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Einkernige Verbindungen 2

Mit 29 Figuren

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Hf	Hafnium-Organische Verbindungen (Erg.-Werk, Bd. 11)
Nb	„Niob“ B 4
Ni	Nickel-Organische Verbindungen 1 (Erg.-Werk, Bd. 16), 2 (Erg.-Werk, Bd. 17), Register (Erg.-Werk, Bd. 18) und „Nickel“ B 3 und C
Np, Pu	Transurane C (Erg.-Werk, Bd. 4)
Pt	„Platin“ C und D
Ru	„Ruthenium“ Erg.-Bd.
Sn	Zinn-Organische Verbindungen 1 (Erg.-Werk, Bd. 26), 2 (Erg.-Werk, Bd. 29), 3 (Erg.-Werk, Bd. 30) und 4 (Erg.-Werk, Bd. 35)
Ta	„Tantal“ B 2
Ti	Titan-Organische Verbindungen (Erg.-Werk, Bd. 10)
V	Vanadium-Organische Verbindungen (Erg.-Werk, Bd. 2) und „Vanadium“ B
Zr	Zirkon-Organische Verbindungen (Erg.-Werk, Bd. 10)

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Vorbemerkungen

Der vorliegende Band setzt die Serie B der Eisen-Organischen Verbindungen fort. Er erfaßt die Literatur vollständig bis Ende 1976, vereinzelt auch bis Mitte 1977.

Der Band beschreibt einkernige Eisenverbindungen, die eine $(\text{CO})_4\text{Fe}$ -Gruppe enthalten; er schließt damit an die Behandlung von Verbindungen mit einer bis drei Carbonyl-Gruppen in den Kapiteln 1.1.4.1 bis 1.1.4.4 des Teiles B1 an (Ergänzungswerk, Bd. 36). Wesentliche Abschnitte des Bandes umfassen Eisen-carbonylhydrid, seine Salze und ihre Anwendung in der organischen Synthese, die Halogenide $(\text{CO})_4\text{FeX}_2$, zahlreiche Beispiele des Verbindungstyps $(\text{CO})_4\text{Fe}^2\text{D}$ und Substanzen, bei denen die $(\text{CO})_4\text{Fe}$ -Gruppe an Elemente der 4. Hauptgruppe des Periodensystems und an Übergangsmetalle gebunden ist. Abschließend werden Verbindungen mit ^1L -Liganden und einige Übergangsmetall-Clustercarbonyle beschrieben.

Eisenpentacarbonyl und weitere Verbindungen mit Liganden des ^1L -Typs bilden den Gegenstand eines anschließenden Bandes der Serie B, der für das Jahr 1978 in Vorbereitung ist.

Bezüglich der Formelschreibweise und der verwendeten Symbole wird auf die Vorbemerkungen in „Kobalt-Organische Verbindungen“ 1 und „Nickel-Organische Verbindungen“ 1 (Ergänzungswerk, Bd. 5 und 16) verwiesen. Die Wiedergabe der Daten in abgekürzter Form, besonders in den Tabellen ohne Verwendung von Dimensionen, wird auf S. 200 erläutert. Weitere Bemerkungen dazu finden sich im Text vor den Tabellen. Verweise auf Seiten, Tabellen und Figuren beziehen sich nur auf diesen Band; Hinweise auf Kapitel (Kennzahlen) gelten sowohl für diesen Band als auch für Teil B1.

Dieser Band enthält ein Summenformelregister (S. 201) und Ligandenformelregister (S. 225), alle Substanzen umfassend, die in den Teilen B1 und B2 der Eisen-Organischen Verbindungen behandelt sind.

Frankfurt am Main
Januar 1978

Ulrich Krüerke

Preface

The present volume continues series B of the organoiron compounds. It covers the literature completely to the end of 1976 and extends occasionally to mid-1977.

This volume describes mononuclear iron compounds containing a $(\text{CO})_4\text{Fe}$ group; thus it follows the treatment of compounds with one to three carbonyl groups in Chapters 1.1.4.1 to 1.1.4.4 of Part B1 (New Supplement Series, Vol. 36). Essential sections of this volume comprise iron carbonyl hydride, its salts and their application in organic synthesis, the halides $(\text{CO})_4\text{FeX}_2$, numerous examples of the $(\text{CO})_4\text{Fe}^{2\text{D}}$ type, and substances containing the $(\text{CO})_4\text{Fe}$ unit bound to Group IVA elements and transition metals. The volume concludes with compounds containing ^1L ligands and with some transition metal cluster carbonyls.

Iron pentacarbonyl and other compounds with ligands of the ^1L type will be the matter of a subsequent volume of the series B, being in preparation for the year 1978.

As to the formulas and symbols used the reader is referred to the prefaces in "Kobalt-Organische Verbindungen" 1 and "Nickel-Organische Verbindungen" 1 (New Supplement Series, Vols. 5 and 16, respectively). The presentation of the data in an abbreviated form, particularly in the tables without use of dimensions, is explained on p. 200. Additional remarks, if necessary, are given in the text heading the tables. Indications to pages, tables, and illustrations refer only to this volume; references to chapters (identification numbers) are to be made to this volume as well as to Part B1.

This volume contains an empirical formula index (p. 201) and a ligand formula index (p. 225) comprising all substances treated in the Parts B1 and B2 of Organoiron Compounds.

Frankfurt am Main
January 1978

Ulrich Krüerke

Inhaltsverzeichnis

(Table of Contents see page II)

	Seite
1.1.4.5 Verbindungen mit vier CO-Gruppen	1
1.1.4.5.1 Das $\text{Fe}(\text{CO})_4$-Radikal und seine Matrix-Verbindungen	1
1.1.4.5.2 $\text{H}_2\text{Fe}(\text{CO})_4$, seine Anionen und Salze	5
$\text{H}_2\text{Fe}(\text{CO})_4$	7
Die $[\text{HFe}(\text{CO})_4]^-$ - und $[\text{Fe}(\text{CO})_4]^{2-}$ -Anionen und ihre Salze	13
Darstellung und Charakterisierung der Anionen und Salze	13
Allgemeine Darstellungsmethoden	13
Die $[\text{HFe}(\text{CO})_4]^-$ - und $[\text{Fe}(\text{CO})_4]^{2-}$ -Anionen	14
Die einzelnen Salze	17
Chemisches Verhalten der Tetracarbonylferrate	25
Allgemeine Eigenschaften	25
Anorganische und metallorganische Reaktionspartner	26
Organische Reaktionspartner	31
Verwendung in der organischen Synthese	33
Addukte und andere Verbindungen	48
1.1.4.5.3 Ionenverbindungen vom Typ $\text{M}[(\text{CO})_4\text{FeX}]$	50
1.1.4.5.4 Verbindungen vom Typ $(\text{CO})_4\text{FeX}_2$	53
Darstellung und Bildung	54
Physikalische Eigenschaften und Struktur	56
Chemisches Verhalten	62
1.1.4.5.5 Verbindungen vom Typ $(\text{CO})_4\text{Fe(X)Y}$	69
1.1.4.5.6 Verbindungen vom Typ $(\text{CO})_4\text{Fe}^2\text{D}$	69
Verbindungen mit N-Donor-Liganden	70
Verbindungen mit P-, As-, Sb-Donor-Liganden	81
Verbindungen mit O-, S-, Te-Donor-Liganden	128
1.1.4.5.7 Verbindungen mit Fe-B-Bindungen	133
1.1.4.5.8 Verbindungen mit Fe-E^{IV}-Bindungen, wobei E^{IV}=Si, Ge, Sn, Pb	135
1.1.4.5.9 Verbindungen mit Fe-E^V-Bindungen, wobei E^V=As und Sb	152
1.1.4.5.10 Verbindungen mit Bindungen zwischen Fe und Übergangsmetallen	153
Verbindungen mit Fe-Hg-Bindungen	153
Verbindungen mit Fe-M-Bindungen, wobei M=Cr, Mn, Re, Pd, Pt, Cu, Ag, Au	162
Verbindungen vom Typ $(\text{CO})_4\text{Fe}(\text{ER}_2)\text{M}'$, M'=Übergangsmetallcarbonyl-Gruppe, E=P, As	169
Weitere Verbindungen unbekannter Struktur	173
1.1.4.5.11 Verbindungen mit einem ¹L-Liganden	173
Salze der $[(\text{CO})_4\text{FeR}]^-$ -Ionen	173
Verbindungen vom Typ $(\text{CO})_4\text{Fe(R)X}$	176
Verbindungen vom Typ $(\text{CO})_4\text{Fe}(\text{}^1\text{L-X})$	183
Verbindungen mit Ionen vom Typ $[(\text{CO})_4\text{Fe}(\text{}^1\text{L-}^2\text{D})]$	188
Verbindungen mit einem $(\text{CO})_4\text{Fe}(\text{}^1\text{L-E})$ -Ringskelett, E=Si, Co	189
1.1.4.5.12 Verbindungen mit zwei ¹L-Liganden	190
1.1.4.6 Clusterverbindungen mit einer $(\text{CO})_n\text{Fe}$-Gruppe	194
Summenformelregister	201
Ligandenformelregister	225

Table of Contents

(Inhaltsverzeichnis s. S. I)

	Page
1.1.4.5 Compounds with Four CO Groups	1
1.1.4.5.1 The $\text{Fe}(\text{CO})_4$ Radical and Its Matrix Compounds	1
1.1.4.5.2 $\text{H}_2\text{Fe}(\text{CO})_4$, Its Anions and Salts	5
$\text{H}_2\text{Fe}(\text{CO})_4$	7
The $[\text{HFe}(\text{CO})_4]^-$ and $[\text{Fe}(\text{CO})_4]^{2-}$ Anions and Their Salts	13
Preparation and Characterization of the Anions and Salts	13
General Methods of Preparation	13
The $[\text{HFe}(\text{CO})_4]^-$ and $[\text{Fe}(\text{CO})_4]^{2-}$ Anions	14
Individual Salts	17
Chemical Behavior of Tetracarbonylferrates	25
General Properties	25
Inorganic and Organometallic Reaction Partners	26
Organic Reactions Partners	31
Applications in Organic Synthesis	33
Adducts and Other Compounds	48
1.1.4.5.3 Ionic Compounds of the $\text{M}[(\text{CO})_4\text{FeX}]$ Type	50
1.1.4.5.4 Compounds of the $(\text{CO})_4\text{FeX}_2$ Type	53
Preparation and Formation	54
Physical Properties and Structure	56
Chemical Behavior	62
1.1.4.5.5 Compounds of the $(\text{CO})_4\text{Fe(X)Y}$ Type	69
1.1.4.5.6 Compounds of the $(\text{CO})_4\text{Fe}^2\text{D}$ Type	69
Compounds with N-Donor Ligands	70
Compounds with P-, As-, Sb-Donor Ligands	81
Compounds with O-, S-, Te-Donor Ligands	128
1.1.4.5.7 Compounds with Fe-B Bonds	133
1.1.4.5.8 Compounds with Fe-E^{IV} Bonds, where $\text{E}^{\text{IV}} = \text{Si, Ge, Sn, Pb}$	135
1.1.4.5.9 Compounds with Fe-E^{V} Bonds, where $\text{E}^{\text{V}} = \text{As and Sb}$	152
1.1.4.5.10 Compounds with Bonds between Fe and Transition Metals	153
Compounds with Fe-Hg Bonds	153
Compounds with Fe-M Bonds, where $\text{M} = \text{Cr, Mn, Re, Pd, Pt, Cu, Ag, Au}$	162
Compounds of the $(\text{CO})_4\text{Fe}(\text{ER}_2)\text{M}'$ Type, $\text{M}' = \text{transition metal carbonyl group, E} = \text{P, As}$	169
Other Compounds of Unknown Structure	173
1.1.4.5.11 Compounds with One ^1L Ligand	173
Salts Containing $[(\text{CO})_4\text{FeR}]^-$ Ions	173
Compounds of the $(\text{CO})_4\text{Fe(R)X}$ Type	176
Compounds of the $(\text{CO})_4\text{Fe}(^1\text{L-X})$ Type	183
Compounds Containing Ions of the $[(\text{CO})_4\text{Fe}(^1\text{L-}^2\text{D})]$ Type	188
Compounds with a $(\text{CO})_4\text{Fe}(^1\text{L-E})$ Ring Skeleton, $\text{E} = \text{Si, Co}$	189
1.1.4.5.12 Compounds with Two ^1L Ligands	190
1.1.4.6 Cluster Compounds Containing One $(\text{CO})_n\text{Fe}$ Group	194
Empirical Formula Index	201
Ligand Formula Index	225

Eisen-Organische Verbindungen, Teil B

Einkernige Verbindungen 2

1.1.4.5 Compounds with Four CO Groups

1.1.4.5.1 The $\text{Fe}(\text{CO})_4$ Radical and Its Matrix Compounds

General literature:

J.J. Turner, J.K. Burdett, R.N. Perutz, M. Poliakoff, Matrix Photochemistry of Metal Carbonyls, *Pure Appl. Chem.* **49** [1977] 271/85.

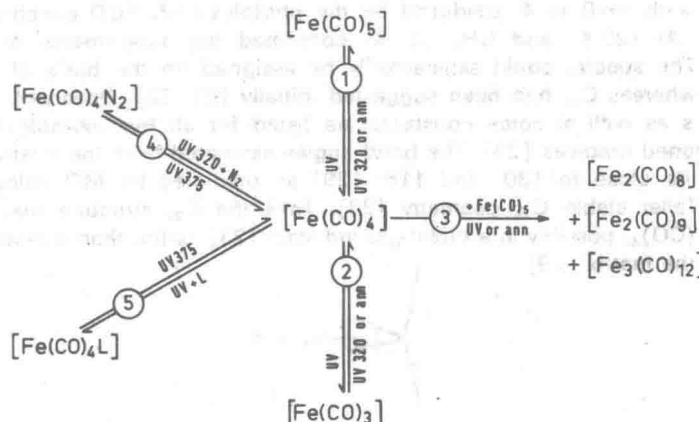
Compounds with Four CO Groups
The $\text{Fe}(\text{CO})_4$ Radical and Its Matrix Compounds

Triiron dodecacarbonyl has been formulated in the older literature as "iron tetracarbonyl, $\text{Fe}(\text{CO})_4$ " [3] since reliable determinations of molecular weight were lacking at that time. The trimeric formula $\text{Fe}_3(\text{CO})_{12}$ was definitely established by Hieber and Becker in 1930 [1]; nevertheless, " $\text{Fe}(\text{CO})_4$ " has been used in stoichiometric equations further on as an abbreviation for $\text{Fe}_3(\text{CO})_{12}$, cf. [2, 4].

The $\text{Fe}(\text{CO})_4$ radical in matrices

Formation and structure: The earliest spectroscopic trace of an "intermediate iron carbonyl species" [7], later shown to be $[\text{Fe}(\text{CO})_4(\text{glass})]$ [29], was the appearance of new CO stretching bands at 1946, 1980 and 1990 cm^{-1} in the IR spectrum of $\text{Fe}(\text{CO})_5$ irradiated in 1:4 methylcyclohexane/isopentane glass at 93 K [7]. Another band observed at 1834 cm^{-1} on melting the glass was first attributed to a "tetracoordinated iron carbonyl" [6] but may have been due to the formation of $\text{Fe}_2(\text{CO})_9$ [22, 29].

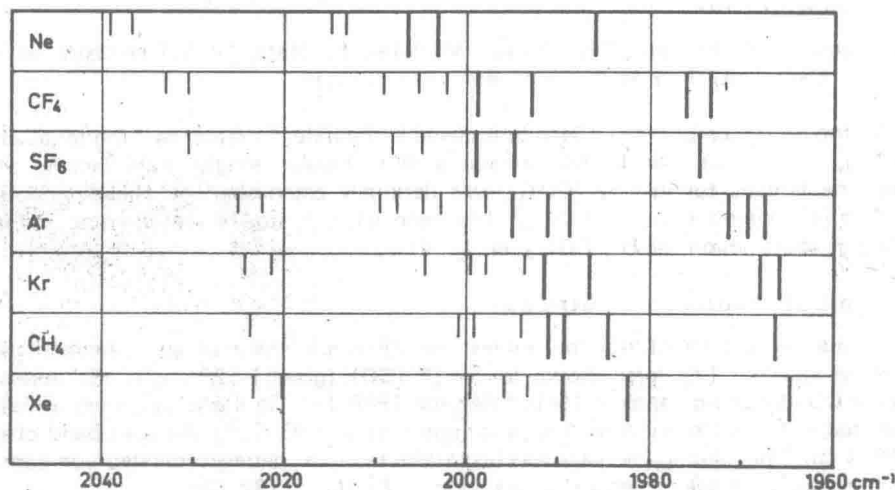
The formation of $[\text{Fe}(\text{CO})_4]$ by photolysis in various matrices at 20 K and its photochemical transformations have recently been studied extensively by IR spectroscopy [21, 22, 29, 39]. The results are summarized in the scheme below [21, 29] using the following symbols: UV=photolysis with a medium-pressure mercury arc, UV 320 and UV 375=irradiation with $\lambda=320$ and 375 nm respectively, ann=annealing matrix at 35 K and L= CH_4 or Xe.



When $\text{Fe}(\text{CO})_5$ is subjected to UV photolysis in various matrices (1:2000 molar ratio) at 4 K (reaction 1), new CO bands of $[\text{Fe}(\text{CO})_4]$ appear in the low frequency region of the original compound, Fig. 1. The liberated, matrix-isolated CO can be detected by its band at 2144 cm^{-1} [22]. Exact values of the bands which show an overall "solvent shift" to low frequencies for both $[\text{Fe}(\text{CO})_4]$ and $[\text{Fe}(\text{CO})_5]$ when the matrix is changed from Ne to Xe are given in [29]:

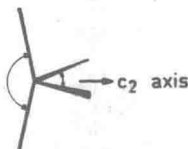
Matrix		SF_6 (35 K)	Ar (20 K)	CH_4 (20 K)	Xe (20 K)
Vibrational modes (C_{2v}) in cm^{-1}	A_1	1999.1	1995.3	1992.3	1989
	B_1	1994.1	1988.5	1985	1983
	B_2	1974.3	1973.3	1966.5	1967

Fig. 1



Schematic representation of the CO stretching frequencies in various matrices for $[\text{Fe}(\text{CO})_5]$ (short lines) and $[\text{Fe}(\text{CO})_4]$ (long lines) [22].

The high-frequency A_1 vibration is very weak or overlaps with other bands, its position has been calculated to be at 2087.88 cm^{-1} . The IR spectra of isotopic species $[\text{Fe}(\text{CO})_n - (^{13}\text{CO})_{4-n}]$ with $n=0$ to 4, produced by the photolysis of ^{13}CO -enriched $\text{Fe}(\text{CO})_5$ in SF_6 (35 K), Ar (20 K) and CH_4 (20 K) confirmed the assignments of IR bands to $[\text{Fe}(\text{CO})_4]$. The spectra could satisfactorily be assigned on the basis of C_{2v} symmetry [29], see I, whereas C_{3v} had been suggested initially [21, 22]. Observed and calculated wavenumbers as well as force constants are listed for all five isotopic species in the above-mentioned matrices [29]. The bond angles estimated from the relative band intensities are quite close to 130° and 115° [29] as predicted by MO calculations based on a Jahn-Teller stable C_{2v} geometry [23]. Thus the C_{2v} structure may well be that of "free" $\text{Fe}(\text{CO})_4$, possibly in a triplet ground state [23], rather than a result of distortion imposed by the matrix [29].



UV spectra of $[\text{Fe}(\text{CO})_4]/[\text{Fe}(\text{CO})_5]$ in Ne, SF_6 , Ar and CH_4 show overlapping bands and a broad absorption at 320 ± 10 nm due to $[\text{Fe}(\text{CO})_4]$ [22].

Reactions of $[\text{Fe}(\text{CO})_4]$ and matrix complexes: After short UV photolysis, e.g. a few minutes in Ne at 4 K, reaction (1) is reversible. Irradiation with light from a Nernst glower or warming the matrix and recooling to 20 K (annealing) causes the bands of $[\text{Fe}(\text{CO})_4]$ and CO to disappear. The photochemical reversal of (1) is essentially a thermal process also due to tail absorption of the 320 nm band of $[\text{Fe}(\text{CO})_4]$. This behaviour has been found in many of the matrices although not always totally reversible [22].

On prolonged photolysis, e.g. 225 min at 20 K, reaction (1) in Ar is no longer reversible; it causes sufficient local melting to allow the CO molecule to diffuse away from the $[\text{Fe}(\text{CO})_4]$ site preventing recombination [22]. As to further photolytic cleavage of $[\text{Fe}(\text{CO})_4]$, reaction (2); and the formation of iron atoms [28], see Chapter 1.1.4.4.1.

$[\text{Fe}(\text{CO})_4]$ appears to be exceedingly reactive [21, 29]. The IR spectra observed on short photolysis of $[\text{Fe}(\text{CO})_5]$ in N_2 , Ar/ N_2 (5%), CH_4 , Kr and Xe matrices and subsequent irradiation with unfiltered light from the Nernst glower at 20 K indicate besides $[\text{Fe}(\text{CO})_4]$ the formation of $[\text{Fe}(\text{CO})_4\text{N}_2]$ and $[\text{Fe}(\text{CO})_4\text{L}]$ (L= CH_4 , Xe and possibly Kr) [29]. No reaction with CH_4 occurs on annealing the matrix; it can be promoted, however, with radiation from a CO laser at 1923 and 1931 cm^{-1} . Among nine possible molecules of $[\text{Fe}(\text{CO})_n(^{13}\text{CO})_{4-n}]$ with different stereochemical arrangements, the few are excited which have $\nu(\text{CO})$ bands at 1922 and 1932 cm^{-1} and yield the corresponding species of $[\text{Fe}(\text{CO})_n(^{13}\text{CO})_{4-n}\text{CH}_4]$ [39]. CO wave numbers are given for the complexes with L= CH_4 and Xe at 20 K [29] including L=hydrocarbon glass [7, 29]. Observed and calculated values for the complexes $[\text{Fe}(\text{CO})_n(^{13}\text{CO})_{4-n}\text{CH}_4]$ are compared and assigned to the different species [29].

Another matrix complex, $[\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4]$, has been cited as product of the photolysis of $\text{Fe}(\text{CO})_5/\text{CH}_2=\text{CH}_2$ (1:10) at high concentration in Ar (100) at 17 K [40].

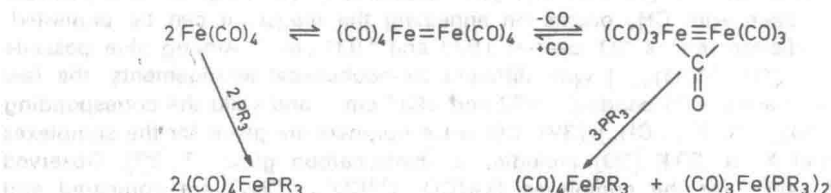
On photolysis of $[\text{Fe}(\text{CO})_5]$ at higher concentration in CH_4 (1:1000) at 20 K, bands appear which can reasonably be assigned to terminal and bridging CO groups of $[\text{Fe}_3(\text{CO})_{12}]$ and $[\text{Fe}_2(\text{CO})_9]$ (2020 to 2060 cm^{-1} and 1820 to 1870 cm^{-1} respectively). Other bands which appear on annealing the matrix belong to $[\text{Fe}_2(\text{CO})_9]$. These results are consistent with $[\text{Fe}(\text{CO})_4]$ being an intermediate in the photochemical formation of polynuclear iron carbonyls [29].

Vacuum UV photolysis of $\text{Fe}(\text{CO})_5$ in Ar (1:8000) at 12 K is believed to give a $[\text{Fe}(\text{CO})_4]^-$ species based on two $\nu(\text{CO})$ at about 1850 cm^{-1} which occur midway between those of $[\text{Fe}(\text{CO})_4]^{2-}$ and $[\text{Fe}(\text{CO})_4]$ [18]; other authors, e.g. [29], did not comment on this interpretation.

$\text{Fe}(\text{CO})_4$ as intermediate species

$\text{Fe}(\text{CO})_4$ was thought quite early to be the first intermediate in the action of light on $\text{Fe}(\text{CO})_5$, e.g. in the standard method of preparing $\text{Fe}_2(\text{CO})_9$ [5]. This is explained by a low energy electronic d-d transition ($5e' \rightarrow 5a_1'$) of $\text{Fe}(\text{CO})_5$ which leads to a weakening of an axial Fe-CO bond [13]. Thus the $\text{Fe}(\text{CO})_4$ radical is frequently formulated in photochemical reactions of $\text{Fe}(\text{CO})_5$ and it is supposed to have been detected by flash spectroscopy [10, 14, 34]. It accounts for the formation of $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$ if produced in sufficiently high concentration. It reacts with olefins to give complexes of the type $^2\text{LFe}(\text{CO})_4$ and it reduces aromatic nitro compounds to nitroso compounds

Amine oxides, preferably $(\text{CH}_3)_3\text{NO}$, appear to be capable of generating the $\text{Fe}(\text{CO})_4$ radical from $\text{Fe}(\text{CO})_5$ as in the presence of dienes a reaction occurs instantly at 0°C in benzene to yield compounds of the $^4\text{LF}(\text{Fe}(\text{CO})_3)$ type [37]. $\text{Fe}(\text{CO})_4$ has also been proposed as intermediate in the back-conversion of $\text{Fe}_2(\text{CO})_9$ in hydrocarbon suspension to $\text{Fe}(\text{CO})_5$ by C^{18}O ; but it seems that some other active intermediate is present which exchanges rapidly with C^{18}O [12]. In fact, similar reactions of $\text{Fe}_2(\text{CO})_9$ with phosphines to give the complex types $(\text{CO})_4\text{Fe}^2\text{D}$ and $(\text{CO})_3\text{Fe}^2(\text{D})_2$ indicate that $\text{Fe}(\text{CO})_4$ cannot be a direct precursor for $(\text{CO})_3\text{Fe}^2(\text{D})_2$ [15]. In analogy to the photochemical behaviour of π -(cyclo- C_4H_4) $\text{Fe}(\text{CO})_3$ dimeric species as shown below may explain the formation of the disubstituted compounds $(\text{CO})_3\text{Fe}^2(\text{D})_2$ under conditions where $(\text{CO})_4\text{Fe}^2\text{D}$ is immune to attack by a ^2D molecule [33]:



$\text{Fe}(\text{CO})_4$ can be generated photolytically from $^2\text{LFe}(\text{CO})_4$ (^2L = olefin) [35] but it also occurs in the thermal dissociation of less stable species, e.g. π -(cis-CHC=CHCl)- $\text{Fe}(\text{CO})_4$ in solution at room temperature. This is evidenced by the spontaneous formation of $\text{Fe}_3(\text{CO})_{12}$ and the reaction with $\text{Fe}(\text{CO})_5$ in excess to give $\text{Fe}_2(\text{CO})_9$ in a non-photochemical way [20], see also [11].

The formation of $\text{Fe}(\text{CO})_4$ has also been inferred from kinetic measurements of the following reactions: the replacement of an olefin ligand in $^2\text{LFe}(\text{CO})_4$ by CO [17] or ^2D ligands as $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$ [24], $\text{Sb}(\text{C}_6\text{H}_5)_3$ [19, 24] and pyridine [24], the transformation of the olefin complexes $(\pi\text{-C}_5\text{H}_5\text{CH=CH-CO-R})\text{Fe}(\text{CO})_4$ into 1,3-heterodiene compounds of the type $(\pi\text{-C}_5\text{H}_5\text{CH=CH-C(R)=O})\text{Fe}(\text{CO})_3$ [30] and the substitution of $(\text{CO})_4\text{FeX}_2$ ($\text{X}=\text{Br}, \text{I}$) with donor molecules to give $(\text{CO})_3\text{Fe}(^2\text{D})\text{X}_2$ [8, 9]. An order of reactivity of $\text{Fe}(\text{CO})_4$ towards various donor molecules and olefins is given in [19, 24].

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1.1.4.5.2 $H_2Fe(CO)_4$, Its Anions and Salts

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$H_2Fe(CO)_4$
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