

# Ligand-field Photolysis of the Fischer Complex, $(OC)_5W=C(OMe)Ph$ : Time-resolved Resonance Raman Spectroscopic Evidence for Alkyl-Metal Interaction Following CO Photodissociation

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Transient resonance Raman spectroscopy suggests that the co-ordinatively unsaturated fragment produced by ligand field photodissociation of the Fischer complex,  $(OC)_5W=C(OMe)Ph$ , undergoes rapid (<10 ns) rearrangement to a species displaying a partial bonding interaction between the methyl group and the metal centre.

Transient vibrational spectroscopy using either fast i.r. detection<sup>1</sup> or the resonance Raman technique<sup>2</sup> has become a significant structural probe of excited states and short-lived species in solution. For metal-centred systems, the former method has been applied<sup>1</sup> to the structural and kinetic investigation of transients produced in metal carbonyl photolysis while the resonance Raman technique has been particularly successful in probing charge-transfer (C.T.) excited states, primarily<sup>2</sup> of  $d^6$  but also, more recently,<sup>3</sup> of  $d^{10}$  metal ion complexes.

We now report the first example of resonant Raman scattering from a transient generated by photolysis in solution with a pulsed laser in the ligand-field absorption bands of the catalytically important metal-carbene complex,  $(OC)_5W=C(OMe)Ph$  (**1**).

Photodissociation of a CO ligand is well-established<sup>4</sup> as a primary process ( $\phi \sim 10^{-2}$ ) from the ligand-field excited states of this and related complexes, but we now present kinetic and spectroscopic evidence that rapid (<10 ns) rearrangement takes place of the initial, co-ordinatively unsaturated photo-fragment, leading to a partial bonding interaction between the metal centre and the methyl group of the carbene moiety.

Figure 1 shows the absorbance difference spectrum of the transient generated by irradiation of Ar-purged solutions of (**1**) in  $CH_2Cl_2$  with a Q-switched pulse ( $\sim 9$  ns duration) from a Nd/YAG laser<sup>5</sup> at 354.7 nm. The transient decayed exponentially (over at least three half-lives) with a lifetime ( $\tau$ ) independent of monitoring wavelength but markedly temperature- and solvent-dependent. Lifetimes measured in argon-purged or CO-saturated solutions were the same within experimental error. The deuteriated complex  $(OC)_5W=C(OCD_3)Ph$  behaved analogously (in  $CDCl_3$  solvent) but the transient decayed more slowly, with  $\tau = 9.1 \mu s$ , at 20 °C, compared to 7.5  $\mu s$  for the undeuteriated complex in the same solvent. Representative lifetime data are summarized in Table 1.

With these transient absorption and dynamics data as a guide, Raman studies of (**1**) were initiated at the S.E.R.C. Central Laser Facility, Rutherford Appleton Laboratory. The Raman spectra were excited by either a continuous (C.W.) Ar<sup>+</sup> laser or an excimer-pumped, pulsed dye laser (Lambda Physik, FL 2002) and detected by an intensified diode array multichannel analyser (EG & G, model 1420) coupled to a triple spectrometer (Spex Triplemate, with a 1200 groove/mm grating). For both C.W. and pulsed laser experiments, argon-purged solutions of complex were flowed through quartz capillaries to minimise sample decomposition.

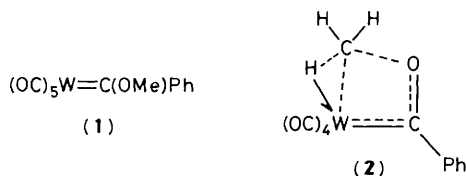
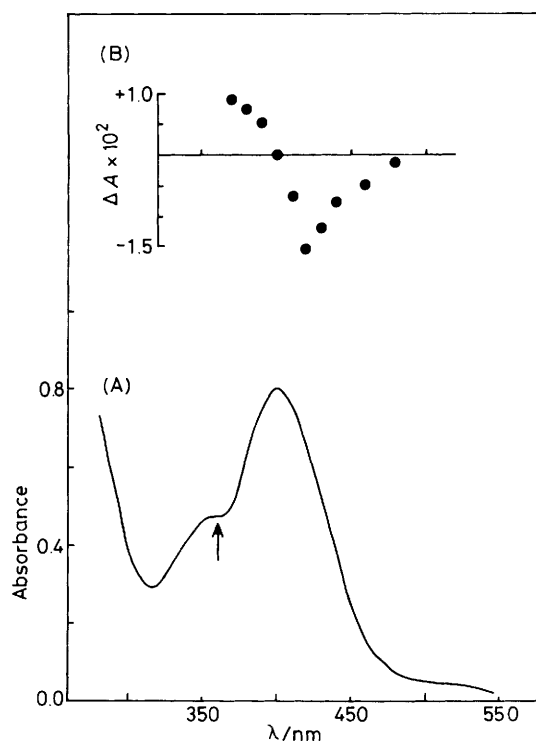
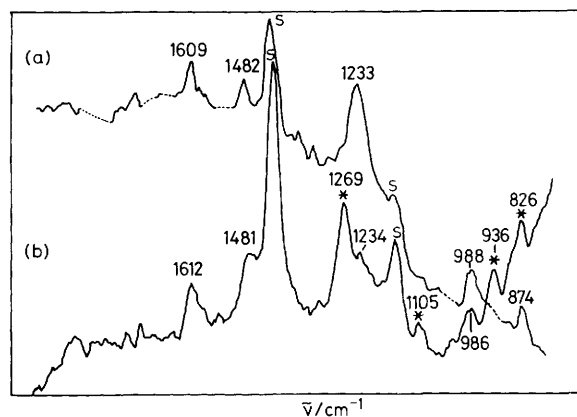


Figure 2 shows examples of the resonance Raman spectra recorded. The C.W. excited spectrum (upper trace) was obtained using the Ar<sup>+</sup> laser at 363.8 nm with the beam defocussed to ensure excitation of ground state Raman spectra only. The bands are due to vibrational modes of the carbene moiety of (**1**) since at this excitation wavelength the resonance enhancement arises from a tungsten  $\rightarrow$  carbene C.T. transition.

The spectrum obtained using the pulsed dye-laser source (Figure 2b) at an excitation wavelength of 360 nm, close to the transient absorption maximum, shows several new features in addition to residual ground state scattering. The new bands are attributable to a transient populated by the laser pulse, the trailing edge of which then probes the resonance Raman spectrum of the species. Time-resolved studies<sup>6</sup> using separate lasers to populate and probe confirm that this is the same



**Figure 1.** (A): Ground electronic state spectrum of  $(OC)_5W=C(OMe)Ph$  in  $CH_2Cl_2$  solution ( $10^{-3}$  mol  $dm^{-3}$ ; 1 cm pathlength). Arrow indicates excitation wavelengths used for resonance Raman spectra. (B): Transient absorbance difference ( $\Delta A$ ) spectrum, (same  $\lambda$  scale as in A) following Q-switched laser photolysis of same solution as in (A), at 354.7 nm (frequency-tripled output from Quanta-Ray DCR-2 Nd/YAG laser); laser pulse energy and duration: 15 mJ, 5–6 ns.

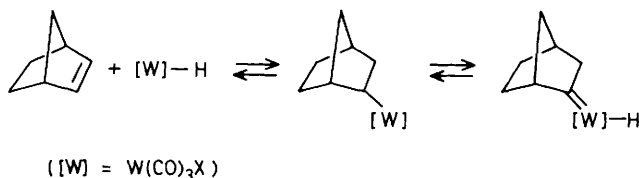


**Figure 2.** Resonance Raman spectra of the Fischer complex in  $\text{CH}_2\text{Cl}_2$ . ( $10^{-3}$  mol  $\text{dm}^{-3}$ ). (a): Ground electronic state spectrum excited at 363.8 nm ( $\text{Ar}^+$  laser, unfocussed beam, 50 mW power at sample). Regions -- indicate positions of spurious background lines in laser source. (b): Transient spectrum excited at 360 nm, using Lambda-Physik FL 2002 excimer-pumped dye laser; pulse duration: 10 ns; energy at sample: 3 mJ. \* denotes features assigned to transient; s denotes solvent Raman scattering. Note: Because of the different laser wavelengths used to excite the Raman spectra, the wavenumber scales in (a) and (b) are not identical. The spectra are displayed together for convenience of comparison.

transient as created in the earlier dynamics studies. Some of the vibrational modes (*vide infra*) of the transient, at 1269, 936, and 826  $\text{cm}^{-1}$ , occur with the same relative intensities as corresponding ground-state features at 1233, 988, and 874  $\text{cm}^{-1}$ , suggesting that they are resonantly enhanced *via* a similar type of electronic transition. The intense transient absorption band at 360 nm (Figure 1) is therefore also assigned as a  $\text{W} \rightarrow$  carbene C.T. transition. The other important feature of the transient Raman spectrum occurs at 1105  $\text{cm}^{-1}$ ; this band has no counterpart in the ground electronic state spectrum but 'grows in' as the focus of the excitation laser beam is increased. Significantly, a similar feature appears in the transient spectrum of the deuteriated ( $\text{OCD}_3$ ) complex, but appreciably shifted to higher frequency, 1181  $\text{cm}^{-1}$ . In contrast, all the other features in this spectrum are shifted by less than 10  $\text{cm}^{-1}$  compared to those of the undeuteriated transient.

Ligand-field (L.F.) ( $^1A_1 \rightarrow ^1B_2$ ) and  $\text{W} \rightarrow$  carbene C.T. ( $^1A_1 \rightarrow ^1A_2$ ) transitions contribute to the absorption intensity in the wavelength region of the laser irradiation and Raman studies just described. Both L.F. ( $^1B_2$ ) and C.T. ( $^1A_2$ ) states will thus be appreciably populated, with the latter, inactive state undergoing fast, non-radiative decay to the ground state. While CO elimination is known<sup>4</sup> to take place from the L.F. state, our results strongly imply that the transient absorption spectrum (Figure 1) is not that of the co-ordinatively unsaturated, 16-electron photofragment,  $(\text{OC})_4\text{W}=\text{C}(\text{OMe})\text{Ph}$ . The fact that CO does not appreciably influence the transient lifetime (Table 1) indicates that access to the co-ordinate site is impeded. On the basis of the kinetic data and the resonance Raman spectra we suggest that this could result from an interaction between the methyl group and the tungsten centre as envisaged in structure (2).

Such a three-centre, 'agostic'<sup>7</sup> interaction has already been invoked<sup>8</sup> to explain the slow back-reaction with CO of the unsaturated primary product,  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{Et}$ , produced by photolysis of the complex  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Et}$ . In the present work, support for the proposed structure (2) comes from the direction of the frequency shifts noted earlier in three of the vibrational modes of the carbene ligand and also the



**Scheme 1**

**Table 1.** Lifetimes<sup>a</sup> of photogenerated transients in  $(\text{OC})_5\text{W}=\text{C}(\text{OMe})\text{Ph}$  in different solvents.

$\tau/\mu\text{s}^b$	Solvent
$11.1 \pm 0.2;^c$ $10.9 \pm 0.2^d$	$\text{CH}_2\text{Cl}_2$
$10.2 \pm 0.1;^c$ $10.3 \pm 0.2^d$	Benzene
$2.9 \pm 0.2;^c$ $3.1 \pm 0.2^d$	Hexane
$4.6 \pm 0.3^c$	Cyclohexane

<sup>a</sup> Measurements at 20.0 °C for *ca.*  $10^{-3}$  mol  $\text{dm}^{-3}$  solutions. <sup>b</sup> Errors are standard derivations. <sup>c</sup> Argon-saturated solutions. <sup>d</sup> CO-saturated solutions.

shift upon deuteration of the feature at 1105  $\text{cm}^{-1}$ , unique to the transient spectrum. The carbene ligand modes at 936  $\text{cm}^{-1}$  (ground state, 982  $\text{cm}^{-1}$ ) and 826  $\text{cm}^{-1}$  (ground state, 874  $\text{cm}^{-1}$ ), assigned<sup>9</sup> respectively to  $\nu(\text{O}-\text{CH}_3)$  and  $\nu(\text{C}-\text{Ph})$  modes are consistent with the weaker bonding in the transient which would be occasioned by the rearrangement suggested in (2), while the band at 1269  $\text{cm}^{-1}$  (ground state, 1233  $\text{cm}^{-1}$ ), assigned<sup>9</sup> to a  $\nu(\text{C}-\text{OCH}_3)$  mode, points to a stronger ( $\text{C}-\text{OCH}_3$ ) bond, compared to the ground state.

As already mentioned, the band at 1105  $\text{cm}^{-1}$  occurs only in the pulsed laser-excited resonance Raman spectrum. This implies that it must be assigned to a vibrational mode in the chromophoric (*i.e.*  $\text{W} \rightarrow$  carbene) part of the transient species. The large frequency shift upon deuteration and the virtual absence of such shifts in any of the other modes suggests that it is likely to be associated largely with the  $\text{CH}_3$  group. However the direction of the shift, to higher rather than to lower frequencies, shows that it cannot be attributable to a 'normal' vibrational mode of  $\text{CH}_3$ . We suggest instead that it is likely due to an unusual deformation of  $\text{CH}_3$  such as could arise from the agostic interaction shown in (2).

The type of interaction proposed in (2) is not new,<sup>7</sup> but the resonance Raman evidence adduced for it in the present work is novel. Some recent<sup>10</sup> nanosecond laser flash photolysis and transient u.v.-visible absorbance studies of the  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Et}$  complex mentioned earlier indicate that the previously suggested<sup>8</sup> rearrangement of the  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{Et}$  photoproduct to an intermediate involving agostic interaction of the  $\beta$ -hydrogen of the Et group with the W centre occurs on a microsecond time-scale. However in the present work, the fact that the resonantly enhanced Raman scattering of the transient occurs from the *same* laser pulse which populates it, shows that the rearrangement leading to (2) must occur within the laser pulse duration, *i.e.* 10 ns or less, a time-scale three orders of magnitude faster than in the above study.

The present results also help to explain some very interesting differences between  $(\text{OC})_5\text{W}=\text{CPh}_2$  and (1) as catalysts for the ring opening polymerization of various norbornenes.<sup>11</sup> One might have expected an identical propagating species, namely  $(\text{OC})_4\text{W}=\text{CHPol}$  (Pol = polymer chain) from these two initiators, and therefore identical polymer. However, the

former gave high *cis*-polymer (92% *cis* double bonds at 45 °C) with intermediate tacticity, whereas the latter gave polymer of intermediate *cis*-content but with very high tacticity, even at 80 °C. These results led us to conclude that the propagating species from the Fischer metallocarbene is of the type:  $(OC)_3XW=CHPol$ , and we now suspect that the permanent ligand, X, is derived in the manner detected here from the initial carbene ligand,  $Ph(MeO)C=$ , which does not therefore initiate the polymerization, as usually suggested.<sup>12</sup> We now suspect that a  $[W]-H$  species ensuing from the agostic interaction leads to the initiating carbene complex *via* a norbornyl derivative (Scheme 1). In complete accord with these ideas, irradiation by a laser pulse at 354.7 nm, or by continuous irradiation, of a  $CH_2Cl_2$  solution of (1) with excess of norbornene markedly enhanced its effectiveness for metathesis polymerization.

The present work has therefore provided some demonstration of the value of resonance Raman spectroscopy as a probe of catalytic transients in solution. We are now carrying out two-laser, time-resolved studies on metal carbenes, including investigations at different probe wavelengths, in order to unravel further the dynamics and to investigate more fully the nature of the transitions giving rise to resonance enhancement of the Raman scattering.

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## References

- 1 S. P. Church, F. W. Grevels, H. Hermann, and K. Schaffner, *J. Chem. Soc., Chem. Commun.*, 1985, 30; B. D. Moore, M. Poliakoff, M. B. Simpson, and J. J. Turner, *J. Phys. Chem.*, 1985, **89**, 850, and references therein.
- 2 P. A. Mabrouk and M. S. Wrighton, *Inorg. Chem.*, 1986, **25**, 526, and references therein.
- 3 J. J. McGarvey, S. E. J. Bell, and J. N. Bechara, *Inorg. Chem.*, 1986, **25**, in the press.
- 4 H. C. Foley, L. M. Strubinger, T. S. Targos, and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1983, **105**, 3064; L. K. Fong and N. J. Cooper, *ibid.*, 1984, **106**, 2595.
- 5 S. E. J. Bell and J. J. McGarvey, *Chem. Phys. Lett.*, 1986, **124**, 336.
- 6 J. Bechara, S. E. J. Bell, and J. J. McGarvey, Annual Report to the Laser Facility Committee (Rutherford Appleton Laboratory, RAL-86-047), 1986, Section B1.3, pp. 7–14.
- 7 M. L. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395.
- 8 R. J. Kazlauskas and M. S. Wrighton, *J. Am. Chem. Soc.*, 1982, **104**, 6005.
- 9 E. O. Fischer, *Pure Appl. Chem.*, 1970, **24**, 407.
- 10 G. K. Yang, K. S. Peters, and V. Vaida, *J. Am. Chem. Soc.*, 1986, **108**, 2511.
- 11 H. H. Thoi, K. J. Ivin, and J. J. Rooney, *J. Mol. Catal.*, 1982, **15**, 245.
- 12 J. J. Rooney and A. Stewart, in 'Catalysis,' ed. C. Kemball (Specialist Periodical Report), The Chemical Society, London, vol. 1, p. 277.