The Structure of $[Fe(CO)_4]$—An Important New Chapter in a Long-Running Story

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In memory of Ernst A. Koerner von Gustorf (1932–1975) and Jeremy K. Burdett (1947–1997)

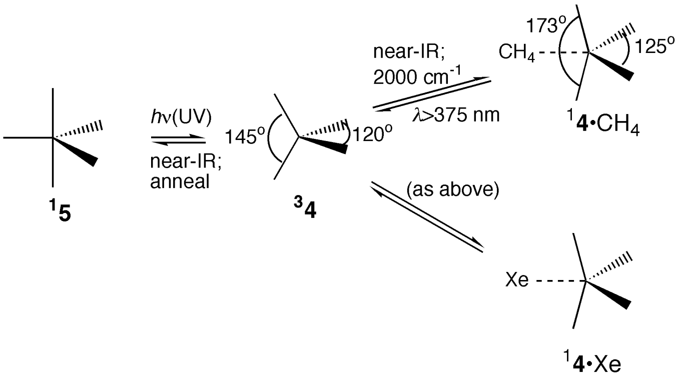
> *"It is of the highest importance in the art of detection to be able to recognize out of a number of facts which are incidental and which are vital."*
> from "The Memoirs of Sherlock Holmes"

$[Fe(CO)_4]$ is a coordinatively unsaturated intermediate usually generated from the stable compound $[Fe(CO)_5]$. Its study has spanned more than 30 years. The recently published paper by Zewail and colleagues[1] in *Angewandte Chemie* represents a major step in the field. Taken together with two recent publications by Fuss and co-workers[2] and Harris and co-workers[3] this paper provides a significant advance in our understanding of $[Fe(CO)_4]$. However, as explained in this Highlight, several questions remain to be answered. For convenience, the discussion is divided into three parts: what was known prior to 1990; what has been discovered since;[4] what happens next.

$[Fe(CO)_4]$ before 1990

The structure and reactions of $[Fe(CO)_4]$ were first established by IR spectroscopy and matrix isolation experiments in 1973/1974.[5] We showed that UV photolysis of $[Fe(CO)_5]$ (^{1}**5**) in low-temperature matrices (ca. 10 K) generates $[Fe(CO)_4]$ with a triplet ground state (^{3}**4**) (Scheme 1; the angles shown for ^{3}**4** are the averages for several matrices with individual errors of $\pm 3°$).

Burdett[6] was the first to show, by rather simple molecular orbital theory, that the expected ground state of $[Fe(CO)_4]$ is indeed a triplet (actually $^3B_2$) with a C_{2v} structure and C-Fe-C bond angles of 135° and 110°, close to the experimental values; the singlet state (^{1}**4**) is somewhat higher in energy. In Ne and Ar matrices, the only further reaction is reversal of the primary photochemical act (i.e. $^3\mathbf{4} \rightarrow {}^1\mathbf{5}$) by either near-IR irradiation or annealing (i.e. warming) of the matrices. On the other hand, with CH_4 and Xe matrices, ^{3}**4** could be converted by a single photon of near-IR or IR ($2000\ cm^{-1}$) radiation into singlet species $^1\mathbf{4}\cdot CH_4$ and $^1\mathbf{4}\cdot Xe$ (Scheme 1; the errors in the bond angles for $^1\mathbf{4}\cdot CH_4$ are $\pm 2°$). There was no evidence for any "uncomplexed" singlet $[Fe(CO)_4]$ (^{1}**4**). It is important to stress that the conversions $^3\mathbf{4} \rightarrow {}^1\mathbf{4}\cdot CH_4$ and $^3\mathbf{4} \rightarrow {}^1\mathbf{4}\cdot Xe$ involve very little energy, implying low activation energies. By contrast, the reverse reactions ($^1\mathbf{4}\cdot CH_4 \rightarrow {}^3\mathbf{4}$, and $^1\mathbf{4}\cdot Xe \rightarrow {}^3\mathbf{4}$) could only be brought about by UV radiation ($\lambda > 375$ nm). With hindsight, one can now see that the interaction of CH_4 and Xe (but not Ne or Ar) with the singlet $[Fe(CO)_4]$ (^{1}**4**) must cause the energies of $^1\mathbf{4}\cdot CH_4$ and $^1\mathbf{4}\cdot Xe$ to be *below* that of ^{3}**4**. Presumably the interaction energy of ^{3}**4** with CH_4 and Xe is insignificant. (In their recent paper, Harris and co-workers[3] point out that there are good theoretical reasons for supposing that interaction of alkanes with triplet metal carbonyl species is negligible, but that interaction with singlet metal species can be significant). It is also noteworthy that in a hydrocarbon glass at 77 K (presumably the nearest low-temperature equivalent to an alkane solvent), only the species $^1\mathbf{4}\cdot$ alkane was produced,[5] that is there was no evidence for ^{3}**4**. Later matrix isolation experiments, using continuous IR lasers, showed that ^{3}**4** could be isomerized by a rather unusual non-Berry pseudorotation mechanism, explained on the basis of a unique example of the Jahn–Teller effect.[7] This low-energy ($<2000\ cm^{-1}$) process is illustrated in Scheme 2, in which X represents a CO group, isotopically enriched with ^{13}C.



Scheme 1. Photochemistry of $[Fe(CO)_5]$ in low-temperature matrices.[5] See text for details.

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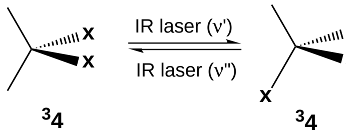

Scheme 2. Wavelength-selective IR laser photoisomerization of $[Fe(CO)_4]$ in low-temperature matrices.[7]

In the mid 1980s, experiments moved into the gas phase where solvent interactions should be absent. Weitz and coworkers[8] carried out experiments with $[Fe(CO)_5]$ in the gas phase, by employing laser UV flash photolysis with fast time-resolved IR detection (TR-IR). The first important point is that, in the gas phase, loss of more than one CO group can occur depending on the photolysis wavelength, whereas in condensed phases the primary photochemical act involves the loss of only a single CO group. The reason for this phase-dependent behavior is well understood in terms of energy transfer from vibrationally excited carbonyl molecules to the solvent or matrix. For the present purposes, the most important observation was that $[Fe(CO)_4]$ could be detected with ν(C–O) frequencies close to those observed for ^{3}**4** in a Ne matrix. This confirmed that the structure of triplet $[Fe(CO)_4]$ (^{3}**4**), which had been deduced from IR matrix frequencies, was not an artefact arising from interactions with matrix. Moreover the gas-phase work showed that ^{3}**4** reacted relatively slowly with either CO or $[Fe(CO)_5]$, a result expected from the spin-forbidden nature of these reactions.

It is also interesting to summarize what was *not* known before 1990:

1) Gas-phase IR studies had revealed no evidence for ^{1}**4**, nor species equivalent to ^{1}**4**$\cdot$Xe or ^{1}**4**$\cdot CH_4$.
2) The photochemical route from ground state $[Fe(CO)_5]$ (^{1}**5**) to ground state $[Fe(CO)_4]$ (^{3}**4**) was unclear, that is did it proceed by a singlet pathway ($^{1}\mathbf{5} \rightarrow [^{1}\mathbf{5}]^* \rightarrow {}^{1}\mathbf{4} \rightarrow {}^{3}\mathbf{4}$) or a triplet pathway ($^{1}\mathbf{5} \rightarrow [^{1}\mathbf{5}]^* \rightarrow [^{3}\mathbf{5}]^* \rightarrow {}^{3}\mathbf{4}$)?
3) Preliminary flash photolysis/IR detection studies on $[Fe(CO)_5]$ in solution had failed to identify any intermediates.[9a]
4) The triplet–singlet energy gap (^{3}**4**/^{1}**4**) was an experimental unknown.
5) There were no really accurate calculations on the structures of ^{3}**4** and ^{1}**4**, including the energy gap, nor were there any estimates of the interaction energies between ^{1}**4** and species such as Xe and CH_4.

[Fe(CO)$_4$] since 1990

In a lecture published in 1992, Grevels reported[9b] preliminary results on the ν(CO) TR-IR spectrum obtained after flash photolysis (309 nm) of $[Fe(CO)_5]$ in CO-saturated cyclohexane. A transient, with an IR spectrum which was very similar to that of ^{1}**4**$\cdot CH_4$ in a matrix, was identified and assigned to ^{1}**4**$\cdot$cyclohexane. This intermediate decayed in about 10 μs. There was no evidence for precursor ^{3}**4**, but this is hardly unexpected given the time-resolution of the experiment (ca. 1 μs).

In 1991/92 Weitz[10] returned to a TR-IR study of $[Fe(CO)_5]$ in the gas phase but using continuously tunable IR diode lasers rather than a line-tunable CO laser. These experiments yielded some fascinating new data about $[Fe(CO)_5]$, its fragments and their kinetics. Interestingly a great deal of the interpretation of the bimolecular reactions, such as $[Fe(CO)_3] + [Fe(CO)_5] \rightarrow [Fe_2(CO)_8]$, was based on earlier matrix isolation experiments[11] on the photochemistry of $[Fe_2(CO)_9]$. However, in the context of this Highlight, the most important observation was detection of a band at 1975 cm^{-1}, assigned to the singlet state of $[Fe(CO)_4]$ (i.e. ^{1}**4**). Although the authors did not comment on the fact, allowing for "matrix shifts", this band is close to the most intense band of ^{1}**4**$\cdot CH_4$, detected in solid CH_4 at 20 K. The chemistry of ^{1}**4** was shown to involve both intersystem crossing (ISC) to ^{3}**4** and reaction with $[Fe(CO)_5]$ to give $[Fe_2(CO)_9]$ in an excited state. The rate of ISC, through collisions with the argon buffer gas, was slower than expected for gas kinetic by a factor of 40, but the reaction with $[Fe(CO)_5]$ was faster, approximately gas kinetic, thereby confirming the spin state of singlet $[Fe(CO)_4]$ (^{1}**4**). In comparison, the corresponding reactions of triplet $[Fe(CO)_4]$ (^{3}**4**) are very slow.[8] Not surprisingly, ^{1}**4** could only be detected when the pressure of buffer gas was low; at higher pressures, ISC to ^{3}**4** was too fast for it to be detected with the time resolution of the experiments (many ns). Thus, these experiments confirm that ^{3}**4** is the ground state with a low-lying singlet state, ^{1}**4**, above it.

In some extremely sophisticated gas-phase experiments, Fuss and co-workers[2] combined femtosecond UV laser excitation with time-of-flight mass spectrometry. They proposed that photolysis of $[Fe(CO)_5]$ at 267 nm proceeds via an excited singlet state ($[^{1}\mathbf{5}]^*$) to yield (in ca. 30 fs) $[Fe(CO)_4]$ in an excited singlet state ($^{1}B_2$), which then rapidly decays (ca. 50 fs), via the $^{1}T_2$ state, to the lowest singlet state ($^{1}A_{1,}$ ^{1}**4**). This is the singlet pathway mentioned above. The Jahn–Teller distortion of the $^{1}T_2$ state was modeled on the earlier non-Berry pseudorotation proposed for ^{3}**4** (Scheme 2).[7] One might have expected to observe the $^{1}A_1$ state decaying to the ground triplet state ($^{1}\mathbf{4} \rightarrow {}^{3}\mathbf{4}$) but the time resolution was too short (< 500 ps) to follow ISC in the gas phase; in practice, what was seen was the very rapid ejection (3.3 ps) of a further CO group from ^{1}**4** to yield $[Fe(CO)_3]$, probably in an excited singlet state (the ground state of C_{3v} $[Fe(CO)_3]$ is almost certainly a triplet, $^{3}A_2$).

This Highlight has been prompted by the latest results on $[Fe(CO)_4]$, in which Zewail and colleagues[1] have used a new apparatus for ultrafast electron diffraction, which combines femtosecond lasers with electron diffraction imaging, to determine absolutely the structure of $[Fe(CO)_4]$. By using 620 nm irradiation, $[Fe(CO)_5]$ is photolyzed by a two-photon process which is of sufficiently low energy to limit the fragmentation pattern (see below for comment about energetics) to only ^{3}**4** and ^{1}**4**, and $[Fe(CO)_3]$ in its ground state ($^{3}A_2$). In an experimental tour de force, they were able to determine the structure of the primary photolysis product and to assign this structure to the $^{1}A_1$ state of $[Fe(CO)_4]$, (^{1}**4**) (Figure 1).

This confirms the singlet pathway proposed by Fuss and coworkers[2] Once more, it would be expected that ^{1}**4** should decay by ISC to ^{3}**4**, but again the time scale (< 200 ps) of these experiments does not permit the detection of the triplet. What

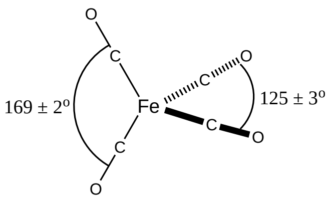

Figure 1. Structure of singlet [Fe(CO)$_4$], (^{1}A$_1$, ^{1}**4**), determined by electron diffraction.[1] The bond lengths [Å] are: CO groups at 169°: Fe-C 1.81 ± 0.03, C-O 1.14 ± 0.05; CO groups at 125°: Fe-C 1.77 ± 0.03, C-O 1.15 ± 0.06. The C-Fe-C angles (169° and 125°) should be compared with those of ^{1}**4**$\cdot$CH$_4$ in the matrix (Scheme 1; 173° and 125°).

is very striking about the structure of ^{1}**4** is that the C-Fe-C bond angles are uncannily close to those determined[5] more than 25 years ago for ^{1}**4**$\cdot$CH$_4$, where angles were calculated from relative IR intensities by using scissors to cut the bands out from the paper trace of the IR spectrum and weighing the paper! Zewail's experiment suggests that, although the interaction of ^{1}**4** with (matrix)CH$_4$ is sufficient to lower the energy of ^{1}**4**$\cdot$CH$_4$ below that of ^{3}**4**, the interaction produces almost no change in the geometry of the singlet [Fe(CO)$_4$] fragment. Thus, these latest gas-phase experiments are entirely consistent with predictions made on the basis of early matrix experiments.

We now turn to the latest experiments in solution. For some time, Harris and colleagues have been highly successful in applying pico- and femtosecond TR-IR to the study of the primary processes in organometallic photochemistry. Their latest paper[3] examines the behavior of several compounds including [Fe(CO)$_5$]. Their TR-IR data revealed an intermediate formed from [Fe(CO)$_5$] within 26 ps and stable for more than 660 ps. The same intermediate was detected in HSiEt$_3$ solution but it reacted within about 1.2 ns to form [HFe(CO)$_4$(SiEt$_3$)]. The IR bands of this intermediate in heptane, 1965 and 1987 cm^{-1}, correspond closely to those observed for ^{3}**4** in a CH$_4$ matrix (1966, 1992/1985 cm^{-1}) (note: *not* ^{1}**4**$\cdot$CH$_4$) and, as the authors claim, it is extremely likely that the intermediate is indeed [Fe(CO)$_4$] in the ^{3}B$_2$ ground state. The intriguing question is: "where is the expected ^{1}**4**$\cdot$solvent?"

If Fuss's and Zewail's gas-phase results apply to the primary steps in solution, then there seems to be only one explanation, namely that ^{1}**4** is indeed produced initially, but that ISC in solution is so fast that only ^{3}**4** is detected. It is worth pointing out that "hot" molecules display "smeared out" IR spectra until relaxation to the equilibrated solution intermediate occurs, a process which takes many ps for metal carbonyls in hydrocarbon solution.[12] Thus, it is just possible that ^{1}**4** is produced initially but it is too "hot" to distinguish spectroscopically, and it converts to ^{3}**4** before detection. Presumably one would have to argue that, on the very fast time scales, ^{1}**4** is just too hot to be stabilized by interaction with the solvent (i.e. there is no "hot" ^{1}**4**$\cdot$solvent). An alternative explanation is that the pathway in solution follows a triplet pathway rather than the singlet pathway observed in the gas phase. Given the matrix behavior of ^{1}**4**$\cdot$Xe and ^{1}**4**$\cdot$CH$_4$, and the fact that only ^{1}**4**$\cdot$alkane can be detected in hydrocarbon glasses,[5] and that ^{1}**4**$\cdot$cyclohexane is detected on the microsecond time scale in room temperature solution,[9b] one would expect that ^{3}**4** should convert to ^{1}**4**$\cdot$heptane over a long time scale. However, this clearly does not happen, at least within about 1 ns, the approximate long time limit of Harris's apparatus. It would be intriguing to look for ^{1}**4**$\cdot$heptane on time scales between 1 ns and 1 μs.[13]

Harris's evidence for ^{3}**4** in solution is consistent with elegant, but perfectly conventional, quantum yield measurements of the photoreaction of [Fe(CO)$_5$] with phosphites[9b] and phosphines, L. [14] At high ratios of L:[Fe(CO)$_5$], which suppress mechanisms involving reaction of [Fe(CO)$_4$] with [Fe(CO)$_5$], photolysis leads to the formation of both [^{1}Fe(CO)$_4$L] and [^{1}Fe(CO)$_3$L$_2$] as primary photoproducts. This is rather surprising since formation of [Fe(CO)$_3$L$_2$] must proceed in solution by a single-photon mechanism; in other words the photochemistry does not involve sequential photolysis of [Fe(CO)$_5$] and [Fe(CO)$_4$L]. The proposed mechanisms[2, 9b, 14] all involve ^{3}**4**, but they differ in what other intermediates are implicated; these include: [^{1}Fe(CO)$_4$] (i.e. ^{1}**4**), [^{1}Fe(CO)$_4$]$\cdot$solvent (i.e. ^{1}**4**$\cdot$solvent), [^{1}Fe(CO)$_3$L]$\cdot$solvent, [^{3}Fe(CO)$_4$L], [^{3}Fe(CO)$_3$L] and [^{3}Fe(CO)$_3$L$_2$]. Very recent picosecond TR-IR results[13] in neat triethylphosphine indicate the presence of [^{3}Fe(CO)$_3$L], but not [^{3}Fe(CO)$_4$L]. Clearly we are some way off pinning down the exact mechanism.

[Fe(CO)$_4$]—The Next Step?

Where does all this leave us? First of all, we have almost entirely ignored recent high-level computational work as well as gas-phase experiments designed to measure the various dissociation energies principally because the results are not always in agreement![15] Thus, although everyone agrees that both ^{3}**4** and ^{1}**4** have C_{2v} structures, the range of bond lengths and bond angles is wide and depends on the details of the calculation. Moreover, although all agree that ^{1}**4** lies above ^{3}**4**, the predicted energy gap varies from about 0.7 to 20 kcal mol^{-1}. Therefore, what would we, as experimentalists, really like to see next? There are three outstanding challenges. It would be marvellous if the structure of gas-phase ^{3}**4** could be unequivocally determined by a "nonsporting" method such as Zewail's diffraction technique; it would be equally enthralling if ^{1}**4** could be unequivocally identified in a "noncomplexing" solvent; finally the ^{1}**4**/^{3}**4** energy gap needs to be measured somehow. We look forward to seeing such results in print!

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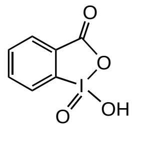
[15] See ref. [1–3] for discussion of values; see also: O. Gonzalez-Blanco, U. Branchadell, *J. Chem. Phys.* **1999**, *110*, 778. It is interesting that calculations in ref. [3] suggest an energy of interaction between ^{1}**4** and C_2H_6 of about 7 kcal mol^{-1}, and a ^{1}**4**/^{3}**4** gap of about 6 kcal mol^{-1}. On this basis, the solvent-stabilized singlet $[Fe(CO)_4]$ (i.e. ^{1}**4** · solvent), has approximately the same energy as ground-state triplet $[Fe(CO)_4]$ (i.e. ^{3}**4**).

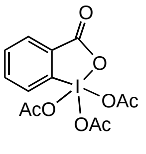
IBX—New Reactions with an Old Reagent

Thomas Wirth*

Hypervalent iodine reagents have attracted increasing interest during the last decade because of their selective, mild, and environmentally friendly properties as oxidizing agents in organic synthesis.[1] 2-Iodoxybenzoic acid (IBX, 1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide **1**) was first reported in 1893[2] but has been rarely used in reactions, probably due to its insolubility in most organic solvents.[3] Dess and Martin transformed IBX (**1**) into the much more soluble Dess–Martin periodinane (DMP, 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one **2**),[3, 4] which has received much attention. Improved procedures for the synthesis of reagents **1** and **2** have been disclosed recently.[5–7]

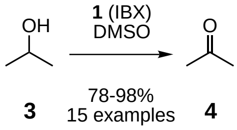


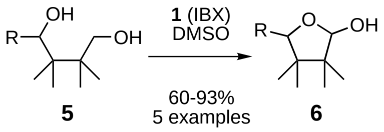
1 (IBX)



2 (DMP)

The broad functional group tolerance of these reagents and high-yielding reactions without over-oxidation have made DMP (**2**) very prominent for the oxidation of alcohols to the corresponding carbonyl compounds. But IBX (**1**) in DMSO was also found to be a highly efficient reagent for the clean oxidation of alcohols **3** to carbonyl compounds **4** even in the presence of thioethers or amines[8, 9] (the number of reported examples are given below the arrows here and in the following). It is also possible to selectively oxidize 1,2-diols to 1,2-diketo derivatives without oxidative cleavage of the glycol C–C bond.[8, 10] The selective oxidation of 1,4-diols **5** to the corresponding γ-lactols **6** can also be realized.[11, 12]





The first step in these oxidation reactions is a fast pre-equilibrium, which can be formally considered as ligand exchange (hydroxy–alkyloxy) on the iodine atom. The product **7** then disproportionates to the carbonyl derivative **4** and the iodosoarene **8** (IBA).[10]

The known paths for the oxidation of alcohols have been extended by recent reports utilizing IBX (**1**) and DMP (**2**)[13] in other transformations. The introduction of an α,β-double bond into carbonyl compounds is sometimes a challenging transformation, which is predominantly performed by using selenium or palladium reagents. A ligand exchange on IBX with the ketone-enolate might be involved in the key step in the mechanism of this new and general procedure. Although the reaction proceeds only at elevated temperatures (65–85 °C), even acid-labile carbonyl compounds can be employed in the process, from which derivatives **9** are obtained in good

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