Shedding Light on Organometallic Reactions: The Characterization of Fe(CO)$_4$, a Prototypical Reaction Intermediate

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The Hatter opened his eyes very wide...but all he said was "Why is a raven like a writing-desk?" ...
"No, I give it up." Alice replied, "What's the answer?"
"I haven't the slightest idea." said the Hatter ...
Alice sighed wearily "I think that you might do something better...than asking riddles that have no answers."

Lewis Carroll

There are many questions that can be asked about a postulated reaction intermediate. Most importantly, does it play an active role in the reaction mechanism? If so, what is its structure and electronic ground state? What types of reactions does the intermediate itself undergo, and what are the kinetics and energetics of these processes?

Over the past few years, questions such as these have prompted the development of several new techniques for studying intermediates in organometallic chemistry, particularly in reactions involving metal carbonyls. Of the many intermediates that have now been characterized, Fe(CO)$_4$ is one of the most significant. Not only does Fe(CO)$_4$ have a fascinating chemistry, but it has also played a crucial part in the development of new experimental techniques: the refinement of matrix isolation techniques,[2] the theoretical understanding of the shapes of coordinatively unsaturated metal fragments,[3] and the successful marriage of flash photolysis to infrared spectroscopy.[4]

There have been major developments since Fe(CO)$_4$ was the subject of an extensive review[2] in 1978, particularly the detection of Fe(CO)$_4$ in the gas phase.[5,6] In this Account we present a critical summary of these new experiments and point out some of the strengths and limitations of the different techniques currently available for studying organometallic reaction intermediates. Overall, we show that key questions about intermediates do have answers but that these answers often lead to another set of intriguing questions.

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Scheme I.
Summary of the Reactions of Matrix-Isolated Fe(CO)$_4$: (i) UV, (ii) Near-IR, (iii) Annealing Matrix, (iv) λ > 375 nm^a
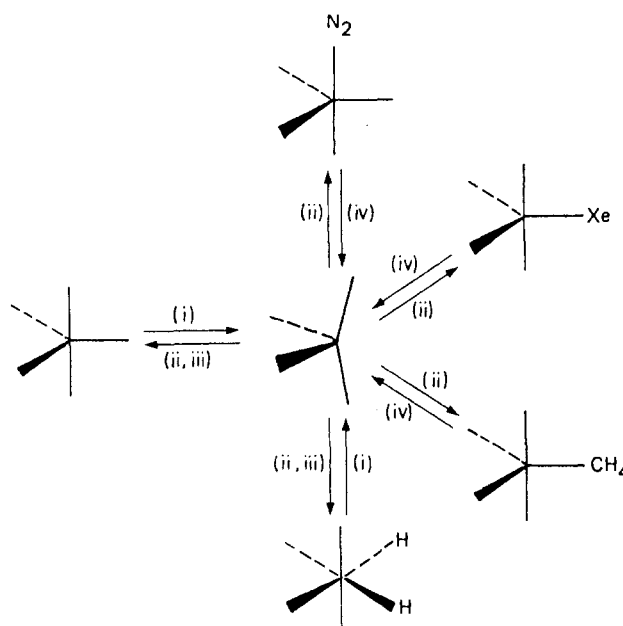
^{a} For detailed references, see text.

Fe(CO)$_4$—The State of the Art

Fifteen years ago little was known about Fe(CO)$_4$ beyond circumstantial evidence that it was an intermediate in the reactions of Fe(CO)$_5$ and Fe$_2$(CO)$_9$. Since then, Fe(CO)$_4$ has been positively identified as an intermediate in several reactions. Fe(CO)$_4$ has been fully characterized in solid matrices at low temperature, where it was found[7] to have a structure with C_{2v} symmetry, 1, and a triplet electronic ground state.[8] This

(1) A general discussion of carbonyl intermediates other than Fe(CO)$_4$ lies outside the scope of this Account. Some species, most notably Cr(CO)$_5$, have been studied in great detail. Useful references can be found in: Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979. Turner, J. J.; Poliakoff, M. *ACS Symp. Ser.* 1983, *No. 211*, 35.
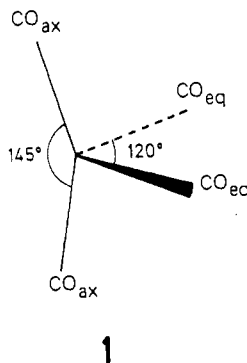
(2) Poliakoff, M. *Chem. Soc. Rev.* 1978, 527.

(3) Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* 1974, *70*, 1599.

(4) For a recent review, see: Poliakoff, M.; Weitz, E. *Adv. Organomet. Chem.* 1986, *25*, 277.

(5) Ouderkirk, A.; Wermer, P.; Schultz, N. L.; Weitz, E. *J. Am. Chem. Soc.* 1983, *105*, 3354.

(6) Seder, T. A.; Ouderkirk, A. J.; Weitz, E. *J. Chem. Phys.* 1986, *85*, 1977.

(7) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* 1974, 2276.

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structure and ground state, although unexpected, have now been rationalized by using both approximate[3,9] and ab initio molecular orbital (MO) arguments.[10] Fe(CO)$_4$ has not yet been detected unequivocally in solution, but in the gas phase, its structure appears to be similar to that in the matrix.[5] Detailed kinetic measurements in the gas phase show that Fe(CO)$_4$ reacts rather slowly with CO, possibly as a result of the triplet ground state.[6] In solid matrices, Fe(CO)$_4$ undergoes several reactions (Scheme I), including a number of IR-laser-induced processes[2,11] which, recently, have also been attributed to the triplet ground state.[12] We now discuss how these facts were established and what questions are still unanswered.

## Structure of Fe(CO)$_4$—Matrix Isolation

Matrix isolation is an "umbrella" term, covering a range of techniques where molecules are trapped in an excess of a relatively inert material, the matrix.[13] In one form, coordinatively unsaturated fragments are generated by photolysis of stable precursor molecules isolated in a frozen gas (e.g., argon or nitrogen) at low temperature, typically 20 K. Once generated in the matrix, the fragments are detected spectroscopically in situ. Matrix isolation was well-known long before it was applied to metal carbonyls, but it is with these compounds in particular that the technique has consistently provided high-quality structural data about molecular fragments.[14]

These data have largely been obtained from a fairly restricted region of the IR spectrum corresponding to vibrations of the carbonyl groups, designated ν(CO). These vibrations, which give rise to IR absorptions in the 2000-cm^{-1} region, can be successfully analyzed without considering any of the other fundamental vibrations of the molecules which all occur at much lower energies, typically <700 cm^{-1}. In general, the number and intensity of ν(C–O) bands of a metal carbonyl fragment provide insufficient evidence to assign a unique structure to the fragment. Thus, the IR spectrum of Fe(CO)$_4$, generated by UV photolysis of the stable carbonyl Fe(CO)$_5$ (eq 1), was initially interpreted in terms of a trigonal, C_{3v} structure, **2**, largely because
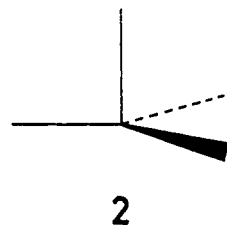
the lower symmetry structure, **1**, seemed less probable.[15]

$$Fe(CO)_5 \xrightarrow{\text{UV, Ar 20 K}} Fe(CO)_4 + CO \qquad (1)$$
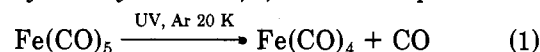
A definitive structural assignment requires additional spectroscopic information. In theory, such information can often be provided by Raman spectroscopy. In practice, however, metal carbonyls are not only very weak Raman scatterers but also highly photosensitive, and with a few notable exceptions,[16] Raman experiments have been singularly disappointing. By contrast, partial ^{13}CO enrichment combined with IR spectroscopy has been extremely successful for determining the structures of fragments. In essence, the procedure involves comparing the observed IR spectrum with those calculated for various possible structures.[17,18] Figure 1 shows this procedure for ^{13}CO-enriched Fe(CO)$_4$, and it is clear that spectrum b, calculated for the C_{2v} structure **1**, agrees better with the observed spectrum a than does spectrum c, calculated for a trigonal structure **2**.

Isotopic enrichment is now being widely applied to metal carbonyl fragments in matrices, and it is timely to restate that the method can only provide convincing evidence for a particular structure (i) if there is good agreement between observed and calculated spectra both in *frequency* and in *relative intensities* of the bands and (ii) if the number of observed IR bands is *significantly larger* than the number of force constants used in the calculation. Even so, the results can sometimes be ambiguous as in the recent case[19] of the fragment CH$_3$Mn(CO)$_4$.

In the case of Fe(CO)$_4$, there is little doubt that structure **1** has been correctly identified, because the assignment of the ν(C–O) spectrum has been tested fairly rigorously. Firstly, the experiment has been repeated using ^{13}C^{18}O enrichment where, because of the greater difference in mass, the bands of the different isotopomers are better resolved.[20] Secondly, IR-laser-induced reactions (see below) have been used to identify sets of bands belonging to individual isotopomers. Fe(CO)$_4$ has the same C_{2v} structure in several different matrices,[7] but before discussing its significance, the structure of Fe(CO)$_4$ in the gas phase should be examined.

(8) Barton, T. J.; Grinter, R.; Thomson, A. J.; Davies, B.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1977**, 841.

(9) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

(10) Daniel, C.; Benard, M.; Dedieu, A.; Wiest, R.; Veillard, A. *J. Phys. Chem.* **1984**, *88*, 4805.

(11) Poliakoff, M. *Spectrochim. Acta, Part A* **1987**, *43A*, 217.

(12) Poliakoff, M.; Ceulemans, A. *J. Am. Chem. Soc.* **1984**, *106*, 50.

(13) For a recent review, which itself contains references to several further reviews of matrix isolation, see: Perutz, R. N. *R. Soc. Chem., Annu. Rep., Sect. C* **1985**, 157.

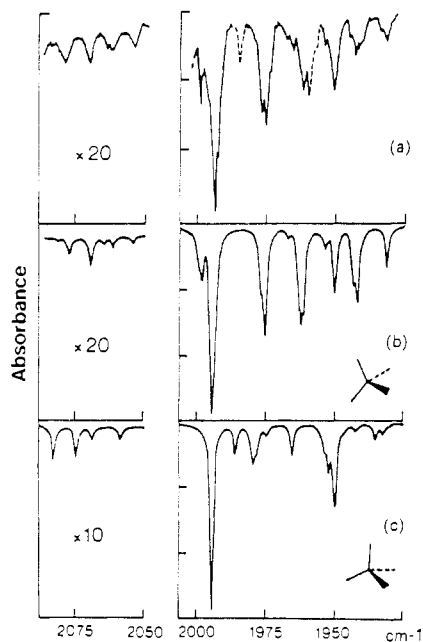(14) See for example: Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1.

(15) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1351.

(16) For a recent example, see: Crayston, J. A.; Almond, M. J.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1984**, *23*, 3051.

(17) Burdett, J. K.; Poliakoff, M.; Dubost, H.; Turner, J. J. *Adv. Infrared Raman Spectrosc.* **1976**, *2*, 1.

(18) The calculation of a spectrum requires a knowledge of bond angles. However, once a spectrum has been tentatively assigned, bond angles can be easily calculated, using a local dipole model, from the relative band intensities in the spectrum of unenriched M(^{12}CO)$_x$. The calculated bond angles are surprisingly insensitive to errors in measurement of intensity and, where comparisons are possible, appear to agree well with experimental values.[17]

(19) Horton-Mastin, A.; Poliakoff, M.; Turner, J. J. *Organometallics* **1986**, *5*, 405.

(20) Davies, B.; McNeish, A.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 7573.

(21) Poliakoff, M. *Chem. Phys. Lett.* **1981**, *78*, 1.

Figure 1. IR spectra showing how the structure of $Fe(CO)_4$ was established. (a) The *observed* spectrum of $Fe(CO)_4$ with partial ^{13}CO enrichment (40%), isolated in a solid SF_6 matrix at 20 K. Bands shown in dotted lines are due to residual $Fe(CO)_5$ precursor. (b) Spectrum, calculated for the C_{2v} geometry, **1**, which gives the best agreement with the observed spectrum. (c) Spectrum, calculated for a C_{3v} geometry, **2**, which provides a poor match to the observed spectra. Reprinted with permission from ref 2. Copyright 1978 Royal Society of Chemistry.

Structure of $Fe(CO)_4$—Time-Resolved IR Spectroscopy in the Gas Phase

A coordinatively unsaturated fragment like $Fe(CO)_4$ will be short-lived in the gas phase, away from the stabilizing influence of the matrix, and so conventional IR apparatus cannot be used to record its spectrum. Although methods for capturing transient IR spectra have existed for some time, it is only recently that these techniques have been applied to organometallic intermediates.[4] The details of equipment vary from one laboratory to another, but in principle, UV flash photolysis (usually by laser) is combined with IR monitoring at one IR wavelength. By repeating the measurement at a series of different IR wavelengths, we can build up a time-resolved IR (TRIR) spectrum "point by point". In general, this TRIR spectrum is a *difference spectrum* with reactants as negative peaks and intermediates as positive peaks.

Figure 2a shows the TRIR spectrum obtained by the flash photolysis of $Fe(CO)_5$ in the gas phase.[5] The rather "angular" appearance of the bands is an artifact of the typically low-resolution TRIR technique, but the lack of rotational fine structure is genuine, the consequence of the large moment of inertia and low-frequency vibrational modes in these metal carbonyl molecules. Even without information from rotational structure, the presence of *two* ν(C–O) bands means that $Fe(CO)_4$ cannot have T_d or D_{4h} symmetry in the gas phase. Furthermore, the similarity in frequency of the gas-phase bands to those of matrix-isolated $Fe(CO)_4$ (Figure 2b) suggests that the structures are the same.

The Electronic Ground State of $Fe(CO)_4$

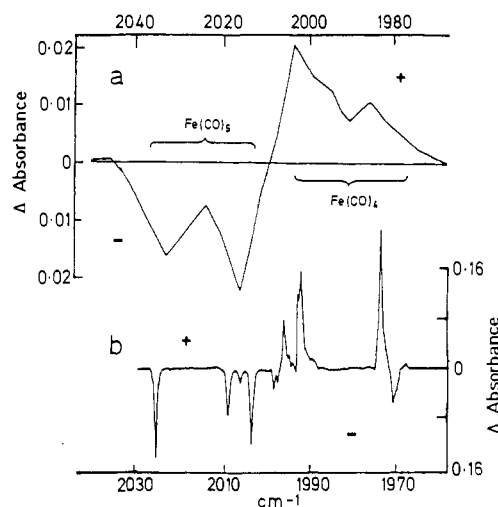Initially, the C_{2v} structure, **1**, was surprising, but simple MO arguments[3,9] were subsequently used to

Figure 2. Comparison of IR spectra of (a) gas phase with (b) low-temperature matrix for $Fe(CO)_5$ and $Fe(CO)_4$. (a) Time-resolved IR (TRIR) spectra, corresponding to a time 3 μs after UV flash photolysis of $Fe(CO)_5$ in the gas phase in the presence of 100 Torr of CO. (See ref 5 for further details.) (b) Fourier transform IR (FT–IR) spectra of $Fe(CO)_5$ and $Fe(CO)_4$ in an Ar matrix at 10 K. (See ref 21 for the rather complicated procedure for generating these spectra, the details of which are not important here.) Note that the Ar matrix has a "solvent" effect which lowers the wavenumbers of the bands by $\sim$10 cm^{-1}; so, to aid comparison of the two spectra, the wavenumber scales have been shifted by 10 cm^{-1} relative to each other.

show that it would be the expected structure for $Fe(CO)_4$ with a $^3B_2$ electronic ground state. Unfortunately, all attempts to detect an electron spin resonance signal due to matrix-isolated $Fe(CO)_4$ have failed, possibly because of a large zero-field splitting.[22] However, a combination of matrix isolation and magnetic circular dichroism (MCD) has provided qualitative confirmation that $Fe(CO)_4$ is indeed paramagnetic.[8]

Both the geometry and triplet ground state of $Fe(CO)_4$ have now been supported by ab initio MO calculations.[10] On the other hand, singlet $Fe(CO)_4$ is predicted to have a D_{4h} square-planar structure.[3,9] This difference means that the Franck–Condon factors for triplet $\rightarrow$ singlet electronic transitions are likely to be unfavorable. $Fe(CO)_4$ does have an observable visible/near-IR absorption band,[20] $\lambda_{max} = 770$ nm (13 000 cm^{-1}), but it is almost certainly due to transitions within the triplet manifold. The difference in geometry between triplet and singlet states is reminiscent of the methylene radical, CH_2, and as is widely known, Hoffmann has made wide use of this similarity in his isolobal analogy.[23] Below, we show that there is also an interesting parallel in the reactivities of $Fe(CO)_4$ and CH_2, but first we consider the formation of $Fe(CO)_3$ and lower fragments.

Formation of $Fe(CO)_3$—Multiple Loss of CO Groups

When matrix-isolated $Fe(CO)_4$ is photolyzed with UV light, $Fe(CO)_3$ is formed,[24] the yield depending on the matrix material (eq 2). ^{13}CO enrichment confirms that
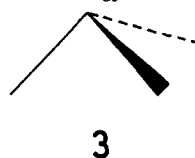
$$Fe(CO)_4 \xrightarrow[\text{matrix, 20 K}]{UV} Fe(CO)_3 + CO \qquad (2)$$
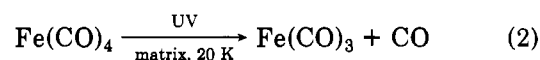
(22) Lionel, T.; Morton, J. R.; Preston, K. F. *J. Chem. Phys.* **1982**, *76*, 234.

(23) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(24) Poliakoff, M. *J. Chem. Soc., Dalton Trans.* **1974**, 210.

Characterization of $Fe(CO)_4$

$Fe(CO_3)$ has a pyramidal C_{3v} structure,[24] **3**, again con-

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sistent with MO predictions.[3] In CH_4 and N_2 matrices, further photolysis provides evidence for formation of $Fe(CO)_x$ species ($x = 2$ or 1) and eventually of Fe atoms.[25] The loss of CO groups appears to be stepwise with one UV photon required to remove each CO group. In matrices there is no evidence for loss of more than one CO group at a time.

Things are quite different in the gas phase. Trapping experiments,[26] particularly with PF_3, show that absorption of a single UV photon can lead to substitution of several CO groups (eq 3). Furthermore, the degree

$$Fe(CO)_5 + xPF_3 \xrightarrow[\text{gas phase}]{UV}$$
$$Fe(CO)_{5-x}(PF_3)_x \quad (x = 1, 2, 3, \text{ or } 4) \quad (3)$$
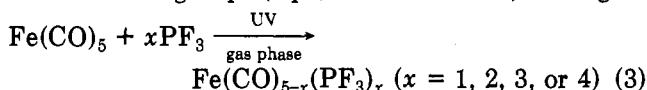
of substitution increases with the energy of the UV photon.[26] Thus, irradiation at 353 nm leads to formation of $Fe(CO)_4(PF_3)$ and $Fe(CO)_3(PF_3)_2$, while higher energy photons from an ArF laser (193 nm) yield predominantly $Fe(CO)_2(PF_3)_3$.

Time-resolved IR measurements confirm that more than one CO group can be lost under these conditions.[6] Bands due to $Fe(CO)_3$ and $Fe(CO)_2$ have been positively identified, although the broadness and overlapping of the IR bands mean that the precise structures of these fragments are uncertain. For a given UV photon energy the relative yield of these fragments is independent of laser power (ca. 1–10 mJ cm^{-2}), indicating that multiphoton processes are not significantly involved. However, just as in the trapping experiments, the yield of the lower fragments increases with the energy of the UV photon, as might be predicted by comparing photon energies with the energy required to form the various fragments[27] (Figure 3).

Thus, in the gas phase, several CO groups can be lost after the absorption of a single UV photon while, in a matrix, only one CO group is lost when one photon is absorbed, irrespective of the energy of the UV photon. The difference between the gas phase and the matrix appears to lie in the rate of vibrational relaxation.[28] It can be seen from Figure 3 that, for all excimer wavelengths shown, there is enough energy in a single photon to remove at least two CO groups from $Fe(CO)_5$. Thus after loss of the first CO group, the $Fe(CO)_4$ fragment would be expected to be "hot", with enough residual internal energy to expel a second CO group. Under the pressure conditions used in gas-phase experiments, the rate of intermolecular energy transfer will be much slower than the intramolecular redistribution of energy required to expel the second CO group. On the other hand, for matrix-isolated molecules the size of $Fe(CO)_4$, the rate of energy transfer to the matrix is likely to be faster than the rate for loss of a CO group following
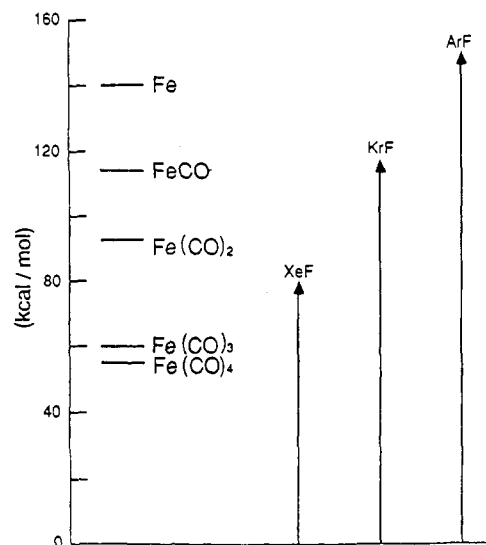
Figure 3. Schematic diagram in which the UV photon energies from rare gas excimer lasers are compared with the energy[27] required for the formation of the various $Fe(CO)_x$ fragments (x = 1–4) from $Fe(CO)_5$; a detailed discussion is given in the text.

intramolecular energy redistribution. This explanation is supported by the observation of TRIR bands due to vibrationally "hot" fragments in the gas phase.[6] Relaxation rates in liquids will be similar to those in matrices, so multiple loss of CO groups during photolysis of $Fe(CO)_5$ in solution is unlikely under normal conditions.

Does $Fe(CO)_4$ Have a Weak Fe–CO Bond?

It can be seen from Figure 3 that ca. 140 kcal mol^{-1} is required to generate Fe atoms from $Fe(CO)_5$, giving an average bond dissociation energy of 28 kcal mol^{-1}. It can also be seen that the amount of energy required to remove one CO group from an $Fe(CO)_x$ fragment varies considerably with the value of x. In particular, a large amount of energy,[29] ~55 kcal mol^{-1}, is needed for $Fe(CO)_5$, but the bond dissociation energy typically quoted for $Fe(CO)_4$ is ~5 kcal mol^{-1}. Does $Fe(CO)_4$ really have such a weak Fe–CO bond?

These bond dissociation energies for $Fe(CO)_x$ species were deduced[27] from a thermodynamic cycle which includes measurements of appearance potentials[30] and electron detachment thresholds for $[Fe(CO)_{x-1}]^-$ ions. The errors in these measurements can be summarized as follows:

bond dissociation energy[30] of $[Fe(CO)_4]^-$		0.8 ± 0.2 eV
−	electron affinity[27] of $Fe(CO)_4$	-2.4 ± 0.3 eV
+	electron affinity[27] of $Fe(CO)_3$	$+1.8 \pm 0.2$ eV
	bond dissociation energy of $Fe(CO)_4$	0.2 ± 0.7 eV
		$(4.6 \pm 16.1$ kcal $mol^{-1})$

Thus, while the bond dissociation energy for $Fe(CO)_4$ may well be less than the average bond dissociation energy for an Fe–CO bond in $Fe(CO)_5$, it is not fair to conclude that $Fe(CO)_4$ is a very weakly bound species. Taking into account the extreme error limits on the bond dissociation energy, $Fe(CO)_4$ could even be bound

(25) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Faraday Trans. 2* 1974, 70, 93.

(26) Yardley, J. T.; Gitlin, B.; Nathanson, G.; Rosan, A. M. *J. Chem. Phys.* 1981, 74, 370.

(27) Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* 1979, 101, 5570.

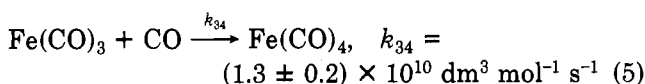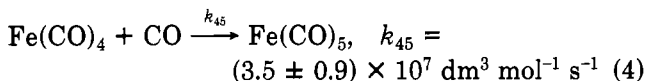(28) Yardley, J. T. *Introduction to Molecular Energy Transfer*; Academic: New York, 1980.

(29) The bond dissociation energy for $Fe(CO)_5$ going to $Fe(CO)_4$ + CO has also been reported as 41.5 ± 2 kcal mol^{-1} by using IR laser pyrolysis techniques. Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* 1984, 106, 3905. This value is also significantly higher than the mean bond dissociation energy.

(30) Compton, R. N.; Stockdale, J. A. D. *Int. J. Mass. Spectrom. Ion Phys.* 1976, 22, 47.

by as much as 20.7 kcal mol^{-1} based on existing appearance potential data.[30] If the appearance potential corresponded to an excited state of $Fe(CO)_3$, the bond dissociation energy for $Fe(CO)_4$ could be even greater.[31] Finally, "hot" $Fe(CO)_4$ is observed to have a significant lifetime in gas-phase TRIR experiments.[6] This seems unlikely behavior for a species with a very low bond dissociation energy.

$Fe(CO)_4$ as a Reaction Intermediate—Gas Phase

Time-resolved IR spectroscopy is, in principle, an excellent technique for measuring the kinetics of reaction intermediates.[4] So far, the most detailed measurements on the $Fe(CO)_x$ species have been for reaction with CO.[6] Surprisingly, the rate of reaction of $Fe(CO)_4$, eq 4, is over 2 orders of magnitude slower than the reaction of $Fe(CO)_3$, eq 5. The difference between

$$Fe(CO)_4 + CO \xrightarrow{k_{45}} Fe(CO)_5, \quad k_{45} =$$
$$(3.5 \pm 0.9) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (4)$$

$$Fe(CO)_3 + CO \xrightarrow{k_{34}} Fe(CO)_4, \quad k_{34} =$$
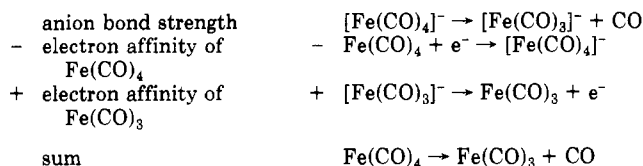$$(1.3 \pm 0.2) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (5)$$

the values of k_{34} and k_{45} reflects significant differences in the preexponential factors,[6] arising from the fact that the reaction of $Fe(CO)_4$ (eq 4) is formally spin-forbidden while the reaction of $Fe(CO)_3$ (eq 5) is not. It is interesting to note that, like $Fe(CO)_4$, *triplet*[33] CH_2 reacts with CO at least 2 orders of magnitude slower than does *singlet*[34] CH_2. Unfortunately, the tuning range of the IR monitoring lasers have so far restricted the reactions of $Fe(CO)_4$ that can be conveniently studied, but this difference in reactivity is not confined to CO. For example, $Fe(CO)_3$ reacts readily with NO but $Fe(CO)_4$ does not.[35]

$Fe(CO)_4$ as a Reaction Intermediate—Matrix Isolation

Molecules, isolated in a matrix at 10 or 20 K, have very little thermal energy, and in favorable circumstances reaction intermediates can be trapped, even if they have a low barrier to further reaction. If energy is then supplied to the trapped intermediate, either by

warming the matrix (so-called annealing) or by irradiation, the energy barrier can be surmounted, and the reaction can go to completion (eq 6).

$$\text{reactant} \xrightarrow{\text{UV}} \text{intermediate} \xrightarrow{\text{"energy"}} \text{product} \quad (6)$$

In this way, $Fe(CO)_4$ has been identified as a definite intermediate in at least five different reactions of matrix-isolated $Fe(CO)_5$, all involving CO substitution (see Scheme I). It is striking that in only two of these reactions are the products known molecules. In one case, the "reaction" is recombination with $CO^{2,15,21}$ (discussed already for the gas phase), and in the other it is the chemically more interesting oxidative addition[36] of H_2. The activation barrier must be extremely low in both cases because the reactions occur when the matrix is annealed.

The third product, $Fe(CO)_4(N_2)$, although so far unknown outside the matrix, is not unexpected, particularly in view of the relatively large number of metal carbonyl dinitrogen complexes that have been generated in liquid noble gas solution.[37] What is interesting is that the activation barrier in this case seems to be rather higher. The reaction cannot be induced by annealing, possibly because N_2 occupies an axial position in the final product (see Scheme I).

The other two products, $Fe(CO)_4Xe$ and $Fe(CO)_4(CH_4)$, are somewhat more exotic.[7] They illustrate one of the more tantalizing aspects of matrix isolation, namely, that sometimes there is enough spectroscopic evidence to suggest that a compound exists but not enough to characterize it fully. Of the two compounds, $Fe(CO)_4Xe$ is the less surprising since it is isoelectronic with a known compound, the stable anion $[Fe(CO)_4I]^-$, but unfortunately, there is no positive IR evidence for the coordination of Xe.

IR spectra show that formation of $Fe(CO)_4(CH_4)$ does not involve oxidative addition of CH_4 and that the molecule contains four CO groups with bond angles, 4,
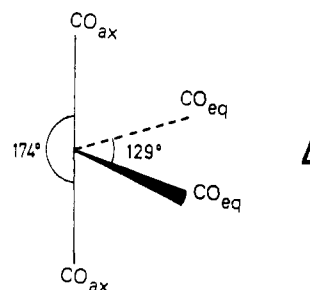
significantly different from those of $Fe(CO)_4$, 1. This suggests that CH_4 may be coordinated in the vacant site.[7] In principle, coordinated CH_4 should be easier than coordinated Xe to detect by IR spectroscopy, but unfortunately, there is no method of selectively trapping two reactants (in this case $Fe(CO)_5$ and CH_4) in the same cage in the matrix. This is one of the most serious limitations to the use of matrix isolation for studying intermediates in bimolecular reactions because, with existing techniques, one requires a huge excess of uncoordinated CH_4 in the matrix to ensure that each $Fe(CO)_4$ fragment has at least one CH_4 molecule close by. Consequently, the absorptions of this uncoordinated CH_4 dominate the spectrum. Thus, the bonding

(31) The thermodynamic cycle for the bond dissociation energy of $Fe(CO)_4$ involves the following steps:

	anion bond strength	$[Fe(CO)_4]^- \rightarrow [Fe(CO)_3]^- + CO$
−	electron affinity of $Fe(CO)_4$	$- \quad Fe(CO)_4 + e^- \rightarrow [Fe(CO)_4]^-$
+	electron affinity of $Fe(CO)_3$	$+ \quad [Fe(CO)_3]^- \rightarrow Fe(CO)_3 + e^-$
	sum	$Fe(CO)_4 \rightarrow Fe(CO)_3 + CO$

However, appearance potentials are very difficult to measure in systems such as these.[30] Consequently, the reported values for the bond dissociation energies have large error brackets[27] which reflect the considerable uncertainty in the appearance potentials.[30] In addition, it has been pointed out that the thermodynamic cycle contains two assumptions:[32] (i) that $[Fe(CO)_3]^-$ is produced in the ground state and (ii) that $Fe(CO)_3$ formed by electron detachment is also produced in the ground state. While the second assumption is almost certainly valid,[32] there is no guarantee that $[Fe(CO)_3]^-$ is produced in the ground state. If the ion were generated in an excited state, the bond dissociation energy for $Fe(CO)_4$ would be underestimated. A detailed discussion of the cycle can be found in: Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 5026.
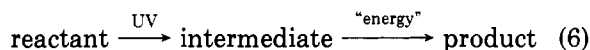
(32) Lineberger, W. C., private communication.

(33) Pilling, M. J.; Robertson, J. A. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 968.

(34) Langford, A. O.; Petek, H.; Moore, C. B. *J. Chem. Phys.* **1983**, *78*, 6650.

(35) Gravelle, S. J.; Weitz, E., unpublished results.

(36) Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410.

(37) See, for example: Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier II, W. B. *J. Am. Chem. Soc.* **1983**, *105*, 3898.

of CH_4 in $Fe(CO)_4(CH_4)$ still remains unclear, although a linear $Fe-H-CH_3$ structure is perhaps the most reasonable guess.

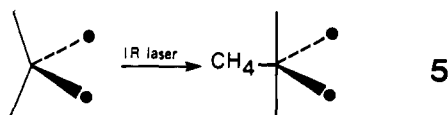All of the reactions in Scheme I can be promoted by near-IR radiation of wavelength corresponding to the 13 000-cm^{-1} absorption band of $Fe(CO)_4$. Formally, at least, these reactions are spin-forbidden, and it is possible that photochemically they could proceed via the singlet state of $Fe(CO)_4$. The energy difference between the singlet and triplet states is unknown, but calculations[10] suggest that it could be less than 13 000 cm^{-1}. However, at least in the case of CO and H_2, the activation barriers seem so low that the singlet state is unlikely to be involved in the thermal addition reactions.

$Fe(CO)_4$ is also postulated as an intermediate in the reactions of $Fe_2(CO)_9$. However, although photolysis of matrix-isolated $Fe_2(CO)_9$ provides excellent evidence[38] for the formation of $Fe_2(CO)_8$, there is no evidence for the formation of $Fe(CO)_4$. This illustrates the second major limitation of matrix isolation, the so-called "cage effect". If photolysis produces two bulky fragments, the matrix cage prevents them from diffusing apart and they recombine. Thus, sadly, matrix isolation will rarely be able to provide information about photofragmentation of polynuclear metal clusters.

The IR-Laser-Induced Photochemistry of Fe(CO)₄

IR-laser-induced reactions are unique to $Fe(CO)_4$, among all matrix-isolated organometallic species, but even so, the reactions merit a brief discussion here to illustrate the potential of experiments in matrices. Full details can be found elsewhere.[2,11,39]

Reactions of $Fe(CO)_4$ can be promoted by IR laser irradiation at frequencies of ~ 2000 cm^{-1}, coinciding with $\nu(C-O)$ IR bands. The effect has been observed in all of the reactions in Scheme I (apart from the reaction with H_2 which has not been studied with IR laser excitation). In each case, the quantum yield is very low. This means that matrix-isolated $Fe(CO)_4$ is only marginally affected by the IR radiation from a normal IR spectrometer. The details of the energy-transfer processes involved are still unclear, but it is now believed that the role of the laser is merely to supply thermal energy to the molecules.[11,39] What is important is that this thermal energy remains localized around the molecule which originally absorbed the IR photon.[40] Only the molecules that absorb at the precise wavelength of the IR laser undergo reaction; all other molecules remain unaffected. This makes IR-laser-induced processes highly selective. For example, one can follow the reactions of particular ^{13}CO isotopomers of $Fe(CO)_4$ and determine the stereochemistry of addition reactions,[39,41] 5.

5

Selective IR excitation also reveals that $Fe(CO)_4$ undergoes *intramolecular* ligand exchange,[20] a process which involves the previously unknown non-Berry pseudorotation, 6. Initially inexplicable, this pseudorotation has now been rationalized on the basis of the Jahn–Teller effect.[12]

6

More detailed experiments[11] show that the pseudorotation, 6, is in competition with addition reactions, 5. It is possible that pseudorotation of the newly formed $Fe(CO)_4$ fragment occurs after the UV photolysis of matrix-isolated $Fe(CO)_5$. The vacant coordination site of $Fe(CO)_4$ would then be rotated away from the ejected CO, and recombination would be prevented.[42] Thus, the fact that $Fe(CO)_4$ is observed at all in the matrix may be an indirect consequence of the triplet ground state which facilitates the pseudorotation.

The triplet ground state of $Fe(CO)_4$ is unusual, even for a coordinatively unsaturated fragment. It would be extremely interesting to know the structures and ground states of $Ru(CO)_4$ and $Os(CO)_4$, the two other group 8 metals. Sadly, these species are still amost totally uncharacterized. Matrix-isolated $Ru(CO)_4$[43] and $Os(CO)_4$[7] cannot easily be generated photochemically from the corresponding $M(CO)_5$ compounds. Apparently, unlike $Fe(CO)_4$, these species are formed but immediately recombine with CO. Might it be that they have singlet electronic ground states and do not pseudorotate within the matrix cage?

Fe(CO)₄ as a Reaction Intermediate—Room-Temperature Solution

Most preparative chemistry is carried out in solution, and so the final stage in the characterization of $Fe(CO)_4$ must involve its detection in solution. This stage seems to be close, but it has not yet been reached. Part of the problem lies in the ease with which insoluble polynuclear species are generated by photolysis of $Fe(CO)_5$. In matrix isolation experiments, the matrix normally prevents polymerization.[7] In the gas phase, cunning design of the cell allows these products to be "flushed away" by the flowing gas.[4,5] In TRIR solution experiments, formation of precipitates still presents technical problems.

TRIR experiments have been carried out with $Fe(CO)_5$ in deuteriobenzene solution where precipitates are not formed.[44] Figure 4 shows the TRIR spectrum of $Fe(CO)_4(C_6D_6)$, the only intermediate observed under these conditions. The decay kinetics of this species are complex but imply the existence of at least one "unseen" intermediate, probably $Fe(CO)_4$. Similar experiments[45]
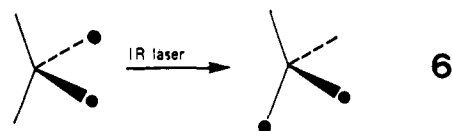
(38) Fletcher, S. C.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* 1986, 25, 3597.

(39) Poliakoff, M.; Turner, J. J. In *Chemical and Biological Applications of Lasers*; Moore, C. B., Ed.; Academic: New York, 1981; Vol. 5, p 175.

(40) It is not clear whether the process involves some heating of the matrix in the immediate environment of the excited molecule, but if it does the effect must be highly localized.

(41) McNeish, A.; Poliakoff, M.; Smith, K. P.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* 1976, 859.

(42) This is similar to the mechanism suggested for $Cr(CO)_5$, although the origin of the pseudorotation is different. Burdett, J. K.; Grzybowski, J. M.; Perutz, R. N.; Poliakoff, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* 1978, 17, 147.

(43) Gregory, M. F.; Poliakoff, M.; Turner, J. J. *J. Mol. Struct.* 1985, 127, 247.

(44) Church, S. P.; Grevels, F.-W.; Hermann, H.; Kelly, J. M.; Klotzbücher, W. E.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* 1985, 594.

(45) Church, S. P.; Grevels, F.-W.; Kiel, G.-Y.; Kiel, W. A.; Takats, J.; Schaffner, K., *Angew. Chem., Int. Ed. Engl.* 1986, 25, 991.
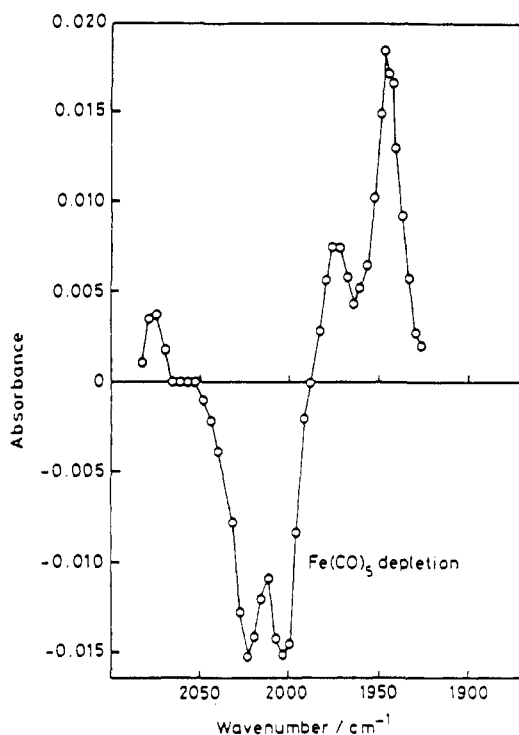
Figure 4. TRIR spectra corresponding to a time 5 μs after the flash photolysis of $Fe(CO)_5$ in C_6D_6 solution at room temperature. The positive bands are assigned to $Fe(CO)_4(C_6D_6)$, presumably formed by the rapid reaction of $Fe(CO)_4$ with the solvent. Reprinted with permission from ref 44. Copyright 1985 Royal Society of Chemistry.

with $Os(CO)_5$ show that $Os(CO)_4(C_6D_6)$ is much shorter lived than $Fe(CO)_4(C_6D_6)$. Could this reflect a difference between $Fe(CO)_4$ and $Os(CO)_4$?

Conclusions

We have shown that intermediates in organometallic reactions no longer need be mysterious. A lot is known

about $Fe(CO)_4$ although there is still more to learn, particularly about its role in reactions in solutions. Characterizing intermediates requires several different experimental techniques, each of which has limitations but which together can provide a large amount of information.

Currently, the most easily detected intermediates are metal carbonyls, but technical developments in the near future should make a wider range of reaction intermediates accessible. For example, new tunable IR sources, already in use for detecting small molecules,[47] will greatly extend the IR regions covered by time-resolved IR spectroscopy. New spectroscopic techniques are becoming available; time-resolved resonance Raman spectroscopy is beginning to be applied to organometallic species,[47] a particularly important development for the detection of very short lived intermediates.

Perhaps we should end on a note of caution. As more is learned about the reactions of particular intermediates, it becomes clearer that reactions are often more complicated than supposed. Closely related reactions do not necessarily have the same mechanism. Intermediates are very reactive. Small energy barriers can alter their behavior. These factors cannot be guessed but they can now be measured!

"I believe I can guess that."
"Do you mean that you think that you can find out the answer to it?" said the March Hare.
"Exactly so" said Alice.

Lewis Carroll

(46) See, for example: Hirota, E. I.; Kawaguchi, K. *Annu. Rev. Phys. Chem.* **1985**, *36*, 53.

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