

# Formation and Reactions of Tetracarbonyl Intermediates of the Fischer Carbene Complex $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}$ . A Laser Flash Photolysis Study Using Time-Resolved Infrared and UV/Vis Spectroscopy<sup>†</sup>

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The results of nanosecond laser flash photolysis (XeCl excimer irradiation at 308 nm) of the Fischer carbene complex  $[(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}]$  (**C<sub>Z</sub>**) in di-*n*-butyl ether and *n*-hexane are reported. Spectrokinetical detection of the intermediates was based on transient absorptions simultaneously recorded in the UV/vis and the IR spectral regions. The primary photoproducts are the unstable isomer **C<sub>E</sub>** produced with a quantum yield of about 30% and a tetracarbonyl complex **I–S**, probably of structure  $[(\text{CO})_4(\text{S})\text{W}=\text{C}(\text{OMe})\text{Ph}]$ , where S is a solvent molecule. The quantum yield of CO photoelimination was estimated as 1.7%. The **C<sub>E</sub>** isomer was found to return to the stable **C<sub>Z</sub>** isomer within a few microseconds, confirming previous results of McGarvey and co-workers. The tetracarbonyl species reacts with cosolutes present in the solution such as N<sub>2</sub>, H<sub>2</sub>O, acetonitrile, and methyl *trans*-crotonate to form secondary complexes of *cis*-tetracarbonyl complex structure  $[(\text{CO})_4(\text{L})\text{W}=\text{C}(\text{OMe})\text{Ph}]$  (**I–L**). The tetracarbonyl complexes react readily with CO. For **I–N<sub>2</sub>** in *n*-hexane the rate constant is  $3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The rate constants of the corresponding reactions with acetonitrile (MeCN) and the olefin are larger by a factor of 2. In the presence of CO the complexes **I–MeCN** and **I–olefin** revert to **C<sub>Z</sub>** in a dissociative reaction mechanism. The rate constants for the elimination of MeCN or olefin are 5 and  $10^5 \text{ s}^{-1}$ , respectively. The **I–olefin** complex irreversibly decomposes with a rate constant of  $8 \times 10^3 \text{ s}^{-1}$ .

## Introduction

While thermal reactions of transition-metal carbene complexes are widely employed in synthetic chemistry,<sup>1</sup> the synthetic potential and, in particular, the mechanisms of their photochemical reactions are much less explored. Only recently<sup>2</sup> McGuire and Hegedus introduced photochemical reactions of *chromium* carbene complexes into organic synthesis. Photolysis of  $[(\text{CO})_5\text{Cr}=\text{C}(\text{XR})\text{R}']$  was proposed<sup>3</sup> to proceed by a thermoreversible intramolecular coupling of a CO and the carbene ligand to form chromium ketene complexes, which are then trapped by, for example, imines, olefins, aldehydes and ketones, or alcohols to afford  $\beta$ -lactams, cyclobutanones,  $\beta$ -lactones, and amino acid esters, respectively.<sup>4</sup>

<sup>†</sup> Dedicated to Professor Jürgen Felsche on the occasion of his 60th birthday.

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(1) See for example: (a) Dötz, K. H. In *Transition Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, 1983; p 191. (b) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Aumann, R. *Angew. Chem.* **1988**, *100*, 1512; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1456. (d) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, J. D., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, p 1065. (e) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 12, p 469.

(2) McGuire M. A.; Hegedus L. S. *J. Am. Chem. Soc.* **1982**, *104*, 5538.

(3) (a) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418. (b) Merlic, C. A.; Xu, D.; Gladstone, B. G. *J. Org. Chem.* **1993**, *58*, 538.

In contrast, the primary reaction step in the photochemical reactions of *tungsten* carbene complexes  $[(\text{CO})_5\text{W}=\text{C}(\text{XR})\text{R}']$  seems to be the photoinduced loss of a CO ligand.<sup>5,6</sup> Subsequent addition of nucleophiles to the resulting coordinatively unsaturated species affords substitution products *cis*- $[(\text{CO})_4(\text{L})\text{W}=\text{C}(\text{XR})\text{R}']$  (L = PR<sub>3</sub>,<sup>7</sup> MeCN,<sup>8</sup> THF,<sup>8</sup> or alkynes<sup>8</sup>). The quantum yield of CO loss from  $[(\text{CO})_5\text{W}=\text{C}(\text{XR})\text{R}']$  is fairly low (approximately 1% at 366 and 313 nm) and drops to less than  $10^{-4}$  at 436 nm.<sup>8,9</sup> This has been explained by the inactivity in photodissociation of the long-wavelength

(4) For recent reviews see: (a) Hegedus L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 12, p 549. (b) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105.

(5) See for example: (a) Casey, C. P.; Vollendorf, N. W.; Haller, K. *J. Am. Chem. Soc.* **1984**, *106*, 3754. (b) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908. (c) Fong, L. K.; Cooper, J. N. *J. Am. Chem. Soc.* **1984**, *106*, 2595. (d) Toledano, C. A.; Rudler, H.; Daran, J.-C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 574. (e) Nandi, M.; Sathe, K. M.; Sarkar, A. *J. Chem. Soc., Chem. Commun.* **1992**, 793. (f) Choi, Y. H.; Rhee, K. S.; Kim, K. S.; Shin, G. C.; Shin, S. C. *Tetrahedron Lett.* **1995**, *36*, 1871.

(6) The photolysis of  $[(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{R}']$  in the presence of *cis*-RN=NR (R = C<sub>6</sub>H<sub>4</sub>X-*p*) proceeds by a different pathway. The proposed mechanism involves initial addition of the azo compound to the carbene carbon to give an adduct that rapidly rearranges to form an isolable zwitterion  $(\text{CO})_5\text{W}^+[\text{NR}-\text{NR}^+=\text{C}(\text{OMe})\text{R}']$ . Photolysis of the zwitterion finally affords diaziridines and imino ethers. See: Maxey, C. T.; Sleiman, H. F.; Massey, S. T.; McElwee-White, L. *J. Am. Chem. Soc.* **1992**, *114*, 5153, and literature cited therein.

(7) Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657.

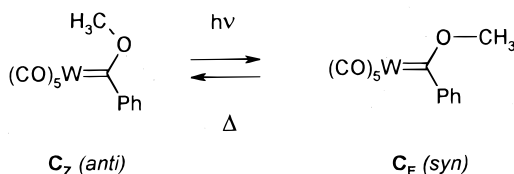
(8) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

metal-to-ligand charge transfer (MLCT) transition and by the only small activity of the ligand-field (LF) excitation due to its rapid radiationless decay to the lower MLCT state. Such small quantum yields may be a major drawback that can limit possible synthetic applications.

Many important thermal reactions of pentacarbonyl carbene complexes such as the Dötz reaction,<sup>1,10</sup> the transfer of the carbene ligand of heteroatom-stabilized carbene complexes to acceptor-substituted olefins<sup>1,11</sup> or dienes,<sup>12</sup> and the formation of carbo- and heterocycles from carbene complexes and enynes<sup>13</sup> are initiated by loss of a CO ligand. Since in these reactions CO dissociation is rate-limiting, the succeeding product-developing steps are not accessible to conventional kinetic investigations. Therefore, the photoinduced access to such CO dissociation products should open up the possibility of detailed studies of these product-developing reaction steps using kinetic laser flash photolysis methods.

Transients generated by photolysis of  $[(\text{CO})_5\text{W}=\text{C}(\text{XR})\text{R}']$  have already been investigated spectroscopically by the groups of McGarvey<sup>14–16</sup> and Stufkens.<sup>17</sup> At room temperature, photolysis of  $[(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{-Ph}]$  in solution yielded a species with a lifetime of several microseconds. The transient was initially assigned a tetracarbonyl carbene structure.<sup>14,15</sup> It was suggested that the vacant coordination site of the intermediate is blocked by an agostic interaction with a C–H bond of the methoxy substituent.

On the basis of the results of matrix isolation studies with  $[(\text{CO})_5[\text{W,Cr}]=\text{C}(\text{OCH}_3)\text{Ph}]$  the primary photoreaction was assigned to an anti/syn isomerization by Servaas et al.<sup>17</sup>



An equilibrium between anti and syn conformers in solution had already been reported before by Kreiter and Fischer<sup>18</sup> on the basis of NMR spectroscopic studies.

(9) Pourreau, D. B.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1985**, *24*, 249.

(10) Dötz, K. H. *Angew. Chem.* **1975**, *87*, 672; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644.

(11) (a) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 1273. (b) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356. (c) Cooke, M. D.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *56*, 279. (d) Wienand, A.; Reissig, H.-U. *Organometallics* **1990**, *9*, 3133, and literature cited therein.

(12) (a) Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653. (b) Wienand, A.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2315. (c) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.*, **1991**, *113*, 8916. (d) Hoffmann, M.; Buchert, M.; Reissig, H.-U. *Chem. Eur. J.* **1999**, *5*, 876, and references therein.

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

(15) Bell, S. E. J.; Gordon, K. C.; McGarvey, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 3107.

(16) Rooney, A. D.; McGarvey, J. J.; Gordon, K. C. *Organometallics* **1995**, *14*, 107.

(17) Servaas, P. C.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* **1990**, *390*, 61.

Continued irradiation of the matrix led to CO loss and to a tetracarbonyl carbene complex with a syn conformation of the carbene ligand. Further irradiation of the tungsten complex gave a species "X", which was tentatively assigned by Stufkens and co-workers to the agostic tetracarbonyl species previously invoked by Bechara et al.<sup>14</sup> Recently, several  $[(\text{CO})_5\text{W}=\text{C}(\text{OR})\text{R}']$  complexes with  $(\text{R}, \text{R}') = (\text{Me}, \text{Me})$ ,  $(\text{Me}, p\text{-tolyl})$ , and  $(\text{Et}, \text{Ph})$  were studied in a variety of solvents.<sup>15</sup> The formation of the syn conformer in its ground state was observed during the laser flash of several nanoseconds. The subsequent thermal regeneration of the anti conformer was found to occur within a few microseconds to several thousands of microseconds depending on the substituents, solvent, and temperature.

We now report results obtained from photolysis of  $[(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{Ph}]$  using a newly set up laser flash spectrometer allowing for simultaneous time-resolved transient detection in the UV/vis and in the 1700–2200  $\text{cm}^{-1}$  infrared region, from which the most significant information on the CO coordination can be obtained.

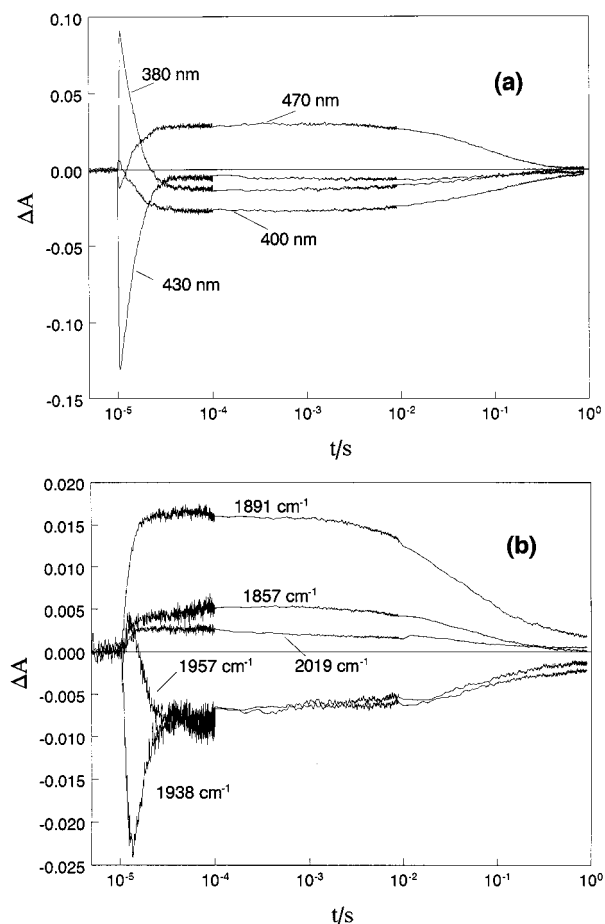
## Results

As a general demonstration of the spectrokinetical features observed on laser flash photolysis of complex **C<sub>Z</sub>** and of the possibility of parallel recording of transient UV/vis and IR signals, characteristic kinetic traces at different wavelengths in di-*n*-butyl ether are depicted in Figure 1. Measurements with 100  $\mu\text{s}$ , 10 ms, and 1 s full scale have been combined to yield signal traces spanning 5 orders of magnitude in time. In the UV/vis spectral range the main changes are observed in the region corresponding to the MLCT band of complex **C<sub>Z</sub>**. Therefore, positive as well as negative  $\Delta A$  steps can be observed. The rise time of these signals is on the order of 20 ns and corresponds to the width of the laser pulse. The subsequent decay of the signals indicates two different transformations: with time constants of about 10  $\mu\text{s}$  and about 0.1 s. After several seconds the signals have decayed essentially to zero, establishing the overall reversibility of the photoinduced processes.

In the  $\tilde{\nu}(\text{CO})$  range of the IR spectrum (cf. Figure 2), too, positive and negative initial signal steps are observed (Figure 1b). The fastest initial signal rise is determined by the time constant of about 1  $\mu\text{s}$  of the detection system (cf. signals at 1938 and 1957  $\text{cm}^{-1}$ ), but there are also frequencies where the rise of the signal is clearly slower than the instrumental time resolution. The rise of the signal at 1891  $\text{cm}^{-1}$  agrees well with the first time-resolved kinetic step in the UV/vis signals showing a time constant of about 10  $\mu\text{s}$ . As with the UV/vis measurements, the slow final decay of the transients is also borne out in the IR. Thus, the signals in Figures 1a and 1b clearly demonstrate that the transient kinetics observed in both spectral regions monitor the same chemical intermediates.

The spectral characteristics of the transients in di-*n*-butyl ether and *n*-hexane are similar. The results of the experiments differ mainly in the kinetics of the intermolecular reactions with CO and other solutes added as reactants. In *n*-hexane interaction of the

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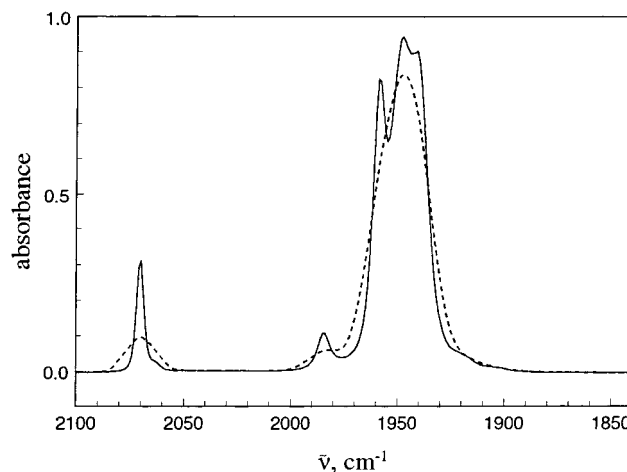


**Figure 1.** Transient absorption signals obtained in a 0.5 mm cuvette upon laser photolysis of **C<sub>Z</sub>** ( $2 \times 10^{-3}$  M) in  $N_2$ -saturated di-*n*-butyl ether at selected wavelengths in the UV/vis (a) and IR (b). Each signal trace spanning 5 orders of magnitude in time was amalgamated from three individual signals measured separately in three different time domains. To avoid distortions of the initial stage of the signal due to the log scale, the zero time of the signal was shifted to  $t = 10 \mu s$ .

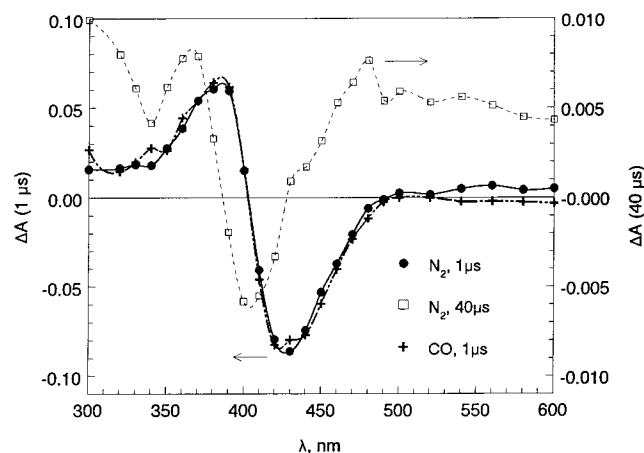
solvent with coordinatively unsaturated intermediates is weaker, and thus reactions of these intermediates with added solutes are faster than in di-*n*-butyl ether. Therefore, we will focus on the experiments in *n*-hexane.

According to the general spectrokinetical picture in di-*n*-butyl ether (Figure 1), the primary intermediates revert to the starting compound and/or transform to secondary intermediates within less than  $20 \mu s$ . Thus, recording transient spectra 1 and  $40 \mu s$  after the laser pulse should provide the spectral characteristics of the primary and secondary intermediates, respectively. Corresponding transient spectra are shown in Figures 3 and 4.

At  $1 \mu s$  delay, the striking feature of both UV/vis and IR spectra is a derivative-type absorption band centered with its inflection point at the wavelength of the main absorption maximum of the starting complex **C<sub>Z</sub>**, i.e., at 402 nm in the UV and at  $1948 \text{ cm}^{-1}$  in the IR (Figure 2). Such spectral features indicate a transformation of the starting complex into a transient with an absorption spectrum only slightly shifted with respect to the former one. In both the UV/vis and the IR region the phase (sign sequence) of the  $\Delta A$  curve signifies a shift of the transient bands to higher frequencies.



**Figure 2.** IR spectra of **C<sub>Z</sub>** in *n*-hexane ( $c = 2 \times 10^{-3}$  M,  $d = 0.05$  cm). Solid line: measured on a FTIR spectrometer with  $2 \text{ cm}^{-1}$  spectral resolution. Dashed line: spectrum calculated from the FTIR spectrum by simulating a triangular slit function of  $14 \text{ cm}^{-1}$  halfwidth as determined by the slit width setting of the IR monochromator used in the time-resolved measurements.



**Figure 3.** UV/vis transient absorption spectra obtained on laser photolysis of **C<sub>Z</sub>** ( $2 \times 10^{-3}$  M) in *n*-hexane. ●, + (left  $\Delta A$  axis) at a delay time of  $1 \mu s$  after the laser pulse: (●) solution saturated with  $N_2$ , (+) solution saturated with CO. □ (right  $\Delta A$  axis) at a delay time of  $40 \mu s$  in  $N_2$ -saturated solution. (In a CO-saturated solution all transient absorptions have completely decayed by  $40 \mu s$ .)

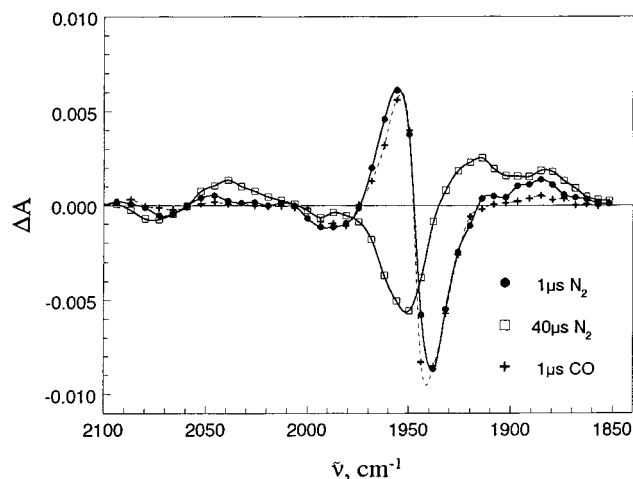
Apart from the dominant derivative-type characteristics at  $1948 \text{ cm}^{-1}$  the  $1 \mu s$  transient spectrum exhibits several other noteworthy features in the IR:

(i) There are positive  $\Delta A$  changes, i.e., new absorptions around  $2045 \text{ cm}^{-1}$  and in the region between  $1850$  and  $1910 \text{ cm}^{-1}$ , all of which are clearly outside the region of IR lines of the precursor complex **C<sub>Z</sub>** (cf. Figure 2).

(ii) Around  $2070 \text{ cm}^{-1}$ , i.e., at the position of the weak  $A_1^{(1)}$  absorption of **C<sub>Z</sub>**, the transient spectrum seems to indicate a superposition of a derivative-type and a bleaching feature. However, due to the weakness of this signal, details cannot be assessed with certainty.

From these spectral features we conclude that at least two early transients are formed in the photolysis of **C<sub>Z</sub>**. One whose UV/vis and IR spectra are only slightly shifted with respect to **C<sub>Z</sub>** gives rise to the derivative-type band. This transient is assigned to an isomer of





**Figure 4.** IR transient spectra obtained on laser photolysis of  $\mathbf{C_Z}$  ( $2 \times 10^{-3}$  M) in *n*-hexane. ●, + at 1  $\mu$ s delay time, (●) with  $\text{N}_2$ -saturated solution, (+) with CO-saturated solution. □ at 40  $\mu$ s delay time with  $\text{N}_2$ -saturated solution.

complex  $\mathbf{C_Z}$ . The other one (denoted  $\mathbf{I-S}$  for reasons to be given below) has IR bands clearly distinct from those of  $\mathbf{C_Z}$ . The IR band positions of  $\mathbf{I-S}$  are listed in Table 1.

After 40  $\mu$ s the spectral intensity in the UV/vis has strongly decreased. Instead of the derivative-type band with the inflection point at the absorption maximum of  $\mathbf{C_Z}$ , we now see a bleaching at this position and positive absorption changes to the right and left of it. This implies that the new transient has an absorption band with a maximum at the same position as  $\mathbf{C_Z}$ , although with a somewhat lower molar extinction coefficient. The absorption is broader and extends to much longer wavelengths. The decrease in intensity most probably implies that a great fraction of the primary intermediates has reverted to the initial complex  $\mathbf{C_Z}$ .

In the IR the  $\Delta A$  spectrum after 40  $\mu$ s clearly indicates bleaching at the positions of the main bands of  $\mathbf{C_Z}$  (2070, 1950  $\text{cm}^{-1}$ ) and positive absorption changes due to new absorptions at the low-frequency sides of these bands.

It seems likely that the long-lived transient is formed in an intermolecular process between the primary transient and the solvent or some other solute. Since in all experiments described so far  $\text{N}_2$  was the only other solute, its possible involvement was tested by substituting argon for nitrogen as protecting gas. This did not cause any change of the transient spectra at delay times as short as 1  $\mu$ s, but it suppressed the formation of the long-lived transient.

In Ar-saturated solutions (cf. Figure 5) after 40  $\mu$ s the spectrum outside the derivative-type band was the same as that of Ar- or  $\text{N}_2$ -saturated solutions at 1  $\mu$ s (cf. Figure 4 for  $\text{N}_2$ ). When argon or nitrogen was saturated with water vapor, the resultant spectrum was unchanged at 1  $\mu$ s and was very similar to the spectrum obtained in solution saturated with dry  $\text{N}_2$ . However, at 40  $\mu$ s the spectral intensity of the  $\text{H}_2\text{O}$ -containing solutions (cf. Figure 5) was significantly enhanced in the region between 1970 and 1850  $\text{cm}^{-1}$ . To distinguish between the long-lived species in solutions with dry nitrogen and with  $\text{H}_2\text{O}$ -saturated gases we will refer to them by the short-hand notations  $\mathbf{I-N}_2$  and  $\mathbf{I-H}_2\text{O}$ ,

respectively. For the frequencies of the IR lines assigned to  $\mathbf{I-N}_2$  and  $\mathbf{I-H}_2\text{O}$  see Table 1.

All observations are consistent with an assignment of the initial transient with the derivative-type  $\Delta A$  spectrum as the E isomer ( $\mathbf{C_E}$ ) of the pentacarbonyl-carbene complex  $\mathbf{C_Z}$ . According to matrix isolation experiments by Servaas et al.<sup>17</sup> in the IR the E isomer shows only very small ( $1\text{--}3\text{ cm}^{-1}$ ) high-frequency shifts relative to the Z isomer. The  $\Delta A$  spectrum deduced from such a shift is perfectly in line with the derivative-type band shape in the initially observed transient IR absorption spectrum. Our pertinent experiments afford the first time-resolved *infrared* detection of the photo-induced  $\mathbf{C_Z} \rightarrow \mathbf{C_E}$  process at room temperature. Some flash spectroscopic investigations with UV/vis transient absorption measurements of complex  $\mathbf{C_Z}$  and related compounds have already been reported by Rooney et al.<sup>16,19</sup> Our UV/vis transient spectrum at 1  $\mu$ s delay (cf. Figure 3) is consistent with their spectra, although their observations were restricted to a spectral range between 370 and 470 nm. According to the latter authors, the decay time of  $\mathbf{C_E}$  at 20  $^\circ\text{C}$  is 2.9  $\mu$ s in *n*-hexane and 25  $\mu$ s in acetonitrile. Our experiments at somewhat higher temperature of approximately 25  $^\circ\text{C}$  yielded slightly shorter values of 1.9  $\mu$ s for *n*-hexane and 14.8  $\mu$ s for acetonitrile. These deviations seem reasonable in view of the activation energy assessed for the  $\mathbf{E} \rightarrow \mathbf{Z}$  process. The decay times exhibit the same solvent dependence as observed by McGarvey's group.

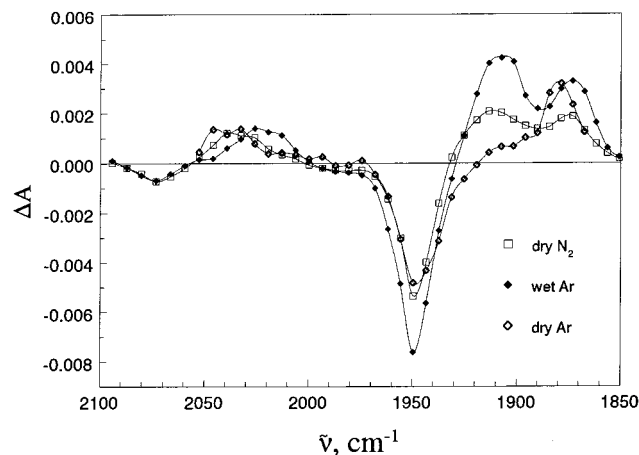
The intermediates  $\mathbf{I-S}$ ,  $\mathbf{I-N}_2$ , and  $\mathbf{I-H}_2\text{O}$  exhibit very similar IR bands, four each, shifted to the low-frequency side of the  $A_1^{(1)}$  and E bands of  $\mathbf{C_Z}$ . The absorptions of  $\mathbf{I-N}_2$  and  $\mathbf{I-H}_2\text{O}$  are at somewhat lower frequencies than those of  $\mathbf{I-S}$ . Thus the lines of the former two species are further away from those of the initial complex  $\mathbf{C_Z}$  and therefore less prone to compensating superposition by negative  $\Delta A$  contributions due to the bleaching of  $\mathbf{C_Z}$ . Thus the signals of  $\mathbf{I-N}_2$  and  $\mathbf{I-H}_2\text{O}$  appear stronger than those of  $\mathbf{I-S}$ . When looking for possible assignments of transients originating from a photoinduced reaction from a pentacarbonyl carbene complex, the possibility of CO loss leading to a tetracarbonyl complex is obvious. The IR transient spectra of  $\mathbf{I-L}$  ( $\text{L} = \text{solvent S, N}_2, \text{H}_2\text{O}$ ) can be readily assigned to *cis*-tetracarbonyl carbene complexes. For comparison, the IR band positions and symmetry assignments of two isolated and structurally well-characterized *cis*-tetracarbonyl carbene complexes *cis*-[(CO)<sub>4</sub>{X}W=C(OMe)-Ph] ( $\text{X} = \text{P}(n\text{-C}_4\text{H}_9)_3$ ,<sup>7</sup>  $\text{CH}_3\text{CN}$ <sup>8,20</sup>) have been included in Table 1. The acetonitrile complex *cis*-[CO]<sub>4</sub>(CH<sub>3</sub>CN)W=C(OMe)Ph] is formed when the pentacarbonyl carbene complex  $\mathbf{C_Z}$  is irradiated in acetonitrile. The formation of the acetonitrile adduct is accompanied by a UV/vis spectral change with an isosbestic point at 420 nm. The absorption maximum of the acetonitrile complex is bathochromically shifted with respect to the MLCT maximum of  $\mathbf{C_Z}$ .<sup>8,15</sup> Our  $\Delta A$  spectra of intermediates  $\mathbf{I-L}$  are in accord with such a spectral change. Thus both IR and UV/vis transient information support the assignment of  $\mathbf{I-L}$  as *cis*-tetracarbonyl carbene

(19) Rooney, A. D.; McGarvey, J. J.; Gordon, K. C.; McNicholl, R. A.; Schubert, U.; Hepp, W. *Organometallics* **1993**, *12*, 1277.

**Table 1.** Infrared Spectral Data for *cis*-Tetracarbonyl Complexes

	A <sub>1</sub> <sup>(1)</sup>	A <sub>1</sub> <sup>(2)</sup>	B <sub>1</sub>	B <sub>2</sub>	ref	solvent
<i>cis</i> -[(CO) <sub>4</sub> {P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> }W=C(OMe)Ph]	2018 m	1925 m, sh	1919 s	1890 vs	7	<i>n</i> -hexane
<i>cis</i> -[(CO) <sub>4</sub> (CH <sub>3</sub> CN)W=C(OMe)Ph]	2024 m	1940 s	1912 m	1880 m	8 <sup>a</sup>	<i>n</i> -hexane
I-S	2040	~1945 <sup>b</sup>	~1910 <sup>b</sup>	1880	this work <sup>c</sup>	<i>n</i> -hexane
I-N <sub>2</sub>	2040	~1940 <sup>b</sup>	1910 <sup>b</sup>	1875	this work <sup>c</sup>	<i>n</i> -hexane
I-H <sub>2</sub> O	2025	1938 <sup>b</sup>	1910 <sup>b</sup>	1875	this work <sup>c</sup>	<i>n</i> -hexane
I-MeCN	2020	1935 <sup>b</sup>	1910 <sup>b</sup>	1880	this work <sup>c</sup>	<i>n</i> -hexane
I-olefin <sup>d</sup>	2020	1935 <sup>b</sup>	1908 <sup>b</sup>	1863	this work <sup>c</sup>	<i>n</i> -hexane
<i>syn</i> -[(CO) <sub>4</sub> W=C(OMe)Ph] <sup>e</sup>	2040	1948		1876	17	CH <sub>4</sub> -matrix at 10 K

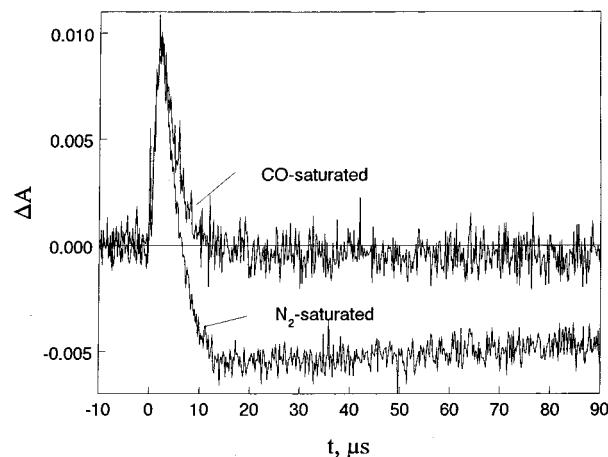
<sup>a</sup> Assignments of the original paper are corrected. <sup>b</sup> Determined from a superposition of the transient  $\Delta A$  spectrum with the spectrum of **C<sub>Z</sub>**. <sup>c</sup> From transient absorption measurements. <sup>d</sup> Methyl *trans*-crotonate. <sup>e</sup> From matrix isolation experiments.



**Figure 5.** IR transient spectra obtained on laser photolysis of **C<sub>Z</sub>** ( $2 \times 10^{-3}$  M) in *n*-hexane at a delay time of 40  $\mu$ s. Solutions saturated with N<sub>2</sub>, Ar, and "wet" Ar, respectively.

complex species. In I-S the solvent (S = *n*-hexane) occupies the sixth coordination site.

**Influence of CO.** To confirm the structural assignments of the transient intermediates, additional flash photolysis experiments in CO-saturated solutions were performed. Spectral traces recorded at 1  $\mu$ s delay time in *n*-hexane saturated with 1 bar of CO are shown in Figures 3 and 4. All spectral features assigned to transient **C<sub>E</sub>** in the UV/vis as well as in the IR are unaffected by the presence of CO, whereas those parts of the  $\Delta A$  spectra assigned to I-S are significantly weakened. Moreover, in the presence of CO intermediate I-N<sub>2</sub> is not formed. Examples of two kinetic traces in the absence and presence of CO are given in Figure 6. At 1956  $\text{cm}^{-1}$   $\Delta A$  of the derivative-type band due to **C<sub>E</sub>** is a maximum, whereas I-N<sub>2</sub> does not absorb. In solutions without added CO, the signal decays within



**Figure 6.** IR transient signals observed on laser photolysis of **C<sub>Z</sub>** ( $2 \times 10^{-3}$  M) in *n*-hexane at 1956  $\text{cm}^{-1}$  in N<sub>2</sub>- and CO-saturated solution, respectively.

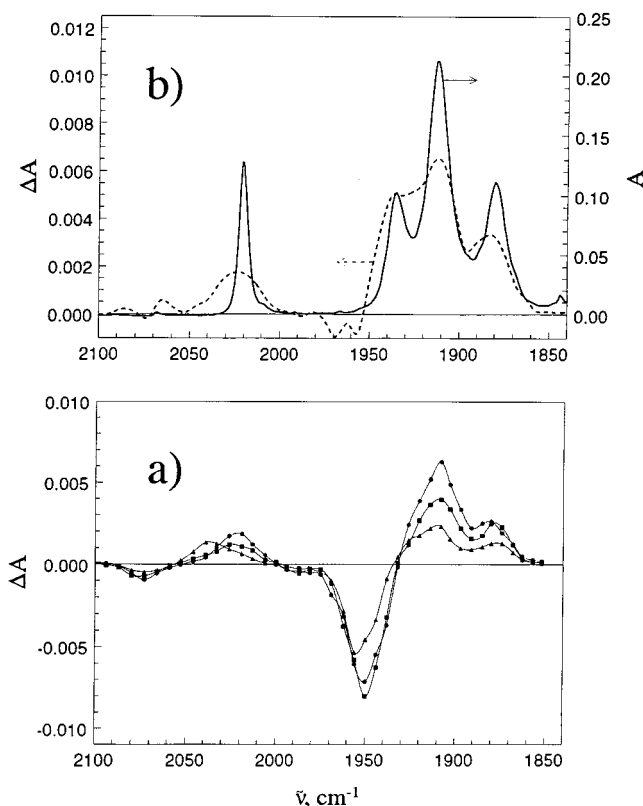
about 10  $\mu$ s and reaches a plateau of negative  $\Delta A$  corresponding to a partial transformation of **C<sub>Z</sub>** into transient I-N<sub>2</sub>. The initial amplitude of the signal and the decay time are independent of the presence or absence of CO. However, in the presence of CO, the decay only reverts to the zero level of  $\Delta A$  and no long-term bleaching occurs. Obviously, the formation of the tetracarbonyl complex I-N<sub>2</sub> is inhibited due to a rapid recombination of tetracarbonyl complex I-S with CO.

In N<sub>2</sub>-saturated solutions the intermediate I-N<sub>2</sub> formed from I-S finally also decays. The kinetics is second-order, indicating recombination of I-N<sub>2</sub> with photoeliminated CO in the solution. The rate constant  $k_{\text{I-N}_2\text{CO}}$  of this process was estimated as  $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>21</sup> This is in reasonable agreement with a value of  $4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  that we obtained from a pseudo-first-order analysis of kinetic experiments with various concentrations of excess CO.

**Reaction of *cis*-Tetracarbonyl Intermediates with Acetonitrile.** Since acetonitrile was known to yield a stable *cis*-tetracarbonyl carbene adduct,<sup>8,15</sup> the reaction of this nucleophile with the tetracarbonyl intermediate I-S or its successor I-N<sub>2</sub> was investi-

(20) We note here that the assignment of a band at 1790  $\text{cm}^{-1}$  to the B<sub>2</sub>-vibration of the complex *cis*-[(CO)<sub>4</sub>(CH<sub>3</sub>CN)W=C(OMe)Ph] in acetonitrile as given by Foley et al.<sup>8</sup> is incorrect. This band was reported to grow in when monitoring a series of IR spectra during the irradiation of **C<sub>Z</sub>** in acetonitrile. When we repeated this experiment in our laboratory, we found that the time dependence of this band was clearly different from that of the other bands assigned to *cis*-[(CO)<sub>4</sub>(CH<sub>3</sub>CN)W=C(OMe)Ph]. While the latter increased linearly at the beginning of the irradiation and passed through a maximum after some time, the rise of the 1790  $\text{cm}^{-1}$  band was preceded by an induction period and then increased monotonically. This is a clear indication that this band belongs to a secondary product. Actually, after long irradiation this band persists together with another sharp band at 1911  $\text{cm}^{-1}$ . The corresponding product, which no longer exhibits the NMR resonances of the carbene ligand, is the *fac*-W(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub> complex, as can be verified by comparing it with the product obtained by irradiation of W(CO)<sub>6</sub> in acetonitrile. The band positions of the *cis*-[(CO)<sub>4</sub>(CH<sub>3</sub>CN)W=C(OMe)Ph] complex in acetonitrile are 2018  $\text{cm}^{-1}$  (m), 1899  $\text{cm}^{-1}$  (s), 1838  $\text{cm}^{-1}$  (sh). These are practically the same as in ref 6: 2017  $\text{cm}^{-1}$  (m), 1900  $\text{cm}^{-1}$  (s), 1840  $\text{cm}^{-1}$  (sh). (Note that in the latter reference the last value is misprinted as 1804  $\text{cm}^{-1}$ .)

(21) The rate constant  $k_{\text{I-N}_2\text{CO}}$  and the rate constant obtained from the second-order analysis of the transient absorption signal ( $k_{\Delta A}$ ) are related by  $k_{\text{I-N}_2\text{CO}} = k_{\Delta A} \Delta \epsilon d$  where  $d = 0.05 \text{ cm}$  is the optical path length of the cuvette and  $\Delta \epsilon \equiv \epsilon_{\text{I-N}_2\text{CO}} - \epsilon_{\text{C}_Z}$  the difference of absorption coefficients of I-N<sub>2</sub> and **C<sub>Z</sub>**. To find the proper conversion factor from the observed  $\Delta A$  spectrum to the  $\Delta \epsilon$  spectrum, it was assumed that  $\epsilon_{\text{I-N}_2} (1948) \ll \epsilon_{\text{C}_Z} = 8600 \text{ M}^{-1} \text{ cm}^{-1}$ , which seems reasonable since most of the IR bands of I-N<sub>2</sub> appear well separated from the lines of **C<sub>Z</sub>** and 1948  $\text{cm}^{-1}$  is the position of the absorption maximum of **C<sub>Z</sub>**. Normalizing the  $\Delta A$  spectrum by the appropriate factor, it was found that at 1891  $\text{cm}^{-1}$ , where the second-order kinetics was evaluated, the absorption coefficient  $\Delta \epsilon$  adopts a value of 2315  $\text{M}^{-1} \text{ cm}^{-1}$ .

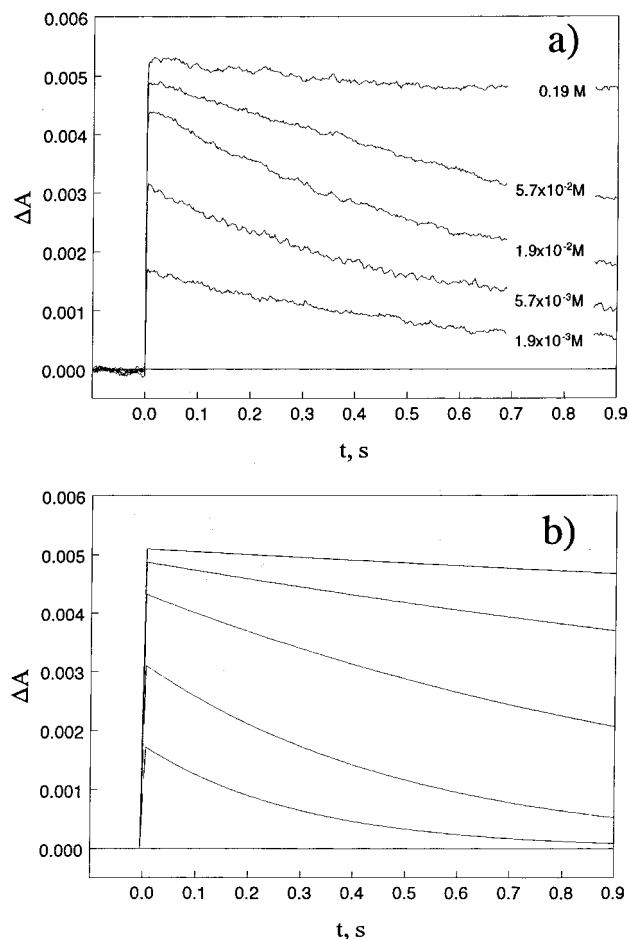


**Figure 7.** (a) Effect of acetonitrile ( $\triangle 5 \times 10^{-5} \text{ M}$ ,  $\blacksquare 9.5 \times 10^{-5} \text{ M}$ ,  $\bullet 1.9 \times 10^{-4} \text{ M}$ ) on IR transient spectra observed on laser photolysis of  $\text{C}_Z$  ( $2 \times 10^{-3} \text{ M}$ ) in  $\text{N}_2$ -saturated  $n$ -hexane at delay time of  $40 \mu\text{s}$ . (b) (---) IR spectrum of  $\text{I-MeCN}$  obtained by correcting the final transient  $\Delta A$  spectrum (symbols  $\bullet$  in a) for the  $\Delta A$  due to the depletion of  $\text{C}_Z$ . (—) FTIR spectrum of the photoproduct obtained on stationary illumination of  $\text{C}_Z$  at  $313 \text{ nm}$  in  $i$ -octane  $0.1 \text{ M}$  in  $\text{MeCN}$ .

gated. Pertinent transient experiments were carried out with increasing concentrations of acetonitrile in  $n$ -hexane.

The transient IR spectra at a delay time of  $40 \mu\text{s}$  for various concentrations of acetonitrile are displayed in Figure 7. There are two isosbestic regions at about  $2030$  and  $1930 \text{ cm}^{-1}$ . The appearing spectrum is assigned to a complex  $\text{I-MeCN}$ . In the region  $1925\text{--}2000 \text{ cm}^{-1}$  its spectrum overlaps with the bleaching of  $\text{C}_Z$ . Here the exact positions of the  $\text{I-MeCN}$  maxima were evaluated by adding to the observed  $\Delta A$  spectrum a spectrum of  $\text{C}_Z$  multiplied by a suitable factor. The factor was chosen in such a way that no negative absorption remained in the resultant spectrum. The positions of the four-band maxima of  $\text{I-MeCN}$  thus obtained are listed in Table 1. They agree well with those determined from the stationary IR spectrum of the *cis*-acetonitrile carbene tetracarbonyl complex.

Direct kinetic information on the association reaction of the *cis*-tetracarbonyl intermediate  $\text{I-N}_2$  with acetonitrile has been derived from kinetic traces at  $2046 \text{ cm}^{-1}$  (a band maximum of  $\text{I-N}_2$ ) and the corresponding maximum of  $\text{I-MeCN}$  at  $2019 \text{ cm}^{-1}$ . After the buildup of the  $\text{I-N}_2$  absorption within approximately  $10 \mu\text{s}$  (due to the  $\text{I-S} + \text{N}_2 \rightarrow \text{I-N}_2$  process) a decay at  $2046 \text{ cm}^{-1}$  and a further rise at  $2019 \text{ cm}^{-1}$  follow. Both have the same time constant. For  $[\text{MeCN}] = 1.9 \times 10^{-4} \text{ M}$  the pseudo-first-order rate constant was determined as  $7.6$



**Figure 8.** (a) Series of IR transient signals measured at  $1903 \text{ cm}^{-1}$  on photolysis of  $\text{C}_Z$  ( $2 \times 10^{-3} \text{ M}$ ) in  $n$ -hexane saturated with  $1 \text{ bar}$  of  $\text{CO}$  and containing various concentrations of acetonitrile. (b) Kinetic simulation. For details see text.

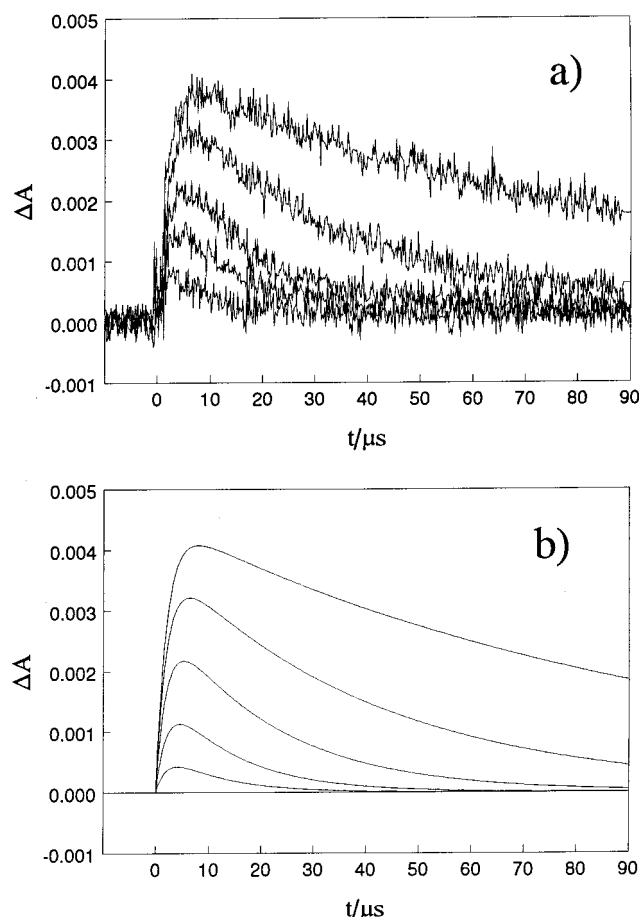
$\times 10^4 \text{ s}^{-1}$ , from which a second-order rate constant of  $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  is derived.

The acetonitrile concentrations employed for observing the conversion from  $\text{I-N}_2$  to  $\text{I-MeCN}$  were fairly low. At higher concentrations of acetonitrile, formation of  $\text{I-N}_2$  is prevented and  $\text{I-MeCN}$  is formed directly from  $\text{I-S}$ . However, the rate of this process is within the time resolution of our IR detection system. Nevertheless, kinetic information about the formation of  $\text{I-MeCN}$  from  $\text{I-S}$  and the reverse of this reaction could be obtained by means of competition experiments with  $\text{CO}$ . The IR band structure of the transient obtained with acetonitrile in  $\text{CO}$ -saturated solutions of  $\text{C}_Z$  was indistinguishable from that in  $\text{CO}$ -free solution, indicating the formation of the same product  $\text{I-MeCN}$  either from  $\text{I-N}_2$  or from its precursor  $\text{I-S}$ .

A representative set of curves at  $1903 \text{ cm}^{-1}$  for various concentrations of acetonitrile in  $\text{CO}$ -saturated solutions is shown in Figure 8a. The significant features are as follows:

- The maximum of the initial signal increases with acetonitrile concentration and approaches a saturation value at high acetonitrile concentrations.
- The decay time of the  $\text{I-MeCN}$  absorption, which varies between fractions of seconds to tens of seconds, increases also with increasing acetonitrile concentration.
- The rise time (not resolved in Figure 8) of all





**Figure 9.** (a) Series of IR transient signals measured at 1903  $\text{cm}^{-1}$  on photolysis of  $\text{C}_Z$  ( $2 \times 10^{-3}$  M) in *n*-hexane saturated with 1 bar of CO and containing various concentrations of methyl *trans*-crotonate. The olefin concentrations are (from below)  $6 \times 10^{-4}$ ,  $2 \times 10^{-3}$ ,  $6 \times 10^{-3}$ ,  $1.9 \times 10^{-2}$ ,  $1.9 \times 10^{-1}$  M. (b) Kinetic simulation. For details see text.

signals is within the time resolution of the IR detection system. The UV/vis channel could not be used to obtain further kinetic information. In this spectral region the short-time kinetics are dominated by the strong signals due to the  $\text{C}_E \rightarrow \text{C}_Z$  reversion process.

**Reaction of *cis*-Tetracarbonyl Intermediates with an Olefinic Reactant.** The analogous experiments have been performed with methyl *trans*-crotonate as an olefinic reactant. The IR spectral change is very similar to that shown for acetonitrile in Figure 7. The frequencies of the IR-band maxima are included in Table 1.

The competition experiment involving CO-saturated solutions and increasing concentrations of olefin yielded the signal traces shown in Figure 9a. In principle, the findings were analogous to those with acetonitrile. However remarkable quantitative differences were observed:

- (i) The decay time of the **I**–olefin adduct is 4–5 orders of magnitude shorter than with acetonitrile.
- (ii) As the olefin concentration increases, the lifetime of the adduct reaches a limiting value of 125  $\mu\text{s}$ .
- (iii) No recovery of  $\text{C}_Z$  occurs with high olefin concentrations, even in the solutions saturated with CO at 1 bar. This may be concluded from observations in the IR region around 1950  $\text{cm}^{-1}$ . Here, at the absorption

maximum of  $\text{C}_Z$ , the transient signals exhibit negative  $\Delta A$ , and a recovery of  $\text{C}_Z$  would be conveniently observed by a returning of the signal to zero (cf. for example Figure 1b).

In accord with these time-dependent observations, a permanent photoinduced loss of  $\text{C}_Z$  is detected when measuring stationary IR spectra after laser photolysis. In *n*-hexane ( $2 \times 10^{-3}$  M in  $\text{C}_Z$  and 0.2 M of methyl *trans*-crotonate) a bleaching of  $5 \times 10^{-5}$  M per laser pulse of 100  $\text{mJ cm}^{-2}$  results. From these data a quantum yield of 1.7% can be estimated for the photo-bleaching of  $\text{C}_Z$  by the olefin. From the IR spectra it can be shown that upon this photolysis the pentacarbonyl complex  $(\text{CO})_5\text{W}(\text{olefin})$  is formed.<sup>22</sup> The yield of this decomposition product amounts to about 20%. Other products containing the carbene moiety, in particular cyclopropanes, have not been detected.

## Discussion

Our observations can be accounted for by the processes represented in Scheme 1. Excitation of the Z isomer of the carbene complex ( $\text{C}_Z$ ) by laser light of 308 nm affords an upper ligand field excited state  $\text{C}_Z^*$  with three possible relaxation pathways: (i) radiationless decay back to the ground state most probably through the intermediacy of the lowest excited MLCT state; (ii) isomerization to form  $\text{C}_E$  in appreciable amounts; (iii) loss of CO in an excited ligand field state and formation of a pentacoordinated tetracarbonyl carbene complex  $(\text{CO})_4\text{W}(\text{cb})$  (**I**).

The coordinatively unsaturated complex **I** either irreversibly recombines with CO to regenerate the initial complex  $\text{C}_Z$  or reversibly combines with L to form a complex  $(\text{CO})_5\text{W}(\text{cb})\text{L}$  (L denoting the solvent S or other coordinating species such as  $\text{N}_2$ ,  $\text{H}_2\text{O}$ , MeCN, or an olefin). It is unlikely that we can detect the pentacoordinated complex **I** in the microsecond regime since  $\text{W}(\text{CO})_5$  or  $\text{Cr}(\text{CO})_5$  complexes generated by photolysis of the corresponding hexacarbonyls<sup>25–29</sup> have been reported to coordinate a solvent molecule within picoseconds. Therefore the first tetracarbonyl-type transient that we see is assigned to the solvent adduct **I**–S. The transformation of **I**–S observed during the first 10  $\mu\text{s}$  in nitrogen-purged solutions can be assigned to the replacement of a solvent ligand by  $\text{N}_2$  to yield the complex **I**– $\text{N}_2$  (or by  $\text{H}_2\text{O}$  yielding **I**– $\text{H}_2\text{O}$  in the case of solutions purged with wet argon). This assignment is substantiated by the spectral features characteristic for

(22) The following bands have been assigned to the  $[(\text{CO})_5\text{W}(\text{methyl trans-crotonate})]$  in *n*-hexane:  $\text{A}_{1g}$  2089 (2093)  $\text{cm}^{-1}$ ,  $\text{E}_g$  2007 (2009)  $\text{cm}^{-1}$ ,  $\text{T}_{1u}$  1977/1955 (1986/1962)  $\text{cm}^{-1}$ ,  $^{13}\text{C}[\text{E}(\text{C}_4)]$  1970 (1976). The band positions are very similar to those obtained by Grevels et al.<sup>23</sup> for  $[(\text{CO})_5\text{W}(\text{methyl acroleate})]$  upon photolysis of  $[\text{W}(\text{CO})_6]$  in solutions containing methyl acroleate. The latter data (values in parentheses) have been verified and supplemented in our laboratory.

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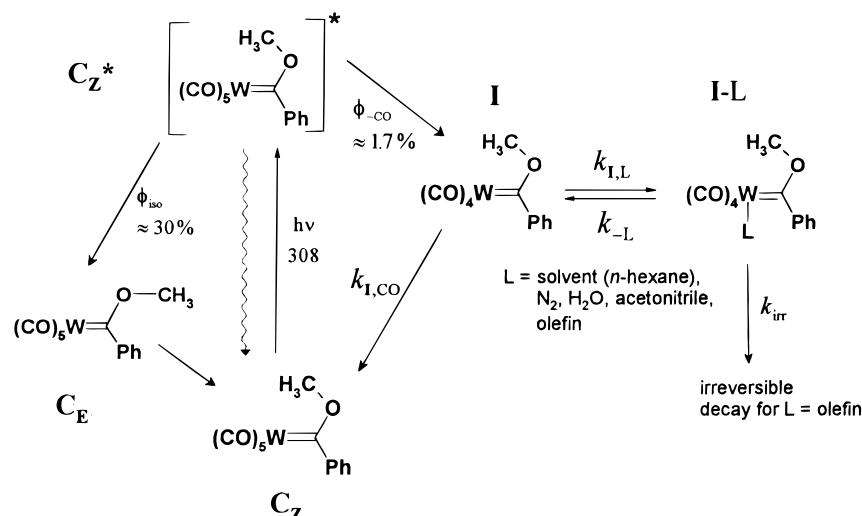
(26) (a) Joly, A. G.; Nelson, K. A. *J. Phys. Chem.* **1989**, *93*, 2876. (b) Joly, A. G.; Nelson, K. A. *Chem. Phys.* **1991**, *152*, 69.

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Scheme 1



tetracarbonyl complexes (cf. Table 1) and by the effect of dry Ar in place of N<sub>2</sub> used for purging the solution. Whether the conversion of I-S into I-N<sub>2</sub> is quantitative or not cannot be definitely decided. The two species I-S and I-N<sub>2</sub> should interconvert through a dissociative mechanism involving the coordinatively unsaturated species I as the intermediate. According to the experimental results, the equilibrium between the three species must be established within 10 μs.

**Quantum Yields.** The photochemical isomerization C<sub>Z</sub> → C<sub>E</sub> has been characterized in some detail by the groups of Stufkens<sup>17</sup> and McGarvey.<sup>16</sup> However, the quantum yield of this process has not been reported. According to Servaas et al.,<sup>17</sup> the IR bands in the CO-stretching region of C<sub>Z</sub> are shifted by 1–3 cm<sup>-1</sup> with respect to those of C<sub>E</sub>. Qualitatively this is in line with our observation of the derivative-type absorption band observed by time-resolved IR at short delay times. By using the Δν̃ values given in ref 17 the concentration of C<sub>E</sub> produced by one laser flash can be estimated.

Since the Δν̃ shifts are small in comparison with the spectral widths of the lines (determined by the spectral resolution of our instrument), the following relation applies:

$$\Delta A_{\text{max}} = -\Delta c d \left( \frac{d\epsilon}{d\nu} \right)_{\text{max}} \Delta \tilde{\nu} \quad (1)$$

where Δc is the concentration change due to the conversion of C<sub>Z</sub> to C<sub>E</sub>, d = 0.05 cm is the optical path length, and (dε/dν̃)<sub>max</sub> is the steepest slope of the IR line. With ν̃<sub>max</sub> = 1956 cm<sup>-1</sup>, Δν̃ ≈ 1 ± 0.5 cm<sup>-1</sup>,<sup>17</sup> (dε/dν̃)<sub>1953</sub> = -(415 ± 30) M<sup>-1</sup> (cf. Figure 2), and ΔA<sub>max</sub> ≈ 0.015<sup>30</sup> we obtain c<sub>C<sub>E</sub></sub> = -Δc<sub>C<sub>Z</sub></sub> = (9 ± 4.5) × 10<sup>-4</sup> M for the experimental conditions pertaining to the signals in Figure 4. From this value and the equivalent concentration of absorbed photons of 3 × 10<sup>-3</sup> M the quantum yield φ<sub>C<sub>Z</sub>→C<sub>E</sub></sub>(308 nm) = 0.3 ± 0.15 for photochemical C<sub>Z</sub> → C<sub>E</sub> isomerization is obtained. With the value of Δc<sub>C<sub>Z</sub></sub> we can also estimate the as yet unknown shift Δλ of

the absorption band at 403 nm associated with the transformation C<sub>Z</sub> → C<sub>E</sub>: By applying the relation analogous to eq 1 and using ΔA<sub>430</sub> = -0.09 (cf. Figure 3), (dε/dλ)<sub>430</sub> = -142 M<sup>-1</sup> cm<sup>-1</sup> nm<sup>-1</sup>, and d = 0.05 cm, we obtain Δλ = -(14 ± 7) nm.

To estimate the quantum yield of photoinduced loss of CO, we need to quantify the resulting transient concentration of tetracarbonyl complexes. As has been described in the Results section, the tetracarbonyl complex intermediate is quantitatively scavenged by the olefin methyl *trans*-crotonate. There is no regeneration of the initial complex from the intermediate I-olefin. Thus the quantum yield of photolysis under such conditions (1.7%) can be also assigned to the quantum yield of primary CO loss. It should be noted that this quantum yield is in fairly good agreement with the value of 1.1% reported by Foley et al.<sup>8</sup> for the photoinduced bleaching of C<sub>Z</sub> under continuous illumination at 313 nm in neat acetonitrile.

From their experiments carried out under low-temperature matrix isolation conditions Servaas et al.<sup>17</sup> concluded that CO loss occurred *after* formation of the C<sub>E</sub> (syn) isomer and that the tetracarbonyl complex generated from C<sub>E</sub> was still in the syn-conformation. By contrast, our observations do imply that CO loss occurs in a one-photon process with C<sub>Z</sub>. This follows from the similarity of the quantum yields for pulsed and continuous illumination. In liquid solution at room temperature the C<sub>E</sub> isomer returns to C<sub>Z</sub> within a few microseconds. Therefore, under stationary illumination the quantum yield for irreversible decomposition initiated by loss of CO should be negligible if only the C<sub>E</sub> isomer could undergo this reaction. Furthermore, a strict linearity between the laser pulse energy and the observed ΔA for the tetracarbonyl intermediates is observed. This would not be compatible with a two-photon mechanism of CO loss which requires C<sub>Z</sub> → C<sub>E</sub> photoisomerization as a first step. Nevertheless, in view of the different orders of magnitude of the quantum yields of photoisomerization and loss of CO, it seems that our observations and those reported by the Stufkens group are compatible. From our results one would expect, for conditions where C<sub>E</sub> is long-lived, i.e., in a low-temperature matrix, that the C<sub>Z</sub> → C<sub>E</sub> conversion

(30) From Figure 4 we obtain ΔA<sub>1956</sub> = 0.006. However, it must be taken into account that due to the short decay time of the signal of only about twice the time constant of the IR detection system, the apparent signal maximum reaches only about 40% of the true value. Thus a corrected ΔA<sub>1956</sub> value of 0.015 should be used.



**Table 2. Rate Constants for Exchange of Solvent or N<sub>2</sub> Ligands by CO**

complex X	$k_{X,CO}[\text{CO}]_{\text{sat},1\text{bar}}, \text{s}^{-1}$	$k_{X,CO}, \text{M}^{-1} \text{s}^{-1}$	ref
[(CO) <sub>5</sub> W( <i>c</i> -hexane)]	$2 \times 10^3$	$2 \times 10^5$ <sup>a</sup>	31
[(CO) <sub>5</sub> W( <i>n</i> -heptane)]	$1 \times 10^4$	$1 \times 10^6$ <sup>a</sup>	32
<i>trans</i> -[(CO) <sub>4</sub> (PPh <sub>3</sub> )W( <i>n</i> -heptane)]	$3.5 \times 10^4$	$3.5 \times 10^6$ <sup>a</sup>	32
<i>cis</i> -[(CO) <sub>4</sub> (PPh <sub>3</sub> )W( <i>n</i> -heptane)]	$1.4 \times 10^5$	$1.4 \times 10^7$ <sup>a</sup>	32
<i>cis</i> -[(CO) <sub>4</sub> (N <sub>2</sub> )W(cb)] = <b>I</b> -N <sub>2</sub>		$3.5 \times 10^8$ <sup>b</sup>	this work
"naked" W(CO) <sub>5</sub> in C <sub>6</sub> F <sub>11</sub> CF <sub>3</sub>		$2 \times 10^9$	33

<sup>a</sup> Assuming a saturation concentration of CO of 10<sup>-2</sup> M. <sup>b</sup> Average value of second-order analysis in solution without excess CO and pseudo-first-order analysis of experiments with excess CO.

should occur first followed, on a longer time-scale, by formation of the CO loss product from **C<sub>E</sub>**. In fact our results do not exclude photoinduced CO loss from the **C<sub>E</sub>** isomer; however, under conditions of low degree of conversion from **C<sub>Z</sub>** to **C<sub>E</sub>** this process is just not significant.

**Recombination of Tetracarbonyl Complex Species with CO.** In Table 2 the CO recombination rate constants are compared with several literature values of related reactions. The reactivity of the coordinatively unsaturated tetracarbonyl carbene complex is only a factor of 10 less than that of a "naked" W(CO)<sub>5</sub> complex and thus ranges among the highest ones. As has been pointed out by Dobson et al.,<sup>32</sup> the relative order of such rate constants of substitution of CO for a weakly bound ligand can be understood on the basis of a dissociative mechanism. The release of the ligand to be replaced is enhanced by bulky substituents *cis* to the leaving ligand. However, the carbene ligand in *cis*-[(CO)<sub>4</sub>(N<sub>2</sub>)W(cb)] (**I**-N<sub>2</sub>) or *cis*-[(CO)<sub>4</sub>(*n*-hexane)W(cb)] (**I**-S) is certainly less bulky than the PPh<sub>3</sub> ligand in *cis*-[(CO)<sub>4</sub>(PPh<sub>3</sub>)W(*n*-heptane)]. Thus other reasons must be responsible for the fast reaction with CO. These reasons presumably are related to the steric and electronic properties of the carbene ligand and its interaction with the metal.

**Competition of CO with Other Potential Ligands.** In CO-saturated solution the lifetime of **I**-S is estimated to be shorter than 0.5 μs. Nevertheless, other potential ligands such as acetonitrile or methyl *trans*-crotonate can compete with CO. The results of the competition experiments, namely, the rise of the signal amplitude of **I**-L and the increase of the decay time of **I**-L with the concentration of L, provide evidence for the reversibility of **I**-L formation and for the dissociative mechanism of the replacement of L by CO. Based on the mechanism represented in Scheme 1 the dependence of the **I**-L-related IR transient signals on [L] shown in Figures 8a and 9a can be simulated and the parameters  $\kappa_L = k_{L,L}/k_{L,CO}$ ,  $k_{-L}$ , and  $k_{\text{irr}}$  can be determined. For the details of the kinetic treatment see the Experimental and Methods Section.

As can be seen in Figures 8 and 9, the overall behavior of the kinetic experiments is very well reproduced by the theoretical curves, although, with a globally<sup>34</sup>

**Table 3. Kinetic Parameters Used in the Global Simulation<sup>34</sup> of the Competitive Kinetics between CO and Ligand L in Figures 8 and 9**

rate constant	ligand	
	acetonitrile	methyl <i>trans</i> -crotonate
$k_{-L}$	5 s <sup>-1</sup>	10 <sup>5</sup> s <sup>-1</sup>
$k_{\text{irr}}$		8 × 10 <sup>3</sup> s <sup>-1</sup>
$\kappa_{L,CO}$	2	2
$k_{\text{I-N}_2,L}$	7 × 10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup> <sup>a</sup>	7 × 10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup> <sup>a</sup>
	4 × 10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup> <sup>b</sup>	

<sup>a</sup> Obtained by multiplying the respective value of  $k_{\text{I-N}_2,CO}$  with  $\kappa_{L,CO}$ . <sup>b</sup> From direct measurement in CO-free solution.

invariant set of parameters, the fit of some of the individual kinetic traces is only approximate.

The ratio of rate constants  $\kappa_L$  for the reaction of the tetracarbonyl intermediate **I** with the ligand L and CO is 2 for both acetonitrile and the olefin. This means that these ligands react 2 times faster with **I** (and consequently with **I**-S and **I**-N<sub>2</sub>) than CO. The values for  $k_{\text{I-N}_2,L} = \kappa_L k_{\text{I-N}_2,CO}$  are given in Table 3. The value of  $k_{\text{I-N}_2,L}$  for L = MeCN compares well with the value of 4 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> estimated from a direct observation of the rise time of the **I**-MeCN IR signal in CO-free solution (cf. Results section). The  $k_{\text{I-N}_2,L}$  values for MeCN and methyl *trans*-crotonate are not far from those of diffusion-controlled reactions and are about 1 order of magnitude larger than the rate constant of 5.5 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> observed for the reaction of [(CO)<sub>5</sub>W-(cyclohexane)] with acetone<sup>31</sup> or of 6.5 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> calculated from the published kinetic data of the reaction of [(CO)<sub>5</sub>W(methylcyclohexane)] with 4-acetylpyridine.<sup>35</sup>

The rate constants  $k_{-L}$  characterize the kinetic stability of the complexes **I**-L toward dissociation. The values (cf. Table 3) indicate a much higher kinetic (and, since the rate constants of formation are equal, also thermodynamic) stability of the acetonitrile than of the olefin complex.

Another remarkable difference between the two **I**-L complexes is the existence of an effective irreversible decay channel to a product other than **C<sub>Z</sub>** in case of the olefin complex. The details of this decay mechanism are not yet clear, except for the fact that the carbene ligand is lost in the course of this reaction and that a [(CO)<sub>5</sub>W-(olefin)] complex has been identified as a product in about 20% yield in *n*-hexane. In di-*n*-butyl ether the complex [(CO)<sub>5</sub>W(solvent)] is formed with about the same yield, as evidenced by the in-situ analysis of the IR spectra. It seems that an understanding of the irreversible decomposition reaction of **I**-olefin is very important for controlling photoinduced coupling of the

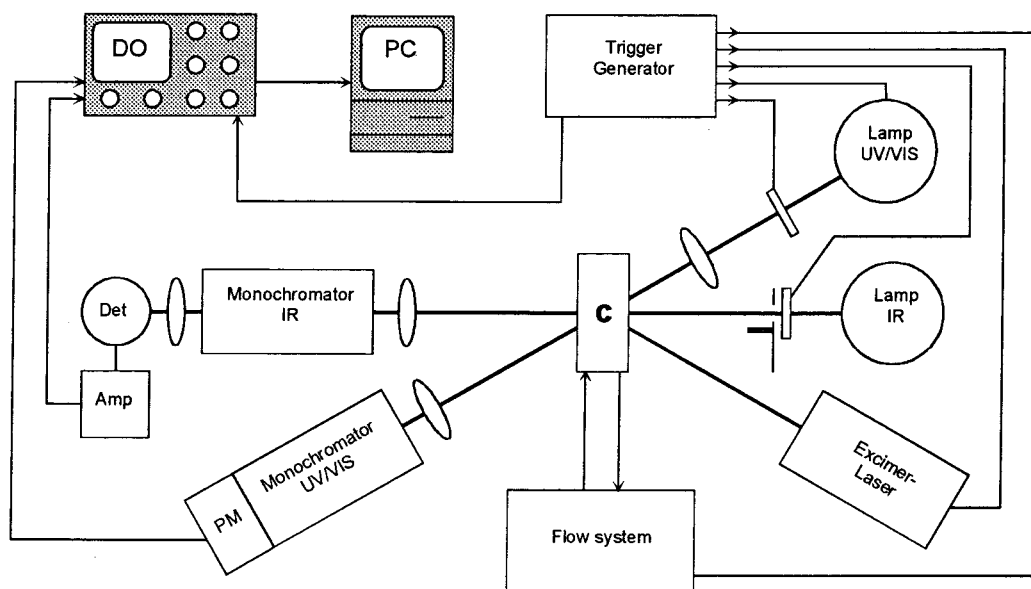
(31) Hermann, H.; Grevels, F.-W.; Henne, A.; Schaffner, K. *J. Phys. Chem.* **1982**, *86*, 5151.

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

(33) Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344.

(34) This term indicates that the same set of values of rate constants has to account for the behavior of a family of kinetic curves. Thus, while suitable sets of individually adjusted rate constants would produce more excellent fits to each curve, the global fit usually yields less good fits to all curves of the family; however the ambiguity in determining the values is reduced.

(35) Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4381.



**Figure 10.** Schematics of the laser flash spectrometer for simultaneous UV/vis and IR transient absorption detection. Abbreviations: **Amp**, ac/dc preamplifier; **C**, optical flow cell; **Det**, MCT detector; **DO**, digital oscilloscope; **PC**, personal computer; **PM** photomultiplier. For details see text.

W-coordinated olefin and the carbene ligand. This reaction mechanism is presently under investigation.

### Conclusion

By using the combination of time-resolved UV/vis and IR spectroscopy it was shown that short-lived carbonyl complex transients can be spectroscopically characterized and their reactions studied even with formation quantum yields as low as 1% and the occurrence of a much more efficient competitive photoprocess. In the UV photolysis of the Fischer carbene complex **C<sub>Z</sub>** at room temperature, photoisomerization and CO loss occur as independent single-photon processes. The quantum yield of isomerization is more than 10 times higher than that of CO photoelimination. Our observations confirm the notion<sup>9,10</sup> that CO elimination has a low quantum yield even if the complex is photoexcited to an LF state. This is due to the competition of CO elimination with electronic relaxation to the lowest excited state, which is predominantly of MLCT character. The LF to MLCT electronic conversion increases the charge on the carbene ligand and seems to favor the Z/E isomerization process.

### Experimental and Methods

**Laser Flash Spectrometer** (for details cf. ref 24). A special setup was developed to allow for laser pulse photolysis with simultaneous observation of UV/vis and IR transient absorbance detection. The schematics of this setup is shown in Figure 10. A XeCl excimer laser (Lambda Physik, LPX 105) was used as the flash photolysis light source. Typically the laser pulse energy was around 100 mJ. The laser beam was focused from an initially  $8 \times 23 \text{ mm}^2$  cross section onto the entrance window of the IR cell of  $10 \times 10 \text{ mm}^2$  by means of two cylindrical lenses. The optical cell was custom-built with two polished, round  $\text{CaF}_2$  windows of 30 mm diameter and 5 mm thickness. The body of the cell was made of V41 steel with connectors to two steel capillaries, allowing for the use of the cuvette as a flow cell. The mechanical properties of the construction allowed for operation of the cell at internal pressures up to 10 bar.

The flow system was fed from a 300 mL steel tank, wherein the sample solutions were flushed with the appropriate gases or gas mixtures made up in a second steel tank preceding the one with the sample solution. The flow of the solution was effected by the gas pressure and controlled by a magnetic valve positioned downstream of the optical cell.

Transient absorption in the UV/vis was monitored by a detection line comprising a pulsed xenon high-pressure lamp (Osram XBO 150 W), quartz optics, monochromator (AMKO, #3.4), and a photomultiplier (Hamamatsu R 955). For IR monitoring, continuous probe light from an IR source (Müller DUO 150) with a cesiuid rod was focused by ZnSe lenses, spectrally analyzed by a grating monochromator (AMKO), and detected by a MCT solid-state device (Infrared Associates Ltd.) operated at 77 K. The IR photosignal was preamplified by a factor of approximately 1000 using a custom-built dc and ac amplifier before feeding this signal and that from the photomultiplier of the UV/vis detection line into a LeCroy 9410 dual channel digital oscilloscope.

Synchronization or suitable time delay of action of the various components of the transient spectrometer was achieved by a home-built trigger generator controlling the following functions: opening and closing of the magnetic valve in the flow-system for a time allowing for the replacement of the solution in the optical cell,<sup>36</sup> opening and closing of the shutters in the UV/vis and IR beams (restricting these opening times to a minimum period required for recording a transient signal prevented undesired photobleaching and heating of the sample solution by the probe light), triggering of the UV/vis probe light pulse, triggering of the laser and of the digital oscilloscope. For further data processing and display the recorded signals were transferred to a personal computer via an IEEE-488 interface. For improving the S/N ratio transient signals were averaged over typically 8–16 single measurements performed at a repetition rate of about 1 Hz.

**Materials and Methods.** Pentacarbonyl[methoxy(phenyl)-carbene]tungsten ( $[(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}]$ , **C<sub>Z</sub>**) was synthesized according to ref 37 and purified by fractionated sublimation

(36) At 1 Hz repetition frequency the volume exchanged between two laser pulses amounts to  $39 \mu\text{L}$ . Thereby about 80% of the illuminated volume of the cuvette is replaced. In view of the low quantum yield of less than 2% permanent decomposition per laser flash this may be considered a sufficient renewal of solution.

(37) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 164.

in vacuo until admixtures of  $[\text{W}(\text{CO})_6]$  were no longer detectable. A very useful and sensitive indicator of  $[\text{W}(\text{CO})_6]$  is the photochemical bleaching of the IR absorption at  $1980\text{ cm}^{-1}$ . Methyl *trans*-crotonate was obtained from Fluka (purum; 98%) and used without further purification. Solvents used were *n*-hexane (SPECTRANAL, Riedel-de Haën, and UVASOL, Merck), acetonitrile (UVASOL, Merck), and di-*n*-butyl ether (Wacker-Chemie, >99.3%). Only the latter was further purified by reflux boiling over metallic sodium for 4 h, distillation, and rectification over metallic sodium under a nitrogen atmosphere. Gases applied to flush and saturate the solutions at 1 bar were  $\text{N}_2$  (5.0 Sauerstoffwerk Friedrichshafen GmbH), Ar (4.8, Messer Griesheim GmbH), and CO (4.7, Messer Griesheim GmbH). Sample solutions were usually  $2 \times 10^{-3}\text{ M}$  in the carbene complex. To saturate the solvent with the applied gas or gas mixture a moderate, solvent-vapor saturated gas stream was passed through 200 mL of sample solution in the supply tank of the flow system for 45 min.

**Kinetic Analysis of Scheme 1.** The initial concentration of the ligand adduct  $\text{I-L}$  is given by

$$[\text{I-L}]_0 = [\text{I}]_0 \frac{k_{\text{I,L}}[\text{L}]}{k_{\text{I,L}}[\text{L}] + k_{\text{I,CO}}[\text{CO}]} = [\text{I}]_0 \frac{\kappa_{\text{L}}[\text{L}]}{\kappa_{\text{L}}[\text{L}] + [\text{CO}]} \quad (2)$$

where  $[\text{I}]_0$  is the total concentration of CO-loss products generated by the laser flash and  $\kappa_{\text{L}} = k_{\text{I,L}}/k_{\text{I,CO}}$ . The decay of  $\text{I-L}$  is exponential with rate constant  $k_{\text{obs}}$ :

$$[\text{I-L}]_t = [\text{I-L}]_0 \exp(-k_{\text{obs}}t) \quad (3)$$

Two channels contribute to the decay: (a) recombination with CO to give  $\text{C}_z$  with an effective rate constant  $k_{\text{C}_z}$  and, possibly, (b) an irreversible decay to other products with a rate constant  $k_{\text{irr}}$ , i.e.,

$$k_{\text{obs}} = k_{\text{C}_z} + k_{\text{irr}} \quad (4)$$

The rate constant  $k_{\text{C}_z}$  is a product of two factors: the rate constant  $k_{-\text{L}}$  of dissociation of the ligand adduct and the probability that the ensuing coordinatively unsaturated intermediate **I** does react with CO in the next step:

$$k_{\text{C}_z} = k_{-\text{L}} \frac{k_{\text{I,CO}}[\text{CO}]}{k_{\text{I,CO}}[\text{CO}] + k_{\text{I,L}}[\text{L}]} = k_{-\text{L}} \left( 1 - \frac{[\text{I-L}]_0}{[\text{I}]_0} \right) \quad (5)$$

From eqs 4 and 5 it follows that the rate constant  $k_{\text{obs}}$  of the decay of  $\text{I-L}$  should decrease linearly with the initial amplitude  $[\text{I-L}]_0$ .

A complete ("global")<sup>34</sup> analysis of the kinetic signals obtained for a series of ligand concentrations requires the determination of  $k_{-\text{L}}$ ,  $k_{\text{irr}}$ , and  $\kappa_{\text{L}}$ . The value of  $\kappa_{\text{L}}$  can be obtained from a plot of the inverse of the initial signal amplitude  $\Delta A_0(\tilde{\nu}_{\text{I-L}})$  at a wavenumber  $\tilde{\nu}_{\text{I-L}}$ , where  $\text{I-L}$  absorbs versus the inverse of the ligand concentration:

$$\frac{1}{\Delta A_0(\tilde{\nu}_{\text{I-L}})} = \frac{1}{\{\Delta A_0(\tilde{\nu}_{\text{I-L}})\}_{\text{max}}} + \frac{[\text{CO}]}{\kappa_{\text{L}}\{\Delta A_0(\tilde{\nu}_{\text{I-L}})\}_{\text{max}}} \frac{1}{[\text{L}]} \quad (6)$$

The intercept of this diagram yields the value  $\{\Delta A_0(\tilde{\nu}_{\text{I-L}})\}_{\text{max}}$ , which corresponds to the complete primary capture of all tetracarbonylcarbene intermediates by L. A plot of  $k_{\text{obs}}$  versus the initial signal amplitude  $\Delta A_0(\tilde{\nu}_{\text{I-L}})$  yields  $k_{-\text{L}}$  and  $k_{\text{irr}}$ :

$$k_{\text{obs}} = k_{\text{irr}} + k_{-\text{L}} - k_{-\text{L}} \frac{\Delta A_0(\tilde{\nu}_{\text{I-L}})}{\{\Delta A_0(\tilde{\nu}_{\text{I-L}})\}_{\text{max}}} \quad (7)$$

The curves shown in Figures 8b and 9b were calculated by eqs 2–5 using parameters (cf. Table 3) obtained in the way just pointed out. For L = olefin (Figure 9) the shortest time resolution available had to be employed for the kinetic measurements. The effect of the finite response time ( $r^{-1} \approx 0.5\text{ }\mu\text{s}$ ) of the IR detection system was taken into account when calculating the kinetic curves. The pertinent equation is

$$[\text{I-L}]_t = [\text{I-L}]_0 \frac{r}{r - k_{\text{obs}}} \{\exp(-k_{\text{obs}}t) - \exp(-rt)\} \quad (8)$$

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