Figure 5.** Influence of deuteration on resonance Raman spectra of  $(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{CH}_3$ , recorded at an excitation wavelength of 363.8 nm in  $\text{CH}_2\text{Cl}_2$  (*ca.*  $10^{-3}$  mol  $\text{dm}^{-3}$ ): (a) Undeuterated species; (b)  $(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)(\text{CD}_3)$ ; (c)  $(\text{CO})_5\text{W}=\text{C}(\text{OCD}_3)(\text{CD}_3)$ .

a pump wavelength of 351 nm and a probe of 420 nm. The transient nature of the 1266 and 935  $\text{cm}^{-1}$  features is clear and the observed decay on a time scale of *ca.* 20  $\mu$ s is consistent with flash photolysis measurements (Table 1).

For purposes of comparison RR spectra were also recorded for the Cr- analogue of **4**,  $(\text{CO})_5\text{Cr}(\text{OMe})(\text{Ph})$ . The spectra were generated using CW and pulsed excitation at 363.8 nm and 355 nm respectively. In the CW-excited spectrum the primary features appear at 935  $\text{cm}^{-1}$ , 997  $\text{cm}^{-1}$ , 1235  $\text{cm}^{-1}$  and 1270  $\text{cm}^{-1}$ , suggesting the presence of both *anti* and *syn* isomers. To establish that this was not simply due to the creation of a photostationary state, RR spectra were also recorded at an excitation wavelength of 457.9 nm. At this wavelength negligible photochemical transformation to *syn* isomer would be expected yet the spectrum (not shown here) clearly displayed features characteristic of both species. NMR studies<sup>1</sup> of  $(\text{CO})_5\text{Cr}(\text{OMe})\text{-Ph}$  do in fact confirm the existence of both isomers in solution under ambient conditions.

Resonance Raman studies were also carried out on samples of **1** with deuterated methyl and methoxy groups. The spectra recorded using CW excitation at 363.8 nm are displayed in Figure 5. When the  $\text{CH}_3$  group alone is deuterated the band at 1264  $\text{cm}^{-1}$  remains unshifted but additional features appear at 1029  $\text{cm}^{-1}$  and 1075  $\text{cm}^{-1}$ . The spectrum recorded when the  $\text{OCH}_3$  and  $\text{CH}_3$  groups are both deuterated shows bands near 1149  $\text{cm}^{-1}$  and 1295  $\text{cm}^{-1}$  as the primary features.

**(c) Low Temperature Matrix Isolation Studies.** When  $(\text{CO})_5\text{WC}(\text{OMe})(\text{Ph})$  was deposited in an argon matrix at 20 K the IR spectrum exhibited CO stretching

**Table 3.** IR Bands ( $\text{cm}^{-1}$ ) for Carbene Complexes in Ar Matrix at 20 K

complex	bands
<i>anti</i> -(CO) <sub>5</sub> WC(OMe)Ph	2074, 1985, 1950, 1223, 1212, 1181, 1149, 993, 876
<i>syn</i> -(CO) <sub>5</sub> WC(OMe)Ph <sup>a</sup>	2074, 1985, 950, 1260, 1191, 1171, 1128, 936, 917, 878
<i>anti</i> -(CO) <sub>5</sub> WC(OMe)Me	2075, 1985, 1950, 1456, 1348, 1255, 1174, 910, 898
<i>syn</i> -(CO) <sub>5</sub> WC(OMe)Me <sup>a</sup>	2075, 1985, 1950, 1340, 1250, 1175, 1099, 1081, 998

<sup>a</sup> Bands observed after matrix irradiation (see text for details); features attributable to CO stretching modes are unshifted between *anti* and *syn* isomers.

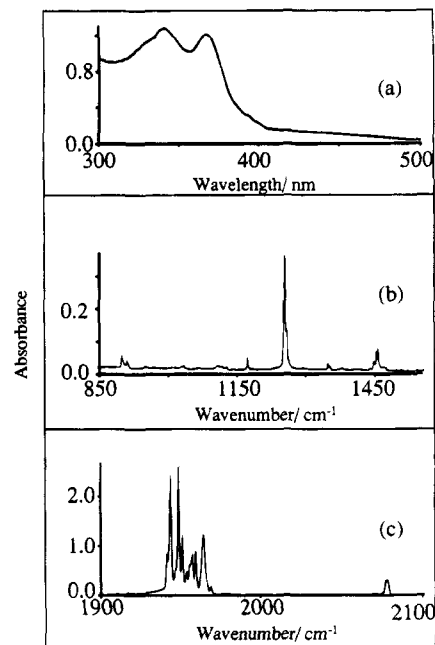
modes at  $2074 \text{ cm}^{-1}$ ,  $1985 \text{ cm}^{-1}$  and at  $1950 \text{ cm}^{-1}$  though with extensive matrix splitting. Several IR bands associated with the carbene moiety were also observed and are summarized in Table 3. Irradiation of the matrix-isolated sample at 434 nm, within the MLCT band ( $\lambda_{\text{max}} = 404 \text{ nm}$ ) resulted in some intensity decrease and frequency shifts in the carbene IR bands as listed in Table 3. Irradiation at 434 nm for 3 h resulted in *ca.* 70% conversion of the *anti* isomer as estimated from the observed decrease in intensity of the carbene band at  $1223 \text{ cm}^{-1}$ . There were no apparent changes in the positions of the CO stretching modes though minor alterations could have been masked by the matrix splitting. As well as the changes in the carbene IR bands upon irradiation a blue shift in the MLCT band from 404 nm to 394 nm was observed. The results are consistent with earlier observations by Stufkens and co-workers on this complex in low temperature matrices<sup>2</sup> and have been attributed to photoconversion of the *anti* to the *syn* isomer of (CO)<sub>5</sub>WC(OMe)(Ph). Irradiation of the sample in the matrix for 3 h within the MLCT band (394 nm) of the *syn* isomer failed to bring about any conversion back to the *anti* form, again consistent with previous work<sup>2</sup>.

The UV and IR spectra for the (CO)<sub>5</sub>WC(OMe)(Me) complex deposited in an argon matrix at 20 K are shown in Figure 6. Irradiation within the MLCT band of the *anti* isomer ( $\lambda_{\text{max}} 368 \text{ nm}$ ) resulted in frequency shifts in several of the carbene IR bands, as shown in Table 3 and also a red shift in the UV spectrum from 368 nm to 375 nm. There was no evidence for CO loss upon irradiation and no apparent changes in the CO stretching region, apart from matrix site splitting as in the case of (CO)<sub>5</sub>WC(OMe)(Ph). The observations are consistent with formation of the *syn* isomer. Irradiation for *ca.* 1.5 h within the MLCT band of the *anti* isomer resulted in about 50% photoconversion as estimated from the decrease in the intensity of the carbene IR bands of the starting material. Interestingly in this case and in contrast to the situation with complex 4, matrix irradiation into the MLCT band of the *syn* isomer (*ca.* 1.5 h at 397 nm) did result in regeneration of the *anti* isomer as judged by the grow-in of features in both the IR and UV/vis spectra (Table 3).

For both complexes the changes in the IR and UV spectra in the matrix experiments are consistent with the data recorded in the solution studies, indicating that the same process is being observed in both media.

## Discussion

**(1) Identification of the Transient.** The time-resolved spectroscopic studies on the three carbene



**Figure 6.** UV and IR spectra recorded for (CO)<sub>5</sub>WC(OMe)(Me) upon deposition in an argon matrix at 20 K: (a) UV spectrum; (b, c)  $\nu(\text{carbene})$  and  $\nu(\text{CO})$  regions respectively. Arbitrary absorbance scales for (b) and (c) indicate relative band intensities.

complexes 1–3 in solution show that excitation into either LF or MLCT bands results in formation of the same single transient in <10 ns. The transient UV/vis and vibrational spectra for both the alkyl- and aryl-substituted carbenes closely resemble the corresponding spectra of the low temperature matrix photoproducts. The rate of decay of the transient is also independent of added CO. The evidence supports the identification of the major photoreaction in these metal carbonyl carbene complexes in solution as an *anti* to *syn* isomerization (eq 1) about the C–OR (R = Me, Et) carbene bond, as established by the matrix studies of Stufkens et al. for the Fischer carbene 4 and its Cr analogue.<sup>2</sup> Free rotation about the C–OR bond is inhibited by the partial double bond character, due to  $\pi$  interaction between the oxygen lone pair and the carbene carbon  $2p_z$  orbital.

## (2) Comparative Kinetics and Spectroscopy of Aryl- and Alkyl-Substituted Carbenes in Solution.

The flash photolysis studies show that the transient lifetimes (Table 1) for the alkyl-substituted carbenes are 1–2 orders of magnitude longer than for the aryl-substituted species. These differences are reflected in the activation enthalpies  $51 \text{ kJ mol}^{-1}$  and  $37 \text{ kJ mol}^{-1}$  for the *syn* to *anti* thermal isomerization measured in cyclohexane solution for (CO)<sub>5</sub>WC(OMe)Me and (CO)<sub>5</sub>WC(OMe)Ph, respectively. Steric interactions by the more bulky aryl group may be one factor influencing the thermal relaxation of the *syn* isomer. However this cannot be the only factor since previous flash photolysis studies<sup>6</sup> on the silyl-substituted carbene, (CO)<sub>5</sub>WC(OEt)(SiPh<sub>3</sub>), show the lifetime of the *syn* isomer to be similar to those determined for the sterically less crowded aryl-substituted carbenes. It appears that the aryl ring must also be exerting an electronic effect, possibly via an alteration during the isomerization of the extent of  $\pi$  delocalization over the carbene ligand. This point is expanded upon below. The kinetic data

in Table 1 also show that the rate of decay of the *syn* isomer is influenced by the solvent, being slower in more polar solvents for both alkyl- and aryl-substituted carbenes. This could be due to an increased stabilization of the *syn* isomer or a decrease in that of the transition state or more likely the result of some contribution from both.

The transient UV/vis spectra are significantly different for the alkyl- and aryl-substituted carbenes. The  $\lambda_{\text{max}}$  of the MLCT absorption for the *syn* isomer of the aryl-substituted complexes shifts to shorter wavelengths compared to the ground state spectrum while for the alkyl-substituted complex the corresponding spectra shift to longer wavelength. The spectral results in the latter case are consistent with those previously reported<sup>6</sup> for the silyl-substituted carbenes and a similar change in the relative stabilities of the HOMO and LUMO might have been expected upon photoisomerization of the closely related aryl-substituted carbenes. The shift to higher energy which is actually observed in the latter therefore suggests the operation of an additional factor in this case. As alluded to earlier, this might arise from a reduction in the degree of  $\pi$  delocalization over the carbene moiety between the *anti* and *syn* isomers. The isomerization of  $(\text{CO})_5\text{WC}(\text{OR})(\text{R}')$  according to eq 1 can involve not only rotation of the alkoxy group but an associated reorientation of  $\text{R}'$ . When an aryl group rotates away from the plane of the carbene in order to minimize its steric interaction with the alkoxy group in the *syn* isomer there will be a reduction in the degree of  $\pi$  interaction of the aryl ring with the carbene carbon  $2p_z$  orbital in the *syn* isomer.<sup>12</sup> This situation does not arise when  $\text{R}'$  is alkyl. Any effect of reorientation of the aryl group might be reflected in frequency changes in vibrational modes of the carbene.

Before discussing the resonance Raman spectra of 1–3 reference is made to the results obtained from studying the spectra of the deuterated analogs of 1. The *anti* isomer of complex 1 exhibits significant shifts in the three bands in its RR spectrum at 1107, 1165 and  $1264\text{ cm}^{-1}$  (Figure 5a) upon successive deuteration of the  $(\text{CH}_3)$  and  $(\text{OCH}_3)$  groups (Figure 5b,c, respectively). However attempts to assign the bands to specific vibrational modes by comparison of the frequency shifts observed upon deuteration with those calculated on the basis of reduced mass considerations were inconclusive. It appears that mode coupling within the carbene moiety is involved but further speculation is unwarranted without additional data. Studies with isotopically labeled species in low temperature matrices are planned to aid band assignment.

The most significant feature of the resonance Raman data for these carbenes is the general similarity in the frequencies of modes assignable to the *anti* and *syn* isomers. This is illustrated for instance by the CW- and pulse-excited spectra for 1 (Table 1 and Figure 2). The notable lack of frequency shifts suggests that the change in position of the alkoxy group which characterises the isomerization between the *anti* and *syn* forms does not significantly perturb the vibrational modes of the com-

plex. Available X-ray data,<sup>13</sup> although for somewhat different systems, appear to be consistent with this conclusion.

The significant shift in the position of a mode between the two isomers which is observed occurs only for the aryl-substituted carbenes. The feature near  $1235\text{ cm}^{-1}$  in the RR spectra of the *anti* forms of 2 and 3 shifts to  $1266\text{--}1270\text{ cm}^{-1}$  in the respective *syn* isomer spectra. The analogous band ( $1264\text{ cm}^{-1}$ ) in the RR spectra of the alkyl-substituted complex 1 (Table 1 and Figure 2) shows no shift in frequency between the spectra of the two isomers. This band is associated<sup>2,15</sup> with modes involving a substantial contribution from a  $(\text{C}_{\text{carbene}}-\text{OMe})$  stretching motion, consistent with its significant intensity in both the RR and IR spectra of these complexes. As proposed above, the flash photolysis experiments suggest that the formation of the *syn* isomer of 2 and 3 requires a further rotation of the aryl group away from the plane of the carbene to minimize the steric interaction between the alkoxy group and the aryl ring. Stabilization of the *syn* isomer would then arise largely<sup>16</sup> from oxygen lone pair donation into the carbon  $2p_z$  orbital with a consequent increase in the C–OMe bond order. Our spectral data are consistent with this although as stated earlier in relation to the results of the isotopic substitution studies, the vibrational spectra of the carbenes are complicated. That a shift in position of this band is only observed for the aryl-substituted carbenes ties in with the proposal that in this case an additional perturbation associated with phenyl ring reorientation is occurring in the course of the *anti* to *syn* isomerization.

**(3) Comparative Spectroscopy of Aryl- and Alkyl-Substituted Carbenes in Cryogenic Argon Matrices.** Stufkens and co-workers reported that isomerization of  $(\text{CO})_5\text{WC}(\text{OMe})(\text{Ph})$ , 4, could be photochemically induced in one direction only, *anti* to *syn*, and we have confirmed this here. The reverse *syn* to *anti* isomerization was not observed, even following direct irradiation into the MLCT band of the *syn* isomer. The only photoreaction observed<sup>2</sup> for the *syn* isomer of 4 in the matrix was CO dissociation via the LF state and it was suggested<sup>2</sup> that the MLCT and LF states of 4 were so close in energy that reaction occurred preferentially from the more reactive LF state irrespective of the state initially populated. However, the matrix isolation studies reported in the present work show that for 1 the isomerization is photochemically reversible. In reported cases of "one-way" photoisomerization in stilbene-type molecules such as that observed in 1-(2-anthryl)-3,3-dimethyl-1-butene the suggested explanation was that a local minimum exists on the excited state potential energy surface close to the geometry of the photochemically inert isomer.<sup>17</sup> We propose here that in the aryl-substituted carbenes the first distortion in the MLCT state upon excitation of the *syn* isomer is a rotation of the aryl ring to a more conjugating position, the driving force being the resulting resonance stabilization. The relative rates of conversion of this localized thermally

(12) X-ray crystallographic studies<sup>14</sup> on  $(\text{CO})_5\text{CrC}(\text{OMe})(\text{Ph})$  show that in the solid state this complex exists as the *anti* isomer, with the phenyl ring lying at  $90^\circ$  to the carbene plane so that there is no  $\pi$  interaction between the phenyl ring and the carbene carbon  $2p_z$  orbital. However this situation may be different in solution where for instance crystal packing effects will not operate.

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equilibrated excited state to either the *anti* or the *syn* forms will depend upon the relative dispositions of the three potential energy surfaces. The data suggest that in the present case decay occurs preferentially back into the potential energy well of the *syn* isomer; the MLCT state of the *syn* isomer is photochemically inert. For the *anti* isomer the solution studies suggest that some degree of conjugation extends over the carbene moiety in the ground state. Therefore, no significant rotation of the aryl ring need occur upon MLCT excitation. The initial excited state rapidly decays via rotation of the C-OMe bond into a lower energy "twisted excited" state in which the original geometry of the complex is lost. From this state decay to either ground state isomer is possible. Hence in the aryl-substituted carbenes the MLCT excited state of the *anti* isomer is photochemically active to isomerization. Support for this explanation of "one way" photoisomerization for  $(\text{CO})_5\text{WC}(\text{OMe})(\text{Ph})$  comes from the matrix experiments on the alkyl-substituted carbene **1**. The MLCT excited states of the *anti* and *syn* isomers of complex **1** are both active to isomerization. This is consistent with the above proposed explanation for "one way" photoisomerization in the aryl-substituted case since "localized" stabilization of the MLCT excited state by increased conjugation cannot operate in complex **1** and both the *syn* and *anti* isomers would be expected to behave like the *anti* isomer of  $(\text{CO})_5\text{WC}(\text{OMe})(\text{Ph})$ .

### Summary and Conclusions

1. The transient observed upon pulsed irradiation in solution into both the LF and MLCT band of these carbenes is assigned as the *syn* isomer. This assignment is supported by comparison with results from experiments carried out in cryogenic matrices. LF excitation provides no evidence in support of a transient arising from CO dissociation, although continuous irradiation experiments<sup>3,5,6</sup> show that the reaction should occur. Presumably the quantum yield for the process is so low that the transient is not detectable.

2. The lifetime of the *syn* isomer is dependent on the polarity of the solvent and on the nature of the ancillary (*R'*) group on the carbene carbon.

3. Distinctive photochemical behaviour is exhibited by the *syn* isomer of alkyl- and aryl-substituted carbenes. The most notable difference is that the MLCT excited state of the *syn* isomer of aryl-substituted carbenes is photoinert, while that of the alkyl-substituted complex leads to photoisomerization. These differences are consistent with the proposal that the isomerization of the aryl-substituted carbenes also involves a reorientation of the aryl ring to a less  $\pi$ -interacting position in the *syn* isomer.

4. There are clear parallels between *anti-syn* photoisomerization of metal carbenes<sup>18,19</sup> as investigated in the present work and the extensively studied *cis-trans* photoisomerization of organic alkenes.<sup>20</sup> However the novel feature which appears in the metal carbene complexes is that although the geometric change is centered on the carbene ligand it is not the direct result of an *intraligand* excitation process. The metal center is in effect acting as an intramolecular photosensitizer resulting in light absorption and the transfer of electron density onto the carbene ligand, thereby facilitating the isomerization.

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