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Time-Resolved Resonance Raman Spectroscopy and Solution Kinetics of Photogenerated Transients in the Metal–Carbene Complex $(OC)_5W=C(OMe)Ph$

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Abstract: Laser flash photolysis and time-resolved resonance Raman (RR) spectroscopy of the metal carbene complex $(CO)_5W{=}C(OMe)Ph$ (**1**) in several solvents are reported. Irradiation within the ligand-field (LF) absorption region of **1** with a Q-switched laser pulse (Nd/YAG, 354.7 nm) results in prompt formation of a transient species with a solvent-dependent lifetime in the microsecond range, measured by rapid response spectrophotometric monitoring. The lifetimes measured in Ar-purged or CO-saturated solutions are the same, within the experimental uncertainties. In acetonitrile solution, fast formation of the substitution product *cis*-$(CH_3CN)(CO)_4W{=}C(OMe)Ph$ (**2**) occurs in addition to the transient species; in the other solvents investigated (CH_2Cl_2, *n*-hexane, benzene), formation and decay of the transient are the only observable processes. A CW laser (Ar^+, 363.8 and 488 nm) is used to obtain the ground electronic state RR spectra of **1** and pulsed excitation, both single- and two-laser pump and probe, to investigate scattering by photogenerated transients. Several features in the pulsed-laser-excited RR spectra occur with the same relative intensities as corresponding bands in the CW-excited ground-state spectra, suggesting that the enhanced scattering arises through resonance with the same type of electronic transition, W→carbene charge transfer (CT), in both ground-state and transient species. The transient RR spectrum also shows a band at 1105 cm^{-1}, with no ground-state counterpart. A similar feature is observed in the transient spectrum of deuteriated **1**, $(CO)_5W{=}C(OCD_3)Ph$, but at a higher frequency, 1156 cm^{-1}. By contrast, all other features in this spectrum are shifted by <10 cm^{-1} compared to those of the undeuteriated transient. Two-laser studies, in which RR spectra are recorded at several delays (150 ns to 20 μs) between the pump (351 nm, excimer) and probe (405 nm, dye) laser pulses, confirm that scattering is due to the same transient as that monitored in the laser flash photolysis experiments. It is proposed that the transient is the result of rapid intramolecular rearrangement, within the laser pulse duration, in the primary CO-dissociated fragment, $[(CO)_4W{=}C(OMe)Ph]$, created by LF excitation. The rearrangement is suggested to involve a two-electron, three-center interaction between the W center and the C–H bonds of the OMe group; this impedes access to the vacant coordination site at the metal but allows the carbene ligand skeleton to retain its essential identity, in line with the resonance Raman spectroscopic evidence. A possible scheme for the [CO]-independent decay of the transient is presented. The fact brought out by the RR evidence, that the transient can be formed by laser excitation throughout the wavelength range (350–405 nm), suggests the existence of two LF transitions in this wavelength interval.

Transient vibrational spectroscopy, involving both time-resolved resonance Raman[1] (TR^3) and transient IR techniques,[2] has grown significantly as a structural probe of metal-centered excited states and transients in solution. However, the TR^3 technique has been mainly deployed as a probe of the excited states of transition metal complexes, especially of metal polypyridyls,[1,3] while use of the IR method has been confined to monitoring photogenerated transients in organometallic complexes. In the latter case interest has focussed on metal carbonyls in which ligand-field (LF) photolysis leads to CO photodissociation and the formation of coordinatively unsaturated species which may then interact rapidly with the solvent.[4] One of the main objectives of the work described in the present paper was to explore how the natural link (arising through the allowed electronic transitions) which exists between transient UV–visible absorbance difference (ΔA) spectroscopy and excited-state resonance Raman (RR) scattering might be exploited in the field of organometallic photochemistry to probe the kinetics and vibrational spectroscopy in solution of organometallic excited states and transients. In a preliminary account[5] of the laser flash photolysis in solution of the Fischer complex, $(CO)_5W{=}C(OMe)Ph$ (**1**), we presented evidence based upon ΔA and single laser RR measurements that LF irradiation of **1** leads to the formation of a species where access to the vacant site created by CO photodissociation is impeded by an intramolecular interaction between the metal center and the methoxy part of the carbene ligand. In this paper the arguments which point to such an interaction are discussed more fully as are the mechanism of formation and decay back to the fully coordinated complex. The results of single laser excitation at a range of wavelengths are reported and also TR^3 spectra. To our knowledge, the latter are the first reported two-laser, time-resolved Raman spectra of a photogenerated organometallic species.

Experimental Section

Laser Flash Photolysis. The laser flash photolysis and transient ΔA measurements used the Nd/YAG Q-switched laser (Quanta-Ray DCR2), Raman wavelength shifting device, boosted xenon arc, and transient digitizer described previously.[6] Solutions (10^{-3} - 10^{-4} mol dm^{-3}) contained in 1-cm quartz cuvettes held in a thermostated copper block (±0.5 °C) were Ar-purged prior to photolysis.

Resonance Raman Spectroscopy. All two-laser experiments were carried out at the Laser Support Facility (LSF) of the Science and Engineering Research Council (Rutherford Appleton Laboratory). Some of the single laser studies were done at Queen's University. Ground electronic state spectra were excited by means of an Ar^+ laser (Innova 90 at the LSF) at wavelengths of 363.8 and 488 nm. For transient studies, an excimer-pumped dye laser (Lambda Physik FL2002E or FL3002E) was used, with the same laser pulse acting as both pump and probe in single color experiments. For two-color, time-resolved studies a second excimer laser (Lambda Physik EMG 150, broad-band output at 351 nm) acted as the pump source. Figure 1 is a schematic diagram of the layout used. Ar-flushed solutions (ca. 10^{-3} mol dm^{-3}) in the appropriate solvent were flowed from a syringe through quartz capillaries (1-mm i.d.) at a rate sufficient to ensure that each pump/probe pulse encountered a fresh volume of sample. Although it was found that solutions could be recycled several times without producing detectable changes in their spectra, fresh samples were used for each experimental run. Raman-scattered photons were collected and dispersed by a Spex Triplemate spectrometer (1200 grooves/mm grating) which was coupled

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(1) Caswell, D. S.; Spiro, T. G. *Inorg. Chem.* **1987**, *26*, 18–22 and references therein.

(2) Poliakoff, M.; Weitz, E. *Adv. Organomet. Chem.* **1986**, *25*, 277–316.

(3) McGarvey, J. J.; Bell, S. E. J.; Bechara, J. N. *Inorg. Chem.* **1986**, *25*, 4325–4327 and references therein.

(4) Dobson, G. R.; Hodges, P. M.; Healy, M. A.; Poliakoff, M.; Turner, J. J.; Firth, S.; Asali, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 4218–4224.

(5) Bechara, J. N.; Bell, S. E. J.; McGarvey, J. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1785–1787.

(6) Bell, S. E. J.; McGarvey, J. J. *Chem. Phys. Lett.* **1986**, *124*, 336–340.

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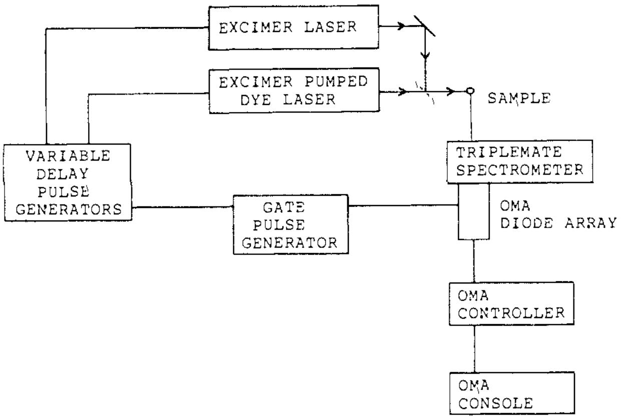

Figure 1. Schematic diagram of set-up for two laser time-resolved resonance Raman scattering studies.

to an intensified diode array detector (EG&G PARC Model 1420) controlled from an OMA II console and gated by a high-voltage pulser. The experiment was synchronized through a linked pair of dual channel pulse generators which triggered both lasers and the gating unit. Time delays between pump and probe laser pulses and synchronization of the gating pulse with the Raman probe pulse were independently monitored by means of a photodiode.

The DCR2 Nd/YAG laser already referred to was used for pulsed, single-color resonance Raman studies at Queen's University. Appropriate pump/probe wavelengths were generated by stimulated Raman scattering in H_2 or CH_4 of the third harmonic output of the laser at 354.7 nm. Raman scattered radiation was dispersed by a triple spectrometer constructed in the laboratory by coupling a double spectrometer (Spex Model 1680, adapted to operate in subtractive dispersion) to a single grating (1200 groove) spectrometer (Spex Model 1870). A diode array detector (Model 1420) with EG&G Model 1463 OMA III controller was used in conjunction with a fast gate pulse generator (EG&G Model 1302). Synchronization was achieved via timing pulses available directly from the Nd/YAG laser.

Materials. Samples of the Fischer complex, $(CO)_5W{=}C(OMe)Ph$, were kindly supplied by Dr. K. Weiss, (Bayreuth, FRG). The deuteriated analogue, $(CO)_5W{=}C(OCD_3)Ph$, was prepared[7] by addition of a catalytic quantity of sodium metal to solutions of Fischer in CH_3OD. Solvent was removed at room temperature under vacuum. Deuteriation was confirmed by mass spectrometry. All solvents were Aldrich Gold Seal grade and were used without further purification.

Results

Transient Absorbance Difference Spectroscopy. When solutions (10^{-3}–10^{-4} mol dm^{-3}) of **1** were irradiated by a laser pulse at 355 nm, exponentially decaying ΔA signals with microsecond lifetimes were observed. At monitoring wavelengths beyond 405 nm transient bleaching was observed while at shorter wavelengths transient absorbance increases occurred. The data measured in CH_2Cl_2 and CH_3CN solutions are typical and ΔA plots for both solutions are displayed in Figure 2a. The lifetimes, τ, were independent of monitoring wavelength but temperature and solvent dependent. In CH_2Cl_2 solutions τ varied from 30.8 μs at 5.8 °C to 4.4 μs at 36.1 °C, while at a fixed temperature (20.0 °C) the following values (in μs) were measured in the solvents indicated, with errors quoted as standard deviations: CH_3CN (25 ± 3); CH_2Cl_2 (11.1 ± 0.2); *n*-hexane (2.9 ± 0.2); 1:1 [*n*-hexane + CH_2Cl_2] (7.4 ± 0.5); benzene (10.2 ± 0.1). A striking and unexpected result was that saturation of solutions of **1** with CO (by vigorous bubbling for 30 min) caused no change in the measured transient relaxation times. The effect was observed and carefully checked in several instances and is illustrated by the following values recorded for CO-saturated solutions, also at 20 °C: CH_2Cl_2 (10.9 ± 0.2); *n*-hexane (3.1 ± 0.2); benzene (10.3 ± 0.2), in very good agreement with the corresponding values measured in the Ar-saturated solutions.

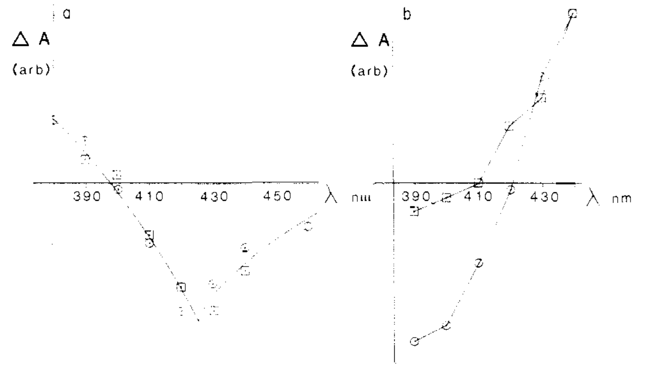

Figure 2. (a) Absorbance difference (ΔA) spectra of the transient generated by laser flash photolysis at 354.7 nm of $(CO)_5W{=}C(OMe)Ph$ in CH_2Cl_2 (○) and CH_3CN (□) solutions. Plotted points were derived from absorbances calculated at maximum signal amplitude of the transient decay immediately following the laser pulse. (b) Absorbance difference spectra for photoproduct formation in CH_3CN solutions of $(CO)_5W{=}C(OMe)Ph$: (○) ΔA values calculated from the spectra in Figure 3. (□) ΔA values derived from the *final* signal levels reached in the transient decay traces in CH_3CN used to obtain the data in (a).

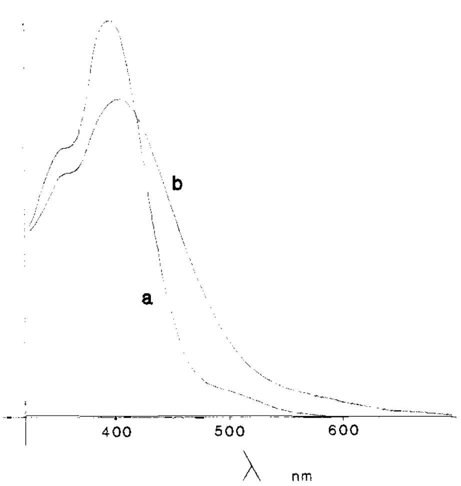

Figure 3. Spectra showing formation of *cis*-$(CH_3CN)(CO)_4W{=}C(OMe)Ph$ following irradiation of $(CO)_5W{=}C(OMe)Ph$ in CH_3CN solution (2 × 10^{-4} mol dm^{-3}) at 354.7 nm: (a) before irradiation; (b) after irradiation with Q-switched laser pulses (10 mJ) at 10 Hz repetition rate for 2 min.

The D^3-Fischer complex, $(CO)_5W{=}C(OCD_3)Ph$, behaved analogously to **1** following pulsed laser excitation, but with somewhat longer lived transients. In $CDCl_3$, the lifetimes for the normal and deuteriated complexes at 20.0 °C were 7.1 and 9.5 μs, respectively. That this was a genuine difference and not the result of impurities in either sample was confirmed by the following measurements carried out in methanol as solvent. First, the transient lifetime for the H^3 complex (**1**) was measured as 18.0 μs at 20.0 °C. Next the lifetime for the D^3-complex transient was recorded as 19.6 μs, also in methanol at 20.0 °C. When a catalytic amount of $CH_3O^-{-}Na^+$ was now added to the latter solution to convert the D^3 complex back to the H^3 form (**1**), and the laser flash experiment repeated, the transient lifetime was found to have changed from 19.6 to 18.1 μs, the same value within experimental uncertainty as had been previously measured for **1** in methanol.

In CH_3CN solutions the transient ΔA signals did not return to the baseline on a microsecond timescale, indicating that a stable photoproduct was being formed. When subjected to a succession of laser pulses at 355 nm (typically at a repetition rate of 10 Hz for a period of 120 s), the solutions gradually deepened in color from yellow to red. Figure 3 shows the shift in λ_{max} to longer wavelengths corresponding to the buildup of a photoproduct. The close agreement shown in Figure 2b between the permanent ΔA signals measured in this and in the above transient experiments indicates that they are due to the same species. The spectral changes, shown in Figure 3 with an isosbestic point at 418 nm, are in good agreement with those reported by Geoffroy et al.[8]

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[7] Schubert, U.; Fischer, E. O. *Justus Liebigs Ann. Chem.* **1975**, *3*, 393–400.

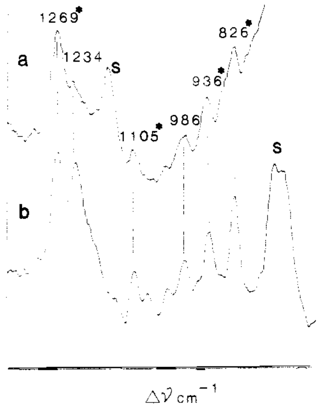

Figure 4. Pulsed laser excited resonance Raman spectra of $(CO)_5W{=}C(OMe)Ph$: (a) in CH_2Cl_2 solution (10^{-3} mol dm^{-3}), λ_{ex} 360 nm, excimer-pumped dye laser, pulse duration 15 ns, energy at sample 3 mJ; (b) in CCl_4 solution (10^{-3} mol dm^{-3}), λ_{ex} 395.6 nm, first Stokes stimulated Raman scattering in CH_4 of third harmonic (354.7 nm) from Nd/YAG laser, pulse duration 6 ns, energy at sample 0.5 mJ. In both spectra, * denotes scattering by photogenerated transient, S: solvent Raman scattering.

following continuous irradiation in the LF absorption region at 366 nm of solutions of **1** in acetonitrile and attributed by them to the stable photosubstitution product, *cis*-$(CH_3CN)(CO)_4W{=}C(OCH_3)Ph$ (**2**). This product is formed[8] by reaction of the acetonitrile solvent with the coordinatively unsaturated species, $(CO)_4W{=}C(OCH_3)Ph$, produced by CO dissociation from a LF excited state of **1**. Figures 2b and 3 therefore provide good evidence that CO photodissociation also occurs under the pulsed laser excitation conditions at 355 nm used in the present work. However, it is clear from our measurements that the stable photoproduct **2** is distinct from the microsecond transient species which, as the ΔA spectra in Figure 2a clearly demonstrate, are formed not only in acetonitrile but also in noncoordinating solvents in which no detectable amounts of permanent photoproduct arise. A central question in the case of acetonitrile is whether **2** forms promptly, during the laser pulse, or is a product of the decay of the transient species. When the monitoring wavelength was set at the isosbestic point between **1** and **2** (418 nm, Figure 3), the exponential decay process alone was observed. Unambiguous observation of a signal due solely to formation of **2** proved more difficult. However, at monitoring wavelengths >600 nm where both **1** and the transient have negligible absorbance but **2** still absorbs to some extent, rapid buildup of the latter on a much faster timescale than decay of the transient was indeed observed. Unfortunately, the size of photomultiplier anode load necessary to observe the small ΔA signals involved compromised the response time of the detector so that buildup within the duration of the laser pulse itself could not be confirmed.

Resonance Raman Spectra

(i) Single-Laser Studies. Ground electronic state Raman spectra of **1** generated by means of the CW Ar$^+$ laser at 363.8 nm were dominated by vibrations characteristic of the carbene part of the molecule (Table I below) since at this excitation wavelength significant resonance enhancement occurs via the W→carbene CT transition which together with a LF transition accounts[8] for the absorption intensity in this spectral region. The Raman spectrum excited at almost the same wavelength (360 nm), but using a pulsed dye laser source exhibited several new bands due to a transient populated by the laser pulse, while retaining features due to residual, unphotolyzed **1**. This pattern of transient and residual ground-state scattering in which the transient is both created and probed by a single laser pulse was also observed in pulsed excitation studies at other wavelengths within the (CT + LF) absorption region of **1**, as shown in Figure 4. Detailed data from the measurements at 360 nm are listed in Table I alongside those from the ground-state spectra recorded at 363.8 nm. The band assignments shown are those proposed by Fischer et al.[9] for IR spectra of **1**. All except one of the bands attributable to the transient have counterparts in the ground-state spectrum and, as Table I shows, occur with the same relative intensities, suggesting that the vibrational modes are resonantly enhanced through the same type of W→carbene CT transition as the ground state of **1**.

Table I. Principal Features (cm^{-1}) in Ground Electronic State and Transient Resonance Raman Spectra of $(CO)_5W{=}C(OCD_3)Ph$ (D^3-Fischer) and $(CO)_5W{=}C(OCH_3)Ph$ (H^3-Fischer) in Solution

D^3-Fischer[a]		H^3-Fischer[b]		
ground[c]	transient	ground[c]	transient[d]	assignment[f]
1235	1268	1233 (1.0)[e]	1269 (1.0)[e]	ν(C–OCH$_3$)
	1156		1105 (0.17)	
983	929	988 (0.36)	936 (0.32)	ν(O–CH$_3$)
864		874 (0.32)	826 (0.35)	ν(C–Ph)

[a] In CDCl$_3$ solution. [b] In CH$_2$Cl$_2$ solution. [c] λ_{ex} 363.8 nm, Ar$^+$ CW laser. [d] λ_{ex} 360 nm, pulsed dye laser. [e] Relative band intensities obtained by normalizing peak heights with respect to the largest peaks (1233 and 1269) in each spectrum. [f] Taken from ref 9.

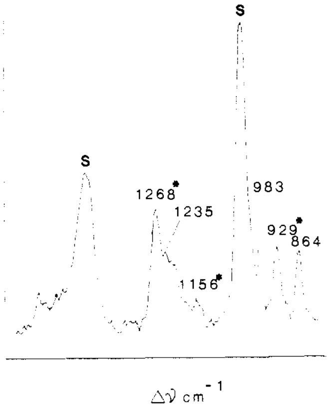

Figure 5. Pulsed laser excited resonance Raman spectrum of $(CO)_5W{=}C(OCD_3)Ph$ in $CDCl_3$ (ca. 10^{-3} mol dm^{-3}), λ_{ex} 370 nm, excimer pumped dye laser, pulse duration 15 ns. * denotes scattering by photogenerated transient, S: solvent Raman scattering.

The resonance Raman spectrum of the deuteriated complex, $(CO)_5W{=}C(OCD_3)Ph$ in $CDCl_3$, recorded using pulsed laser excitation at 370 nm, is shown in Figure 5. Although a strong solvent peak at 1026 cm^{-1} masks part of the lower frequency region, the spectrum generally resembles that of undeuteriated **1**. The principal bands are also listed in Table I for comparison with those of **1**. Significantly, most of the features visible and attributable to either parent complex or transient are shifted by small extents only (<10 cm^{-1}) from their respective positions in the corresponding RR spectra of **1**. The one exception[10] is a band at 1156 cm^{-1} which appears at 1105 cm^{-1} in the transient spectrum of **1**, the only feature in that spectrum with no obvious ground-state counterpart.

(ii) Two-Laser Time-Resolved Studies. Although it seems reasonable to assume that the same transient species is being observed in both the UV–visible ΔA and the RR scattering studies, the difference in time scale of the two experiments (Raman scattering being recorded within a single-laser pulse of 10–15 ns duration but ΔA being measured over a period of several microseconds) made it desirable to check this assumption. A series of two-laser TR^3 studies was therefore carried out. Samples of **1** in CH_2Cl_2 were photolyzed at 351 nm and Raman scattering from the photogenerated transient was probed by a second pulse at 405 nm from a dye laser, at a series of time delays after photolysis. Investigations with the probe beam alone, however,

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[8] Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064–3073.

[9] Fischer, E. O.; Maasbol, A. *Chem. Ber.* **1967**, *100*, 2445–2456.

[10] This band position supercedes the value 1181 cm^{-1} reported in ref 5, which was derived from spectra of inferior signal:noise to those reported here.

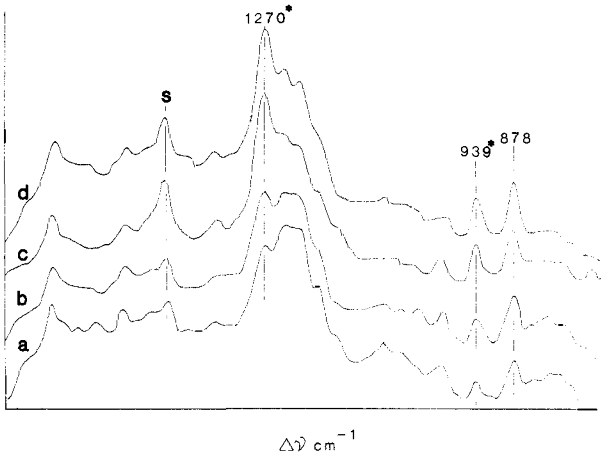

Figure 6. Pulsed laser excited resonance Raman spectra of $(CO)_5W{=}C(OMe)Ph$ in CH_2Cl_2 (ca. 10^{-3} mol dm^{-3}) at λ_{ex} 405 nm, excimer pumped dye laser. Spectra (a–d) show growth of transient (*) features with increasing laser beam focus (S: solvent Raman scattering).

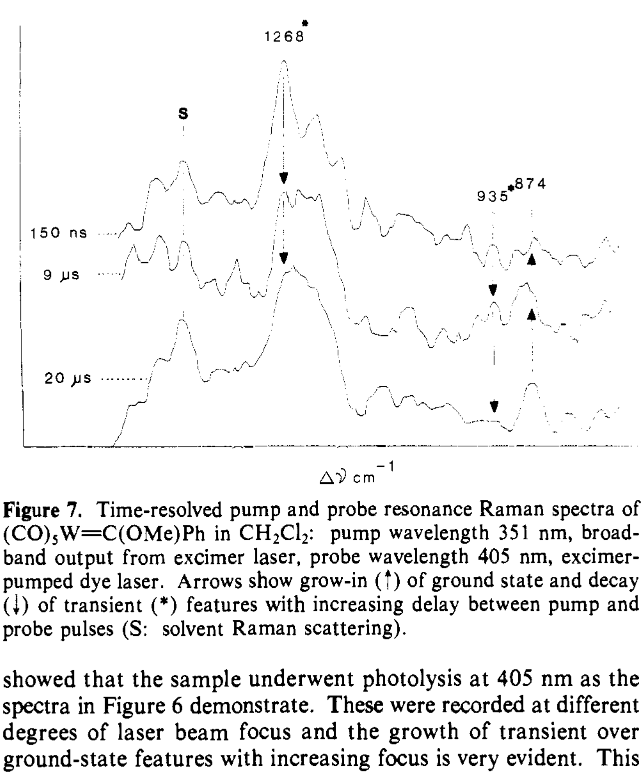

Figure 7. Time-resolved pump and probe resonance Raman spectra of $(CO)_5W{=}C(OMe)Ph$ in CH_2Cl_2: pump wavelength 351 nm, broadband output from excimer laser, probe wavelength 405 nm, excimer-pumped dye laser. Arrows show grow-in (↑) of ground state and decay (↓) of transient (*) features with increasing delay between pump and probe pulses (S: solvent Raman scattering).

showed that the sample underwent photolysis at 405 nm as the spectra in Figure 6 demonstrate. These were recorded at different degrees of laser beam focus and the growth of transient over ground-state features with increasing focus is very evident. This secondary photolysis problem was minimized in the two-laser experiments by using a well-defocused beam and the lowest possible probe pulse energy, consistent with detectable Raman scattering.

A series of TR^3 spectra obtained at different pump-probe time delays with 405-nm probe pulses is shown in Figure 7. While the signal/noise ratio of these spectra is lower than that obtained in the single-laser experiments at the same wavelength, it is quite clear that the same transient features appear in the spectrum recorded at shortest delay as were observed in single-laser experiments. These transient features decay over a period of several microseconds and there is a corresponding growth in those associated with the unphotolyzed complex. In practice, complete recovery to a spectrum containing no characteristic transient features was not observed, owing to secondary photolysis by the probe beam, which occurs to some extent even under low power conditions. Nevertheless, the long time-delay spectrum does strongly resemble spectra obtained under low power with the probe laser alone. The spectra in Figures 6 and 7 thus show that the same transient species which is formed within the pulse duration in single laser experiments decays over several microseconds back to the unphotolyzed Fischer complex and so may be reasonably identified with the transient observed in the UV–visible ΔA experiments.

The possibility was also considered of using the two-laser TR^3 technique to confirm the rapid buildup, suggested by the ΔA measurements referred to earlier, of the acetonitrile photoproduct **2**. However, preliminary experiments to determine the RR spectrum of **2** at an appropriate wavelength (488 nm, where **2** is much more strongly absorbing than **1**) showed that apart from a somewhat greater degree of resonance enhancement of the scattering from **2** at 488 nm, the spectrum was practically indistinguishable from that of **1**.

Discussion

Previous work by Geoffroy et al.[8] and Fong and Cooper[11] has established that CO dissociation is the dominant primary process arising from population of the ligand-field (LF) states of metal carbonyl carbene complexes. As already noted above, our observation of prompt formation of *cis*-$CH_3CN(CO)_4W{=}C(OCH_3)Ph$ as a result of laser irradiation at 355 nm of **1** in acetonitrile is in good accord with the earlier work[8] and provides clear evidence for CO dissociation under our conditions at this wavelength. Nevertheless, it does not eliminate the possibility that the LF state from which CO dissociation occurs is very short-lived and that the microsecond transient is due to a long-lived charge-transfer excited state of the complex. However, in all the other solvents investigated only the transient species is observed and since CO dissociation would reasonably be expected in these media also, then this implies that the transient is indeed formed through CO loss. The single laser resonance Raman spectra show that this species must form within the duration of a nanosecond laser pulse while the TR^3 spectra show that it subsequently decays on a microsecond time scale back to **1**. As emphasized in the Results section, the very similar patterns of resonance enhancement displayed by the Raman spectra of the ground state of **1** and of the transient species strongly suggests that the enhancement in the latter case must arise through the same type of W→carbene CT transition as the ground state. This in itself would effectively rule out the possibility that the transient is a (thermally equilibrated) MLCT excited state. There are two reasons why we believe the transient cannot simply be the coordinatively unsaturated entity present immediately after CO dissociation: (1) acetonitrile photosubstitution arising through attack at the vacant coordination site is apparently complete within a matter of nanoseconds whereas the transient species exists for microseconds; (2) the rate of regeneration of **1** is independent of CO concentration in the solution, rather than CO-dependent as it would be if transient and CO reacted to form **1** in a rate-determining step. Both these observations suggest that the vacant site is "blocked" in the transient. However, this cannot be attributed merely to solvent coordination at the site (with transient decay then corresponding to rupture of the solvent–complex bond followed by fast CO attack) since (i) in acetonitrile the solvent-coordinated species (**2**) is a stable entity, readily distinguishable from the transient which in this and all the other solvents investigated decays on a microsecond time scale; and (ii) the vibrational frequencies of bonds within the carbene moiety of the transient are shifted by 10's of cm^{-1} from those of **1** (Table I) whereas the resonance Raman spectra of **1** and the photoproduct **2** are practically indistinguishable (vide supra). This latter observation suggests that replacement of CO by solvent at the metal center causes a minor perturbation only of the bond strengths within the carbene skeleton.[12]

Interaction between solvent and the vacant site created by CO photodissociation in metal carbonyls, $M(CO)_6$, and substituted metal carbonyls, $M(CO)_5L$, is now a widely reported phenomenon,[13] ranging in degree from direct "Lewis base" coordination

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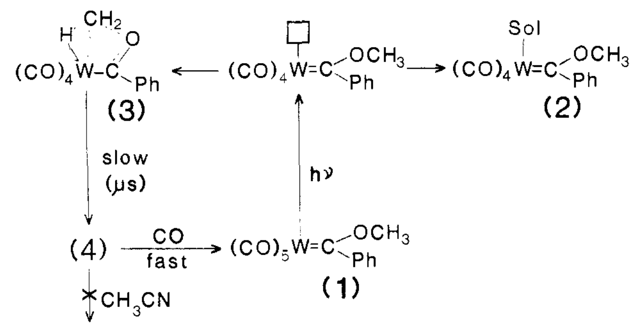
[11] Fong, L. K.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 2595–2599.

[12] Similar investigations now in progress of the methyl analogue of **1**, $(CO)_5W{=}C(OMe)Me$, show that replacement of CO by solvent causes subtle changes only in the RR scattering pattern.

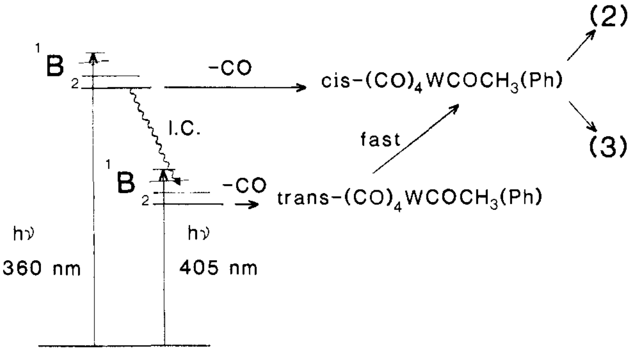
[13] Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6751–6753 and references therein.

Scheme I. Proposed Reaction Sequence Following Ligand-Field Photolysis of the Fischer Complex (**1**) in Solution: □, Vacant Coordination Site



as in the formation of the acetonitrile substitution product (**2**), to "quasicoordination"[4] by solvents normally regarded as noncoordinating. In Scheme I which we now propose to account for the present observations, creation of a blocked site in the nascent, coordinatively unsaturated species is considered to come about through an incipient, intramolecular interaction between the "16-electron" tungsten center and the C–H bond of the adjacent methoxy group to give the cyclic species **3**. This "self-solvation"[14] occurs in competition with intermolecular formation of the solvent-coordinated species **2**. In the case of acetonitrile our ΔA measurements suggest that **2** and **3** form at comparable rates within the laser pulse duration whereas in the other, noncoordinating solvents the formation of species **3** is the dominant process. The type of three-center, two-electron interaction suggested in **3**, between an alkyl C–H bond and an electron-deficient metal center, has already been quite commonly invoked.[15] A very recent example,[14] related in some respects to the present situation, concerns the complex, $(\eta\text{-}C_5H_5)(CO)_3W{-}CH_2CH_3$, where in the coordinatively unsaturated CO loss species arising from LF photolysis an interaction was suggested[16] between the metal center and the β hydrogen of the ethyl group. In species **3** in Scheme I the vacant coordination site is blocked and the tungsten center has a formal electron count greater than 16. Polarization of the C–H bond should result in a concomitant decrease in the strength of the $O{-}CH_3$ bond and an increase in that of the $C{-}OCH_3$ bond. While the shifts in the vibrational frequencies (see Table I) are in line with this expectation, in suggesting that the $O{-}CH_3$ and $C{-}OCH_3$ bonds are respectively weaker and stronger in **3** than in **1**, the structure proposed in **3** should be regarded as a formalism only. The essence of it is that the metal center withdraws some electron density from a C–H bond in the methoxy group to form a cyclic entity with a blocked coordination site but with the carbene ligand skeleton remaining more or less intact. Hence, the proposal also accommodates the observation that vibrational modes in the transient resonance Raman spectrum have counterparts in that of the parent complex. The large frequency shift (to 1156 cm^{-1}) which the 1105-cm^{-1} vibration undergoes (Table I) upon deuteriation implies that the feature is intimately associated with the $-CH_3$ region of the transient although the direction of the shift suggests that it is not attributable to a "normal" vibrational mode of $-CH_3$. The fact that it only appears in the spectrum of the transient is significant. As discussed already, resonance enhancement is largely attributable to W→carbene transitions in both the transient and the Fischer complex **1** so that the same vibrational modes would be expected to appear in both spectra. The absence of the 1105-cm^{-1} band from the ground-state spectrum would suggest a negligible change in C–H bond character (and thus lack of resonance enhancement) in the $-CH_3$ group on going from the ground state to the charge-transfer state, the transition through which enhancement of the other primarily stretching modes of the carbene skeleton arises. However, in the transient structure **3** where a tungsten–CH_3 group interaction is proposed, the corresponding charge-transfer transition would be expected to influence the bonding not only in the carbene skeleton but also between the metal and the $-CH_3$ group so that resonance enhancement of CH_3 modes could occur through transitions to virtual states of this type.

Scheme II. Internal Conversion (I.C.) and CO Photodissociation from Laser-Populated LF Excited States of the Fischer Complex (**1**)



Scheme I proposes the return of the transient **3** to the fully coordinated Fischer complex **1** to occur via a rate-limiting rearrangement to a species **4** which rapidly recombines with CO (but not with CH_3CN, since no photosubstitution product (**2**) forms on the time scale of the transient decay). While this proposal provides a formal explanation for the observation noted above that the transient lifetimes are independent of the CO concentration in solution, we can only speculate about the rearrangement and the structure of **4**. One tentative suggestion is that complete cleavage of the C–H bond involved in the interaction proposed in **3** occurs to give a cyclic species with a metal–hydride bond, $(CO)_4\overline{W(H)\text{-}CH_2\text{-}O\text{-}C}Ph$, in which if the proton is "mobile", moving between W^- and the carbene carbon, (rather than covalently bound to the metal), attack at the formal W^- center by a π-acceptor like CO might be encouraged, compared to CH_3CN. Selective reactivity by transient species among simple two-electron donors such as CO and PPh_3 has been reported in other systems.[17]

Concerning the initial photolysis step in **1** which results in CO dissociation, some discussion[8,11] still centers on the assignment of the LF transitions in the absorption spectrum of the complex. Two low-lying LF transitions are expected and on the basis of quantum yield measurements for CH_3CN substitution at various wavelengths, Geoffroy et al.[8] assigned the 352-nm band to the lower energy of these, corresponding to the one-electron transition (in the assumed C_{2v} symmetry), $^1B_2\ (...2a_1{}^1b_2{}^1) \leftarrow {}^1A_1\ (...b_2{}^2)$, involving population of a d_{z^2} orbital. Hence, 352-nm excitation should result in axial W–CO bond labilization and hence trans CO loss. The formation of entirely cis substitution product was attributed to either fast trans to cis interconversion in the initially formed coordinatively unsaturated species prior to acetonitrile attack or to trans → cis conversion of the product. However, Fong and Cooper[11] from a study of the spectra of a series of complexes related to **1** but where the positions of *both* bands were more easily determined, have assigned the 352-nm band of **1** to the higher energy transition, $^1B_2\ (...3a_1{}^1b_2{}^1) \leftarrow {}^1A_1\ (...b_2{}^2)$, corresponding to population of a $d_{x^2-y^2}$ orbital. On this basis excitation in the 350–360-nm region would be expected[11] to lead directly to cis CO loss without the need to postulate any fast trans → cis interconversion. The resonance Raman results presented here suggest that there is indeed a second, allowed LF transition at lower energies than the 352-nm band. From the fact that transient formation (involving CO dissociation) is observed after photolysis of **1** at either 355 or 405 nm, we conclude that the 352-nm band is due to a transition to the upper LF state and that at least some of the absorption by the complex at 405 nm may be due to a second, lower lying LF transition. Species **3**, shown in Scheme I, can only

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[14] Yang, G. K.; Peters, K. S.; Vaida, V. S. *J. Am. Chem. Soc.* **1986**, *108*, 2511–2513.

[15] Brookhart, M. L.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.

[16] Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6005–6015.

[17] Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 436–442.

form if a cis vacancy is present, a trans vacancy being too remote to allow such interaction. Since 405-nm photolysis also leads to **3** within the laser pulse duration but via the lower LF state (expected to give trans CO dissociation), it appears that trans to cis interconversion of the vacant site must occur within a few nanoseconds. These conclusions are summarized in Scheme II. Our resonance Raman results, however, permit no definitive conclusions about the rate of internal conversion[11] (IC) between the two $^1B_2$ states shown. If IC were too slow to compete with CO dissociation induced by 360-nm photolysis, species **3** would form rapidly from the cis CO loss entity within the duration of the laser pulse. If IC were fast enough to compete with CO loss, this would result in population of the lower lying LF state which, as the experiments at 405 nm suggest, would again lead to formation of **3** within the laser pulse duration. Thus no unequivocal statement can be made about the rate of IC between the two LF states.

Summary

Laser flash photolysis at 354.7 nm in the ligand field absorption region of $(CO)_5W{=}C(OMe)Ph$ in solution results in prompt formation of a transient with a microsecond lifetime. Evidence for primary photodissociation of CO is presented, in agreement with earlier steady-state photolysis studies,[8] but the transient decay is independent of CO concentration in solution. It is concluded on the basis of both kinetic and resonance Raman spectroscopic evidence that the transient is the result of rapid intramolecular rearrangement, within the laser pulse duration, in the primary CO-dissociated photofragment. This rearrangement "blocks" the vacant coordination in the latter, by way of a proposed two-electron, three-center interaction between the electron-deficient tungsten and the C–H bond of the OMe group. The interaction distinguishes the chemical and kinetic behavior of the transient from that of the initial, coordinatively unsaturated entity, $[(CO)_4W{=}C(OMe)Ph]$, while at the same time allowing the carbene ligand skeleton effectively to retain its integrity. Although the mechanism for decay of the transient remains a matter for speculation, its essential nature as expressed in the previous sentence is an important conclusion. A significant part of the evidence for it derives from a central feature of resonance Raman spectroscopy, namely, that the observed pattern of enhancement in vibrational modes can be linked to resonance with a particular electronic transition, hence enabling well-founded identification of a key chromophore in the scattering species. The present study shows that this "localization" of structural information, which is a natural feature of RR spectroscopy, can be turned to substantial advantage in elucidating the nature of transient species.

We are currently extending the RR and kinetic investigations to analogues of the Fischer complex and are also examining the possibility of probing the carbonyl vibrational modes as a complement to transient IR methods.

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Registry No. 1, 37823-96-4; **1**-d_3, 109388-47-8; **2**, 85221-50-7; CH_2Cl_2, 75-09-2; *n*-hexane, 110-54-3; benzene, 71-43-2; acetonitrile, 75-05-8.

1,2-Migrations in Free Radicals Related to Coenzyme B_{12} Dependent Rearrangements

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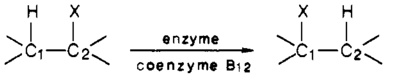
Abstract: The free radicals $XC(CH_3)(COOR)CH_2^{\bullet}$, where X = C(=O)Me (**1**), C(=O)SEt (**2**), C(=O)OEt (**3**), $C(=CH_2)Me$ (**4**), and C_6H_5 (**5**), were generated by reaction of the corresponding bromides with $(n\text{-Bu})_3SnH$. The rates of rearrangement involving 1,2-migration of X (to form $^{\bullet}C(CH_3)(COOR)(CH_2X)$) were measured in competition with trapping by $(n\text{-Bu})_3SnH$. The measurements yielded the following rearrangement rate constants, k_r, and activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$: (**1**) 1.2×10^4 s^{-1} at 45 °C, 11.0 kcal/mol, −4 cal/mol·K; (**2**) 23.5 s^{-1} at 60.5 °C, 13.8 kcal/mol, −11 cal/mol·K; (**3**) <10 s^{-1} at 113 °C; (**4**) 3.0×10^5 s^{-1} at 45 °C, 10.0 kcal/mol, −2 cal/mol·K; (**5**) 5.0×10^3 s^{-1} at 61 °C. From the results of crossover experiments it is concluded that the rearrangements of **1** and **2** are intramolecular processes, probably proceeding through cyclopropyloxy radical intermediates or transition states. The carbanions corresponding to **1**–**5** (i.e., $XC(CH_3)(COOR)CH_2^-$, generated by reduction of the corresponding bromides with sodium naphthalene) also rearrange rapidly but, in each case, with some contribution from migration of the ester group. This represents the first demonstration of spontaneous 1,2-migration of a thioester group in a free radical and models the coenzyme B_{12} dependent methylmalonyl-CoA mutase rearrangement. The results support a free-radical rearrangement mechanism for the latter reaction.

Coenzyme B_{12} (5′-deoxyadenosylcobalamin, abbreviated $AdCH_2$–B_{12}) serves as a cofactor in several enzymatic reactions, a common feature of which is the interchange of a hydrogen atom and another substituent [X = OH, NH_2, C(=O)S–coenzyme A, $C(=CH_2)COOH$, or $CH(NH_2)COOH$] on adjacent carbon atoms, as depicted schematically by eq 1.[1,2]



$$>\overset{H}{C_1}-\overset{X}{C_2}< \xrightarrow[\text{coenzyme } B_{12}]{\text{enzyme}} >\overset{X}{C_1}-\overset{H}{C_2}< \qquad (1)$$

Several lines of evidence have provided persuasive support for a mechanistic scheme, the minimal features of which are depicted by eq 2 and 3.[2-5]

$$AdCH_2\text{–}B_{12} \xrightleftharpoons{\text{enzyme}} AdCH_2^{\bullet} + B_{12r} \qquad (2)$$

An aspect of the mechanism that continues to be controversial is whether the rearrangement step itself, i.e., the 1,2-migration of X, actually occurs at the free-radical stage (i.e., $S^{\bullet} \rightarrow P^{\bullet}$, directly), as depicted in eq 3, or via additional intermediates (for

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[1] For leading references, see: (a) Dolphin, D., Ed. *B_{12}*; Wiley: New York, 1982. (b) "Vitamin B_{12}", *Proc. Eur. Symp., 3rd* **1979**.

[2] Halpern, J. *Science (Washington, D.C.)* **1985**, *227*, 869, and references cited therein.

[3] Babior, B. M. *Acc. Chem. Res.* **1975**, *8*, 376.

[4] Golding, B. T. Reference 1a, Vol. 1, p 543, and references cited therein.

[5] Abeles, R. H. Reference 1b, p 373.

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