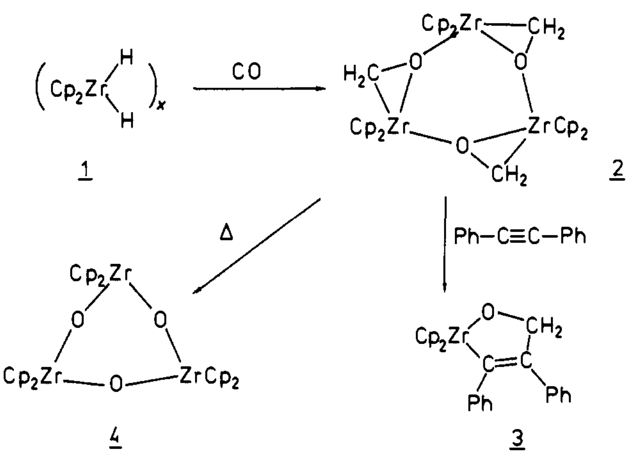
Scheme I



many unsaturated organic substrates under C–C bond formation. In contrast to the examples described previously, here such reactions are characterized by substantial activation barriers. Slow conversions of **2** take place above 180 °C with a variety of alkenes and alkynes forming complex mixtures of as yet unidentified organometallic compounds. Treatment of **2** with excess tolane at 200 °C is an exception and a 1:1 adduct [**3**: ^1H NMR (C_6D_6) δ 7.5 (m, 10 H, Ph), 5.9 (s, 10 H, Cp), 4.6 (s, 2 H, CH_2)] of (η^2-formaldehyde)zirconocene and diphenylacetylene is formed.[12,13] At that temperature the cyclotrimer **2** itself is thermally labile. The favorable alternation of oxygen atoms and zirconium metal centers in the ring system of **2** is retained on thermolysis: at 200 °C the trimeric (η^2-formaldehyde)zirconium complex is slowly converted ($\tau_{1/2} \sim 3$ h) to the known $Cp_2Zr{=}O$ trimer **4** (Scheme I).[14] The formation of the major reaction product **4** (≥80% yield) is accompanied by the appearance of a complex mixture of different organometallic components. These exhibit ^1H NMR features similar to the complex reaction mixtures obtained upon thermolysis of **2** in the presence of alkenes (see above). As the composition of these minor products has not yet been established, the fate of CH_2 groups "lost" in the thermolysis of **2** remains obscure at present. The unexpected loss of all three carbon monoxide derived methylene groups[15] from **2** by simply heating the complex may eventually lead to a new understanding of the factors controlling Fischer–Tropsch-type processes on a well-defined molecular level.[16] At present this is being actively pursued in our laboratory.

Registry No. 1, 85442-81-5; **2**, 85442-82-6; **3**, 85442-83-7; **4**, 70693-90-2.

Supplementary Material Available: Tables of positional and thermal parameters for **2** and a list of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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[12] ≥80%, accompanied by ca. 20% of **4** as judged by ^1H NMR. Hydrolysis (aqueous NH_4Cl) of the mixture yields (*E*)-2,3-diphenylpropenol (63% isolated yield based on consumed starting material **2**): ^1H NMR ($CDCl_3$, Me_4Si) δ 1.74 (s, OH), 4.46 (d, 2 H, CH_2, $^4J_{HH} = 1.5$ Hz), 6.69 (t, 1 H, =CH—), 6.93–7.46 (m, 10 H, Ph).

[13] We have recently shown that bis[(η^2-benzophenone)zirconocene] at 70 °C rapidly dissociates to give a monomeric (η^2-ketone)zirconocene species.[11] Here the isolation of oligomer **2** derived from an odd number of $Cp_2Zr(CH_2O)$-units (**5**) could indicate as well the presence of monomeric (η^2-formaldehyde)zirconocene as a reactive intermediate at some stage of the reaction. The formation of **3** by trapping thermally generated **5** with the added scavenger tolane would be in accord with this supposition.

[14] Average Zr–O bond length 1.959 Å; Zr–O–Zr angle (mean value) for 4: Fachinetti, C.; Floriani, C.; Chiese-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767–1775.

[15] See for a comparison: Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829–5831. Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Ibid.* **1981**, *103*, 5596–5598. Erker, G.; Rosenfeldt, F. *Tetrahedron Lett.* **1981**, *22*, 1379–1382.

[16] There has been strong evidence that hydrocarbon products in Fischer–Tropsch processes could be obtained from reactions of methylene groups on a metal surface. Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181–6182.

Observation of Coordinatively Unsaturated Intermediates following the Pulsed UV Photolysis of $Fe(CO)_5$

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Organometallic photochemistry is currently an area of vigorous investigation. One reason for this interest is the catalytic activity of photogenerated coordinatively unsaturated species.[1] A great deal of effort has gone into characterizing the nascent photoproducts, including elegant studies involving photochemically generated coordinatively unsaturated organometallics trapped in low-temperature inert-gas matrices.[2] Experiments have also been performed in the gas and liquid phases in an attempt to record the transient spectrum of photolytically generated coordinatively unsaturated species. Despite early problems of impurities coordinating with the photofragment(s), a few reports now exist where transient photofragments have been spectroscopically observed.[3] Other experiments have been successful in chemically trapping coordinatively unsaturated species following gas-phase pulsed UV photolysis of $Fe(CO)_5$ and $Cr(CO)_6$.[4]

In this communication we report the first gas-phase infrared spectrum of the carbonyl-stretch region of coordinatively unsaturated iron carbonyls generated via pulsed UV photolysis of $Fe(CO)_5$. The apparatus used in this study is schematically depicted in Figure 1. The basic experimental configuration is that of a pulsed UV–continuous-wave (CW) infrared double-resonance apparatus. UV pulses of a few millijoules per square centimeter are produced via an excimer laser. Almost collinear with the excimer beam is the output of a line-tunable liquid-N_2-cooled CW CO laser. The output of this laser is uniformly attenuated and diffused to produce a beam of ~10 mW/cm², which after passing through the flow cell is incident on an InSb detector. The detector and amplifier combination were carefully chosen to provide rapid response ($\tau \simeq 35$ ns) and linearity over a large dynamic range of incident power. A mixture of 3–30 mtorr of $Fe(CO)_5$ in Ar and/or CO is photolyzed in the 10-cm Teflon flow cell. A change of approximately 10^{11} $Fe(CO)_5$ or coordinatively unsaturated iron carbonyl molecules are necessary to produce a single-pulse transient with a signal to noise ratio of unity.

The transient absorption spectrum generated as a consequence of photolysis of $Fe(CO)_5$ with 248-nm light is displayed in Figure 2. The spectrum is produced by recording transient absorptions as a function of frequency as the CO laser is scanned over a portion of its wavelength range. Four spectral features are apparent and can be assigned by reference to matrix and chemical trapping data.[2,4,6] Feature 1 is the parent absorption. As the parent is

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† Alfred P. Sloan Fellow 1978–1982.

[1] R. L. Whetten, K. J. Fu, and E. R. Grant, *J. Am. Chem. Soc.*, **104**, 4270–4272 (1982); R. L. Whetten, K. J. Fu, and E. R. Grant, *J. Chem. Phys.*, **77**, 3769–3770 (1982); J. C. Mitchener and M. S. Wrighton, *J. Am. Chem. Soc.*, **103**, 975–977 (1981); M. A. Schroeder and M. S. Wrighton, *ibid.*, **98**, 551–558 (1976).

[2] M. Poliakoff, *Chem. Soc. Rev.*, **7**, 527–540 (1978), and references therein; J. J. Turner, J. K. Burdett, R. N. Perutz, and M. Poliakoff, *Pure Appl. Chem.*, **49**, 271–285 (1977), and references therein.

[3] W. H. Breckenridge and N. Sinai, *J. Phys. Chem.*, **85**, 3557–3560 (1981); L. J. Rothberg, N. J. Cooper, K. S. Peters, and V. Vaida, *J. Am. Chem. Soc.*, **104**, 3536–3537 (1982); R. Bonneau and J. M. Kelly, *ibid.*, **102**, 1220–1221 (1980); A. B. Callear, *Proc. R. Soc. London, Ser. A*, **265**, 71–87 (1961).

[4] W. Tumas, B. Gitlin, A. M. Rosan, and J. T. Yardley, *J. Am. Chem. Soc.*, **104**, 55–59 (1982); G. Nathanson, B. Gitlin, A. M. Rosan, and J. T. Yardley, *J. Chem. Phys.*, 74, 361–369 (1981); J. T. Yardley, B. Gitlin, G. Nathanson, and A. M. Rosan, *ibid.*, 74, 370–378 (1981).

[5] G. L. Geoffroy and M. S. Wrighton, "Organometallic Photochemistry", Academic Press, New York, 1979; M. S. Wrighton, Ed., "Inorganic and Organometallic Photochemistry", American Chemical Society, Washington, D.C., 1978, ACS Adv. Chem. Series, Vol. 168.

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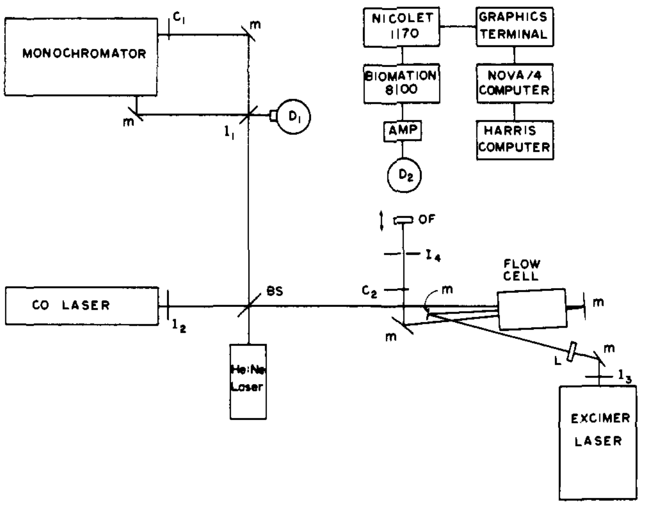

Figure 1. Schematic of the double-resonance experimental setup. D_1 and D_2 are indium antimonide detectors, with D_2 being the high-speed detector. In all cases: m = mirror, I = iris, C = chopper, BS = beam splitter, L = lens, and DF = diffuser. The choppers are only used for alignment purposes and for determining the intensities of the CO laser lines. The diffuser is used to keep the CO laser power constant as a function of frequency.

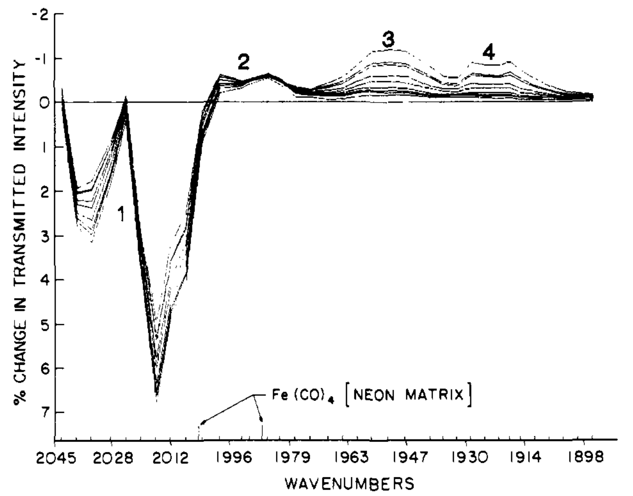

Figure 2. Portion of the infrared spectrum shown following photolysis of 30 mtorr of $Fe(CO)_5$ in 5 torr of argon with a KrF excimer laser pulse. Adjacent traces are taken at 3-μs intervals. The largest excursion from the base line for features 2-4 is the first trace with that trace taken 3 μs after the excimer laser pulse. Nine traces are shown in addition to the base line. Also shown is the position of the $Fe(CO)_4$ absorption in a neon matrix. The tic marks above the abscissa indicate the frequencies of the CO laser lines that were used to construct the traces. Features 1-4 are identified in the text as $Fe(CO)_5$, $Fe(CO)_4$, $Fe(CO)_3$, and $Fe(CO)_2$ absorptions, respectively. Percent change in transmitted intensity refers to CO laser intensity.

photolyzed, the transmitted intensity of the CO laser increases. Thus immediately following photolysis the parent produces a negative going peak. The parent absorption *decreases* further following the photolysis pulse due to the reaction with coordinatively unsaturated species. These reactions may lead to the formation of stable polynuclear iron-containing species such as $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$.[5] Reactions of the type $Fe(CO)_3 + Fe(CO)_5 \rightarrow 2Fe(CO)_4$ also may occur, and further study is necessary to assign their relative importance with respect to loss of parent. Some initially photolyzed $Fe(CO)_5$ is regenerated on a longer time scale than shown in Figure 2. This occurs via recombination of coordinatively unsaturated species with photolytically produced CO. However, in the absence of added CO,

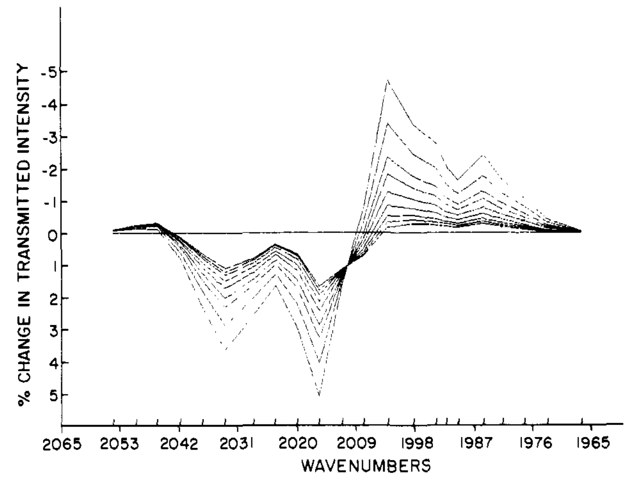

Figure 3. Portion of the infrared spectrum shown following photolysis of 30 mtorr of $Fe(CO)_5$ in 100 torr of CO with a KrF excimer laser pulse. Adjacent traces are taken at 3-μs intervals. The first trace is the one with the largest excursion from the abscissa. Nine traces are shown with the first being 3 μs after the excimer laser pulse photolyzes the sample. The tic marks above the abscissa indicate the frequencies of the CO laser lines that were used to construct the traces.

recombination *does not* compete effectively with the aforementioned reactions, and only a very small fraction of photolyzed $Fe(CO)_5$ is regenerated.

Feature 2 is assigned as $Fe(CO)_4$ and will be discussed further in reference to Figure 3. Features 3 and 4 are assigned as $Fe(CO)_3$ and $Fe(CO)_2$ absorptions, respectively. The frequency of the $Fe(CO)_3$ carbonyl stretch in an argon matrix, 1935 cm^{-1}, is quite close to the frequency of the peak assigned to $Fe(CO)_3$.[6] The presence of a more highly coordinatively unsaturated species than $Fe(CO)_3$ has also been reported in the matrix. This absorption, at lower frequency than the $Fe(CO)_3$ absorption,[6] is assigned to $Fe(CO)_2$ by reference to chemical trapping studies that report no significant Fe(CO) following photolysis at 248 nm.[4]

Figure 3 depicts the $Fe(CO)_5$ and $Fe(CO)_4$ absorptions following photolysis of a mixture of 30 mtorr of $Fe(CO)_5$ and 100 torr of CO. At these CO pressures the initially generated $Fe(CO)_2$ and $Fe(CO)_3$ react very rapidly with the large excess of CO to generate $Fe(CO)_4$. $Fe(CO)_4$ then reacts more slowly with CO to regenerate $Fe(CO)_5$. The kinetics of these reactions will be the subject of another publication.[7] For these conditions, $Fe(CO)_2$ and $Fe(CO)_3$ have already reacted on the fastest time scale shown in Figure 3. The isobestic point clearly indicates that a simple pseudo-first-order reaction occurs where $Fe(CO)_4$ combines with CO to regenerate $Fe(CO)_5$. This observation coupled with data on the frequency of absorption in a neon matrix,[6] which is shown in Figure 2, allows for the unequivocal assignment of the feature in Figure 3 that causes a transient increase in absorption to $Fe(CO)_4$. Interestingly, even with a 3000-fold excess of CO all initially photolyzed $Fe(CO)_5$ is *not regenerated*, implying that the formation of polynuclear metal species is exceedingly rapid and efficient. Finally, the splitting of the $Fe(CO)_4$ spectral feature is significant in that very similar splitting is observed in the matrix. In the matrix, this splitting is one factor that indicates that $Fe(CO)_4$ posesses a C_{2v} geometry. The implications of a similar splitting in the gas phase is that matrix effects do not significantly perturb the gas-phase geometry of $Fe(CO)_4$ and $Fe(CO)_4$ is likely C_{2v} in the gas phase as well as in the matrix.[6]

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Registry No. $Fe(CO)_5$, 13463-40-6; $Fe(CO)_4$, 15281-98-8; $Fe(CO)_3$, 52491-41-5; $Fe(CO)_2$, 71701-41-2.

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[6] M. Poliakoff, *J. Chem. Soc., Dalton Trans.*, 210–212 (1974); M. Poliakoff and J. J. Turner, *ibid.*, 2276–2285 (1974).

[7] A. J. Ouderkirk and E. Weitz, accepted for publication.