

Gmelin Handbook of Inorganic Chemistry

8th Edition

viii

Fe Organoiron Compounds

Part C7

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8th Edition

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8th Edition

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The following listing indicates in which volumes these compounds are discussed or are referred to:

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Au	Organogold Compounds (1980)
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Hf	Organohafnium Compounds (1973)
Nb	Niob B 4 (1973)
Ni	Nickel-Organische Verbindungen 1 (1975), 2 (1974), Register (1975), Nickel B 3 (1966), C 1 (1968), C 2 (1969)
Np, Pu	Transurane C (partly in English; 1972)
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Ru	Ruthenium Erg.-Bd. (1970)
Sb	Organoantimony Compounds 1 (1981), 2 (1981), 3 (1982)
Sc, Y, La to Lu	D 6 (1983)
Sn	Zinn-Organische Verbindungen 1 (1975), 2 (1975), 3 (1976), 4 (1976), 5 (1978), 6 (1979), Organotin Compounds 7 (1980), 8 (1981), 9 (1982), 10 (1983), 11 (1984), 12 (1985)
Ta	Tantal B 2 (1971)
Ti	Titan-Organische Verbindungen 1 (1977), 2 (1980) 3 (1984), 4 and Register (1984)
U	Uranium Suppl. Vol. E 2 (1980)
V	Vanadium-Organische Verbindungen (1971), Vanadium B (1967)
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Gmelin Handbook of Inorganic Chemistry

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Fe Organoiron Compounds

Part C7

Polynuclear Compounds 7

With 134 illustrations

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Preface

The present volume is a continuation of Series C on the polynuclear organoiron compounds. It covers the literature completely to the end of 1984 and includes many references to the literature up to mid-1985.

For technical reasons, the present volume C7 was edited before volume C6, which will deal with a part of the trinuclear organoiron compounds, i.e., all those containing ligands of the 1L type up to compounds with the $Fe_3(CO)_{11}$ unit. Therefore, the present volume C7 begins with $Fe_3(CO)_{12}$ and concludes the second part of the trinuclear compounds, followed by tetranuclear compounds as another quite extended group of products, and all compounds with more than four iron atoms.

The particular features of cluster compounds with four or more iron atoms, and the limited number of different types of carbon ligands (nL) occurring with these clusters, obviated the usual arrangement of compounds by the type of nL ligand and necessitated the arrangement within each main section on typical structural elements. This was possible due to the X-ray diffraction studies available now in this field. More information is given in the introductory remarks for the tetranuclear compounds on p. 194.

It has not always been possible to indicate the compounds in a chapter exactly by general formulas in the chapter heading. In these cases the user is referred to the introductory remarks at the beginning of the chapter, where the compounds are more precisely characterized.

Formulas and symbols have been explained in the prefaces to "Kobalt-Organische Verbindungen" 1, New Suppl. Ser., Vol. 5, and "Nickel-Organische Verbindungen" 1, New Suppl. Ser., Vol. 16. Much of the data, particularly in tables, is given in abbreviated form without dimensions; for explanations see p. VIII. Additional remarks, if necessary, are given in the texts heading the tables. The location of substances in other organoiron volumes is given in the form "B4, 1.1.6.1", i.e., Series B (mononuclear compounds), Volume 4, Section 1.1.6.1, or "C3, 2.4.1.1.1", i.e., Series C (polynuclear compounds), Volume 3, Section 2.4.1.1.1.

The volume contains an empirical formula index on p. 383 and a ligand formula index on p. 395.

Frankfurt am Main, December 1985

Ulrich Krüerke

Explanations, Abbreviations, and Units

Many compounds in this volume are presented in tables in which numerous abbreviations are used and the units are omitted for the sake of conciseness. This necessitates the following clarification.

The term "special" in the second column of the tables indicates preparative methods which are described under the further information section following the table.

Temperatures are given in °C, otherwise K stands for Kelvin. Abbreviations used with temperatures are m.p. for melting point, b.p. for boiling point, dec. for decomposition, and subl. for sublimation. Terms like 80°/0.1 mean the boiling or sublimation point at a pressure of 0.1 Torr. **Densities** D are given in g/cm³. D_c and D_m distinguish calculated and measured values, respectively.

NMR represents **nuclear magnetic resonance**. Chemical shifts are given as δ values in ppm; reference substances and signs for δ are shown in the scheme below.

	increasing field →		
		I	
		$\delta = 0$ for	
¹ H	+	Si(CH ₃) ₄	—
¹¹ B	+	BF ₃ · O(C ₂ H ₅) ₂	—
¹³ C	+	Si(CH ₃) ₄	—
¹⁹ F	+	CFCl ₃	—
³¹ P	+	H ₃ PO ₄	—

Coupling constants J in Hz appear usually in parentheses behind the δ value, along with the multiplicity and the assignment, and refer to the respective nucleus. If a more precise designation is necessary, they are given as, e.g., ⁿJ(C,H) or J(1,3) referring to labelled formulas.

Multiplicities of the signals are abbreviated as s, d, t, q (singlet to quartet), quint, sext, sept, oct (quintet to octet), and m (multiplet); terms like dd (double doublet) and t's (triplets) are also used. Assignments referring to labelled structural formulas are given in the form C-4, H-3, 5. The numbering deviates in some cases from official nomenclature so that corresponding values for compounds in the same chapter can be more easily compared.

Mössbauer spectra are represented by ⁵⁷Fe- γ and ¹¹⁹Sn- γ ; both the isomer shift δ (vs. Na₂[Fe(CN)₅NO] or BaSnO₃ at room temperature) and the quadrupole splitting Δ are given in mm/s; the experimental error has generally been omitted. Other reference substances for δ are indicated after the numerical value, e.g., $\delta = 0.23$ (Fe).

Optical spectra are labelled as IR (infrared), R (Raman), and UV (electronic spectrum including the visible region). IR bands and Raman lines are given in cm⁻¹; the assigned bands are usually labelled with the symbols ν for stretching vibration and δ for deformation vibration. Intensities occur in parentheses either in the common qualitative terms (s, m, w, vs, etc.) or as numerical relative intensities. The UV absorption maxima, λ_{\max} , are given in nm followed by the extinction coefficient ϵ (L · cm⁻¹ · mol⁻¹) or log ϵ in parentheses; sh means shoulder.

Solvents, or the physical state of the sample, and the temperature (in °C or K) are given in parentheses immediately after the spectral symbol, e.g., R(solid), ¹³C NMR (C₆D₆, 50 °C). Common solvents are given by their formula (C₆H₁₂ = cyclohexane) except THF, which represents tetrahydrofuran.

References, quoted in the last column, are occasionally also placed in the first and second column if statements from different sources must be distinguished.

Figures give only selected parameters. Barred bond lengths (in Å) or angles are mean values for parameters of the same type.

Other symbols occasionally used are Cp* for substituted cyclopentadienyl, Fp for $(C_5H_5Fe(CO)_2)_2$, fc for $Fe(C_5H_5)_2$, and CO_t and CO_b for terminal and bridging carbonyl groups, respectively.

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Organoiron Compounds, Part C

Polynuclear Compounds 7

3 Trinuclear Compounds (continued)

A selection of General References relating to n-nuclear compounds with $n \geq 3$ is given at the beginning of Chapter 4 on p. 192.

3.1 Compounds with Ligands Bonded by One Carbon Atom (continued)

Trinuclear compounds with 1L ligands are mostly carbonyl compounds containing other non-carbon ligands as terminal or bridging groups. Therefore, they are arranged by the increasing number of carbonyl ligands. $Fe_3(CO)_n$ compounds with $n < 12$ are going to be described in previous chapters (3.1.1 to 3.1.9) and, for technical reasons, will be edited as Volume C6 after the present volume C7. Thus the present volume begins with $Fe_3(CO)_n$ compounds where $n \geq 12$.

3.1.10 Compounds with Twelve Carbonyl Ligands

3.1.10.1 Triliron Dodecacarbonyl, $Fe_3(CO)_{12}$

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The series authored by M.I. Bruce, Advan. Organometal. Chem. **12** [1974] 380/407, **11** [1973] 448/71, and **10** [1972] 274/346, provide a source of information for the period between 1950 and 1972.

3.1.10.1.1 Preparation and Formation

$\text{Fe}_3(\text{CO})_{12}$ is prepared from $\text{Fe}(\text{CO})_5$ by two methods. In Method I, the anion $[\text{HFe}(\text{CO})_4]^-$ is oxidized by various oxidation agents, followed by acidification. In Method II, $\text{Fe}(\text{CO})_5$ is treated with tertiary amines (disproportionation), also followed by acidification.

Method I was developed by Hieber and co-workers [3, 6, 8, 14, 16]. Detailed preparative instructions for improved scaled-up versions with yields between 40 and 90 g are given in [24, 29, 33, 52].

The anion $[\text{HFe}(\text{CO})_4]^-$ is prepared from $\text{Fe}(\text{CO})_5$, CH_3OH , and 50% aqueous NaOH (see B2, p. 13). To avoid base reactions of the product, the solution is buffered with NH_4Cl before oxidation [14, 16, 28]. Various oxidizing agents have been tested: MnO_2 , KMnO_4 , $\text{K}_2\text{S}_2\text{O}_8$ [8], and H_2O_2 [8, 9]. If H_2O_2 is used as the oxidizing agent, the yield is improved by addition of equimolar amounts of urea to stabilize the hydrogen peroxide [8]. Optimum yield is obtained with specially prepared active MnO_2 [8]. In the earlier literature, it is prepared from MnSO_4 with Br_2/NaOH [6, 8, 24], but the use of Br_2 can be avoided by treating aqueous KMnO_4 with excess $\text{C}_2\text{H}_5\text{OH}$ [21, 23, 52]. The MnO_2 suspension is added to the solution of $[\text{HFe}(\text{CO})_4]^-$, and cooled with ice. An exothermic reaction occurs and the mixture becomes deep red. To guarantee complete oxidation, the reaction mixture is stirred for at least 1 h. The excess of MnO_2 is best removed with aqueous FeSO_4 acidified with H_2SO_4 . Addition of NaHSO_3 is less suitable since it diminishes the yield due to carbonyl sulfide formation [14, 16, 19]. Upon addition of 50% H_2SO_4 to the oxidized solution $\text{Fe}_3(\text{CO})_{12}$ precipitates. After washing the filtered product (see below) the yield is 70 to 90% [29], but only 60 to 70% in the scaled-up version starting with ~ 0.8 mol $\text{Fe}(\text{CO})_5$ [33].

Method II, the action of strongly basic amines on $\text{Fe}(\text{CO})_5$, followed by acidification, is a large scale operation with little manipulation.

A slight excess of $\text{N}(\text{C}_2\text{H}_5)_3$ and $\text{Fe}(\text{CO})_5$ are stirred in air-free water at 80 °C for 10 h to give the polynuclear salt $[\text{NHR}_3][\text{HFe}_3(\text{CO})_{11}]$ which is treated in methanolic solution with a 1:1 $\text{HCl}/\text{H}_2\text{O}$ mixture for several hours on a waterbath until $\text{Fe}_3(\text{CO})_{12}$ is floating on the surface. The yield, $\sim 70\%$, is somewhat variable and rather sensitive to the conditions [34].

The salt ($R = C_2H_5$ or *N*-methylpyrrolidine) can also be treated with $HCOOH$ or CH_3COOH between ambient temperature and $60^\circ C$ or with solutions of CCl_3COOH in CH_3COOH or HCl in CH_3OH [13]. It is noted that the procedure is cheaper and takes less time if the polynuclear anion is prepared with alkali hydroxide and aqueous NH_3 . $Fe(CO)_5$ and aqueous $NaOH$ (1:2 mole ratio) are stirred at $20^\circ C$ for 1 h, NH_3 solution (mole ratio $Fe(CO)_5:NH_3 = 1.3$) is added, and the mixture is kept at $50^\circ C$ for 2 h. Acidification with 50% H_2SO_4 gives $Fe_3(CO)_{12}$ in a yield of 65% based on $Fe(CO)_5$ [39].

The $Fe_3(CO)_{12}$ prepared by Method I is first washed with hot, dilute H_2SO_4 and then (for both methods) successively with water, methanol or ethanol, and petroleum ether, pentane, or hexane [8, 13, 24, 29, 33, 34, 39, 52]. The product is sometimes obtained as a fine pyrophoric powder when dry. This can be avoided by extraction of the crude material with petroleum ether or pentane in a Soxhlet apparatus which results in a highly pure compound with comparatively large crystals [14, 16, 29, 34]. Recrystallization is from toluene or acetone [11], acetone/water [28], ether/hexane [40], or benzene/petroleum ether, followed by chromatography on Florisil with pentane as the eluent [37]. For complete absence of traces of water and ethanol it is dried for several hours at $25^\circ C/0.1$ Torr [33]. Highly pure $Fe_3(CO)_{12}$ is obtained by sublimation at $60^\circ C$ in the high vacuum [29, 33, 52].

$Fe_3(CO)_{12}$ is also obtained in about 10% yield by heating $Fe_2(CO)_9$ in toluene either in an evacuated tube at $90^\circ C$ [11] or in a flask at $70^\circ C$ [10] which results in good crystals on cooling (also see earlier reports in "Eisen" B, 1930, p. 482). Sonication of $Fe(CO)_5$, neat or in hydrocarbon solvents, produces $Fe_3(CO)_{12}$ along with finely divided iron powder. Initial formation of an $Fe(CO)_3$ species which reacts sequentially with two $Fe(CO)_5$ molecules in solution is suggested [53].

Small amounts of $Fe_3(CO)_{12}$ are formed along with $Fe_2(CO)_9$ as the main product upon ^{60}Co - γ irradiation of liquid $Fe(CO)_5$ [26] or dilute cyclohexane solutions at 20 to $25^\circ C$ [27, 30, 31]. The $Fe_2(CO)_9$ to $Fe_3(CO)_{12}$ ratio depends on the nature of the solvent, and the formation of $Fe_3(CO)_{12}$ is nearly completely suppressed in aromatic solvents like benzene or toluene [31, 35, 36] (also see C2, pp. 25/6). From the fact that $Fe_3(CO)_{12}$ forms even at $-18^\circ C$ from liquid $Fe(CO)_5$, and that addition of $Fe_2(CO)_9$ does not increase the yield (given in G=number of molecules formed per 100 eV), a primary reaction mechanism is deduced [26, 31]. The influence of the solvent on energy transfer is unknown [27, 30, 35, 36]. The influence of various additives upon the $Fe_2(CO)_9$ to $Fe_3(CO)_{12}$ ratio in cyclohexane and benzene is shown in a table [36].

Neutron irradiation of $Fe(CO)_5$ gives radioactive $Fe_3(CO)_{12}$ along with approximately 41% of retention. The yield of $Fe_3(CO)_{12}$ was rather difficult to determine unambiguously, since the target compound was decomposed (presumably by the γ radiation) to an extent of about 2%, to give $Fe_3(CO)_{12}$. After correction for this direct chemical production, the authors estimated the activity of ^{59}Fe found as $Fe_3(CO)_{12}$ to be 24% of the total [37].

UV photolysis of $Fe(CO)_5$ in a CH_4 matrix (1:1000) at 20 K produces IR bands assignable to both $Fe_2(CO)_8$ and $Fe_3(CO)_{12}$ [41]. In flash photolysis studies on $Fe(CO)_5$ rapid ($< 10^{-4}$ s) formation of $Fe_3(CO)_{12}$ is observed [49]. Illumination at 10 K of a polycrystalline sample of $Fe_2(CO)_9$ with the 514.5 nm light of an Ar^+ ion laser produces a Raman band at 240 cm^{-1} , which may originate from $Fe_3(CO)_{12}$ [47]. $Fe_3(CO)_{12}$ is also formed as the only product upon laser photolysis of silica-adsorbed $Fe(CO)_5$. Subsequent trimerization of a weakly bonded $Fe(CO)_4 \cdots SiO_2$ intermediate is supposed [54, 57], also see [58].

Direct synthesis of metal carbonyls by laser evaporation of iron to Fe atoms and reaction with CO in a THF matrix gives only 0.2% $Fe_3(CO)_{12}$ besides $Fe(CO)_5$ (0.4%) and traces of $Fe_2(CO)_9$ [42, 43, 45]. It is probable that a reactive $Fe(CO)_4 \cdot THF$ complex yields the polynuc-

lear carbonyls on warming up the matrix, instead of direct combination of Fe atoms with CO, because $\text{Fe}(\text{CO})_4 \cdot \text{THF}$ also forms $\text{Fe}_3(\text{CO})_{12}$ when worked up under similar conditions [42, 43].

Addition of acids to solutions of the anion $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ mainly gives $\text{Fe}_3(\text{CO})_{12}$, H_2 , and small amounts of $\text{Fe}(\text{CO})_5$, Fe^{2+} , and CO [14 to 16]; from dilute acetic acid solution of the anion, $\text{Fe}_3(\text{CO})_{12}$ precipitates only slowly [22]. In the older literature, the salts from $\text{H}_2\text{Fe}_3(\text{CO})_{12}$ and amines, alcohols, and other donor-type molecules are erroneously formulated as "pure coordination compounds", which decompose upon acidification with dilute H_2SO_4 or concentrated HCl [1, 2, 5, 7] or in contact with air [1, 4]. " $\text{Fe}(\text{CO})_3$ " instead of $\text{H}_2\text{Fe}_3(\text{CO})_{12}$ was assumed to be the red-colored precursor in the reaction of acids with " $\text{H}_2\text{Fe}(\text{CO})_4$ " [6] or in the self-decomposition of $\text{H}_2\text{Fe}(\text{CO})_4$ [9]. Later it was observed that the oxygen in the air is necessary for the formation of $\text{Fe}_3(\text{CO})_{12}$ from solutions of $\text{H}_2\text{Fe}(\text{CO})_4$. In the absence of oxygen, mainly $\text{Fe}(\text{CO})_5$ is formed [12]. $\text{Fe}_3(\text{CO})_{12}$ also occurs when a mixture of $\text{Na}[\text{HFe}_2(\text{CO})_8]/\text{H}_2\text{Fe}_2(\text{CO})_8$ is stirred with an excess of 6 N HCl [28, 44], or when the salts of the anion $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ are acidified [17, 22] in the presence of air [17]. These reactions are also formulated via $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ as an intermediate [22]. The preparative Methods I and II are optimized versions of the reactions mentioned in this paragraph.

$\text{Fe}_3(\text{CO})_{12}$, recognizable by the green color of the solution, is formed in many reactions of $\text{Fe}_2(\text{CO})_9$ with either inorganic, organometallic, or organic compounds at room temperature or above. The formation probably occurs by thermal dissociation of $\text{Fe}_2(\text{CO})_9$ into $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4$, followed by trimerization of the unsaturated species [20]. This species was reported to be trapped and characterized in a zeolite matrix (Z) by adsorption of $\text{Fe}(\text{CO})_5$ on a dehydrated HY zeolite at 25 °C: $\text{Z-OH} + \text{Fe}(\text{CO})_5 \rightarrow \text{Fe}(\text{CO})_5(\text{ads.}) + \text{Z-[OH} \cdots \text{Fe}(\text{CO})_4]$. Subsequent heating of the sample under vacuum at 60 °C initiates the migration of the $\text{Fe}(\text{CO})_4$ moieties and aggregation to form $\text{Z-[}(\text{OH})_3 \cdots \text{Fe}_3(\text{CO})_{12}]$ [50].

The half-life of $\text{Fe}_2(\text{CO})_9$ in benzene at 21 °C (resulting in only $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$) was estimated to be 1.6 h [46]. It is described that thianthrene, 2,6- and 3,5-diphenylthiopyran-4-ones, diphenylsulfide, and thiophene catalyze the conversion of $\text{Fe}_2(\text{CO})_9$ to $\text{Fe}_3(\text{CO})_{12}$ [32]. The formation also seems to be enhanced with $\text{Fe}(\text{CO})_5$ as the solvent [35].

The decomposition of organoiron carbonyls often gives $\text{Fe}_3(\text{CO})_{12}$ besides $\text{Fe}(\text{CO})_5$. The extensive literature of these reactions and of the reactions with $\text{Fe}_2(\text{CO})_9$ is not given here. Some examples may be found in the chapters on the chemical reactions of the diverse organoiron compounds.

The standard enthalpy of formation is calculated to be $\Delta H_f^\circ = -442 \pm 4 \text{ kcal/mol}$ ($-1849 \pm 16 \text{ kJ/mol}$) from thermal decomposition and iodination over the range 494 to 544 K [38], also see [44, 48, 51]. Moreover, see the metal-metal and metal-ligand bond enthalpy terms in 3.1.10.1.3.1, p. 18 [56].

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