

# Cover Essay

## (Cyclobutadiene)iron Tricarbonyl—A Case of Theory before Experiment

### I. Introduction: Hans Reihlen Discovers (Butadiene)iron Tricarbonyl, an Early Forerunner of (Cyclobutadiene)iron Tricarbonyl

One hundred years after Zeise's report of the first  $\pi$ -olefin complexes, salts of the  $[\text{Cl}_3\text{Pt}(\text{C}_2\text{H}_4)]^-$  anion,<sup>1</sup> the first conjugated diene complex of a transition metal, ( $\eta^4$ -1,3-butadiene)iron tricarbonyl, was prepared. Hans Reihlen (Figure 1),<sup>2</sup> a professor of inorganic chemistry at the University of Tübingen in Germany, had been engaged in studies of transition metal carbonyls and nitrosyls during the period 1927–1931. At that time the nature of the bonding of CO to the metal atom in metal carbonyls was still uncertain. Langmuir in 1921 had suggested that the CO molecule was a two-electron donor, bonded to the metal atom via its carbon atom.<sup>3</sup> In contrast, Reihlen thought that the metal carried a positive charge, a result of donating one electron to the CO ligand, which he viewed as a pseudohalogen atom. This, in Reihlen's view, required the formation of C–C bonds between two or three CO ligands.<sup>4</sup> Since neutral molecules such as pyridine could displace some of the CO ligands in a metal carbonyl, Reihlen thought such CO substitution should stop at the  $\text{L}_2\text{Fe}(\text{CO})_3$  stage, since, as he said, "otherwise the iron would be mono- or zerovalent." Reihlen also considered it to be uncertain whether the CO ligand was bound to the metal by a M–C or M–O bond. His rationale for experiments to examine this question was as follows:<sup>4</sup>

"The question, if in mononuclear carbonyls at least some of the CO groups are bonded to the metal via C or O, could be resolved if it were possible, in the case of iron pentacarbonyl, to replace one or more CO groups by olefin molecules without changing the character of the compounds as strongly as in the case of substitution (of CO) by methyl alcohol."

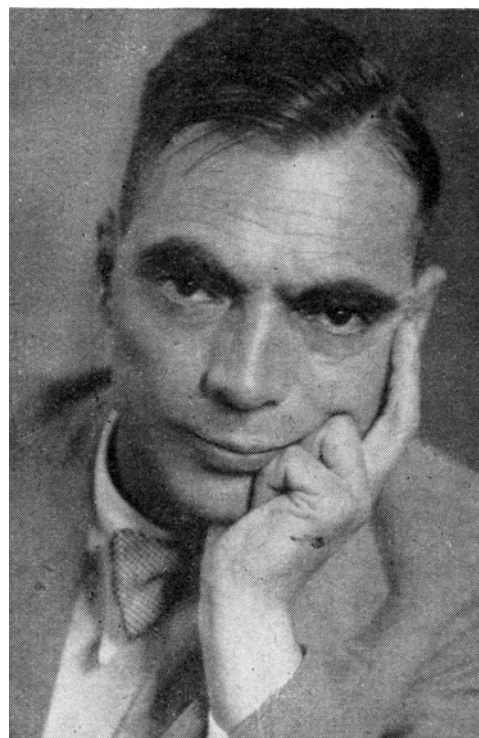
(The latter reaction also was studied by Reihlen et al. and reported in the same paper to give a complex with an O-bonded methanol ligand,  $(\text{OC})_3\text{Fe}(\text{CH}_3\text{OH})$ .)

(1) See the cover molecule essay dealing with this species: Seyferth, D. *Organometallics* 2001, 20, 2.

(2) Hans Reihlen (1892–1950). Chemistry studies begun at the University of Tübingen, interrupted by military service in World War I, resumed at the University of Greifswald, Ph.D. 1920, *Habilitation* 1922. In 1924 at the University of Frankfurt, 1928 Professor (*Extraordinarius*) at the University of Tübingen. Research in coordination chemistry: studies in stereochemistry, Pt(II) and Pd(II) complexes (1926–1936), Th, Fe, Cr, Sb, and Cu complexes, metal carbonyls and nitrosyls (1927–1931), metal cyanide complexes. Military service in World War II. Obituary: Rüdorff, W. *Angew. Chem.* 1950, 62, 545.

(3) Langmuir, I. *Science* 1921, 54, 59.

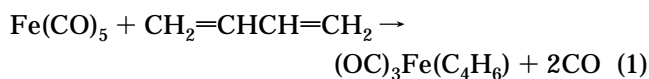
(4) Reihlen, H.; Gruhl, A.; Hesslein, G. v.; Pfrengle, O. *Liebigs Ann. Chem.* 1930, 482, 161.



**Figure 1.** Hans Reihlen (from *Angew. Chem.* 1950, 62, 545; reproduced by permission of Wiley/VCH).

This reasoning led Reihlen to try thermal reactions of  $\text{Fe}(\text{CO})_5$  with cyclohexene, isobutene, and styrene in a sealed tube at 100–140 °C. No reactions occurred, although styrene polymerized at 140 °C. Curiously, Reihlen did not try photochemical activation, although the  $\text{Fe}(\text{CO})_5/\text{CH}_3\text{OH}$  reaction had been found to be induced by UV irradiation. Had he done so, he might have obtained  $(\text{C}_6\text{H}_5\text{CH}=\text{CH}_2)\text{Fe}(\text{CO})_4$ , since Koerner von Gustorf et al. were able to prepare this complex by the photochemical procedure in 1966.

Since monoolefins did not react, Reihlen turned to 1,3-dienes, and here the reaction with 1,3-butadiene was successful (eq 1). The diene (2 molar equiv) was con-

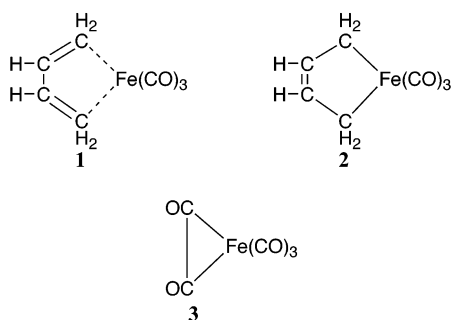


densed into a bomb tube containing  $\text{Fe}(\text{CO})_5$  (1 molar equiv). The sealed (under nitrogen) tube then was heated at  $\sim 135$  °C for 24 h, after which time the tube was cooled to  $-10$  °C and opened. After evaporation of unreacted butadiene, the liquid residue was distilled between 120 and 180 °C. Redistillation with a fine nitrogen bleed at reduced pressure gave first some

Fe(CO)<sub>5</sub> and then, at 29.5–30 °C under high vacuum, a light yellow liquid. When 30 cm<sup>3</sup> of butadiene was used, 6.5 g of this product was obtained. The product had an unpleasant odor, was soluble in organic solvents and insoluble in water, and reacted very vigorously with concentrated H<sub>2</sub>SO<sub>4</sub> and with HNO<sub>3</sub>. The product was of limited stability and began to decompose within a few days at room temperature, even when light and oxygen were excluded. A cryoscopic molecular weight determination was in agreement with the simple formula (OC)<sub>3</sub>Fe(C<sub>4</sub>H<sub>6</sub>), as was its elemental analysis (C, H, Fe).

Isoprene and 2,3-dimethyl-1,3-butadiene also reacted with Fe(CO)<sub>5</sub> under these conditions, but pure products of the type (OC)<sub>3</sub>Fe(diene) could not be obtained. Instead, materials of stoichiometry (diene)<sub>n</sub>Fe(CO)<sub>3</sub> (*n* = 2, 3) were isolated, which apparently were inseparable mixtures of the expected (diene)Fe(CO)<sub>3</sub> complex and 1,3-diene dimers and oligomers.

Reihlen did not express great surprise at having obtained such a novel compound and did not mention the known platinum–olefin complexes at all. He concluded that the great similarity of (OC)<sub>3</sub>Fe(C<sub>4</sub>H<sub>6</sub>) with Fe(CO)<sub>5</sub> indicated that at least the two displaced CO ligands had been bonded to iron as Fe–CO, not Fe–OC. He offered two possible cyclic structures for (OC)<sub>3</sub>Fe(C<sub>4</sub>H<sub>6</sub>), **1** and **2**, and raised the question that



perhaps the two displaced CO groups also might have been bonded in a cyclic manner, presumably as **3**. Consideration of structure **2**, he noted, was justified “in particular, in view of the organochromium compounds” (meaning, of course, Hein’s “polyphenylchromium” compounds in which M–C single bonds were believed to be present).

Thus, Reihlen’s ideas about metal carbonyl structure and bonding (far from the mark though they were) resulted in an important milestone of organometallic chemistry: the preparation of the first 1,3-diene transition metal complex. Reihlen did not appear to appreciate the novelty and the importance of his discovery: at least, he did not comment on it in his paper and he did not pursue the matter further. (1,3-Butadiene)iron tricarbonyl does not appear to have stimulated the interest of other chemists at the time. The coverage of organometallic compounds in Krause and von Grosse’s 1937 monograph<sup>5</sup> is encyclopedic, with references through the 1936 literature, but its short chapter on organoiron compounds does not include (butadiene)iron tricarbonyl. In the metal carbonyl chapter of their monograph on

inorganic chemistry,<sup>6</sup> Emeléus and Anderson devoted only one sentence to Reihlen’s complexes, without any special comment: “Reihlen has described compounds formed by heating iron pentacarbonyl with diolefins—e.g., dimethylbutadiene, MeCH=CH–CH=CHMe—in which one molecule of the olefin displaces two molecules of carbon monoxide—Fe(CO)<sub>3</sub>C<sub>6</sub>H<sub>10</sub>.” (They chose here one of the two examples that did not give a pure (diene)Fe(CO)<sub>3</sub>, and they got the olefin wrong—it was 2,3-dimethylbutadiene.) Perhaps if the reactions of isoprene and 2,3-dimethyl-1,3-butadiene had given pure (diene)Fe(CO)<sub>3</sub> products, these compounds, as a class, might have attracted some interest on the part of Reihlen and those who read his paper. However, (1,3-butadiene)Fe(CO)<sub>3</sub> was the only such compound that could be isolated in pure form, a curiosity whose structure and bonding were not known and which, to make it worse, was not stable at room temperature for more than a few days. So, it made no impact on organometallic chemistry at the time and no further papers on it were published during the next 28 years. (Butadiene)iron tricarbonyl was, however, the subject of a 1946 U.S. patent assigned to Texaco.<sup>7</sup> The product, prepared by Reihlen’s procedure, a yellow liquid with a boiling point of 50 °C at 10 mmHg, was not isolated in pure form, since its composition, derived from its elemental analysis, was given as [Fe(CO)<sub>3</sub>]<sub>5</sub>[C<sub>4</sub>H<sub>6</sub>]<sub>6</sub>. It was claimed to be an effective antiknock agent, but it certainly was not a practical one, since it was necessary to protect hydrocarbon fuels that contained it against the action of oxygen and light.

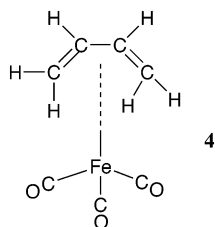
The discovery of ferrocene in 1951 and the determination of its novel sandwich structure in 1952 resulted in an explosive growth of the field of organotransition metal chemistry, and Peter Pauson, the discoverer (with Kealy) of the first laboratory synthesis of ferrocene, after having studied the reaction of iron carbonyls with cyclopentadiene, became interested in the tricarbonyl-iron derivatives of conjugated dienes.<sup>8</sup> The preparation of (butadiene)iron tricarbonyl was repeated. In Hallam and Pauson’s preparation, the product crystallized in part during its distillation under vacuum, and it could be recrystallized from ligroin or methanol at –78 °C to give pale yellow crystals, with melting point 19 °C, that were indefinitely stable when stored in a refrigerator. The compound is diamagnetic, and its UV and IR spectra suggested that it contained essentially an intact, unaltered butadiene ligand, which spoke against Reihlen’s preferred structure **2**. It could be recovered unchanged from its solutions in pyridine and glacial acetic acid and even from concentrated sulfuric acid. No reaction occurred on attempted hydrogenation in the presence of Adam’s catalyst or on attempted Diels–Alder reaction with refluxing maleic anhydride. Hallam and Pauson suggested structure **4** for (butadiene)iron tricarbonyl, which contains a planar (or nearly so) butadiene molecule in a cisoid configuration with the iron atom below the C<sub>4</sub>H<sub>6</sub> ligand plane and equidistant from its four carbon atoms. The authors believed that such a structure “will lead to a metal–carbon bond of a

(6) Emeléus, H. J.; Anderson, J. S. *Modern Aspects of Inorganic Chemistry*, 1st ed.; George Routledge & Sons: London, 1938; Chapter XII, p 428. In the second edition, published by Routledge and Kegan Paul in 1952, Reihlen’s work is not mentioned at all.

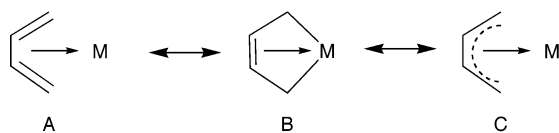
(7) Veltman, P. L. U.S. Patent 2,409,167, 1946; *Chem. Abstr.* **1947**, 41, 595.

(8) Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1958**, 642.

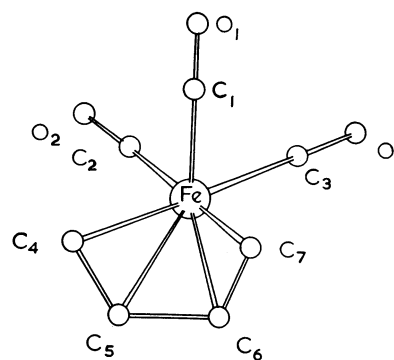
(5) Krause, E.; von Grosse, A. *Die Chemie der metallorganischen Verbindungen*; Gebrüder Bornträger: Berlin, 1937.



type closely related to that in ferrocene". Their suggested structure was confirmed by an X-ray crystallographic study at  $-40\text{ }^{\circ}\text{C}$  by Mills and Robinson<sup>9</sup> (Figure 2), who found that the butadiene ligand is planar. The iron atom was determined to be equidistant ( $2.1 \pm 0.04\text{ \AA}$ ) from the four C atoms of the butadiene ligand. Mills and Robinson concluded "that the bonding is essentially that of a  $\pi$ -complex", with C–C distances "in agreement with the complete delocalization of the  $\pi$ -electrons from the formal diene structure". A  $^{13}\text{C}$  NMR study<sup>10</sup> confirmed (via the  $^{13}\text{C}$ – $^1\text{H}$  coupling constants) that all the C–H bonds in (butadiene)iron tricarbonyl involve essentially  $\text{sp}^2$ -hybridized carbon atoms. However, other data suggested that there was slight rotation about the  $\text{C}_1$ – $\text{C}_2$  and  $\text{C}_3$ – $\text{C}_4$  bonds of the  $\text{C}_4\text{H}_6$  ligand. Such steric distortion from planarity has as a result that the Fe– $\text{C}_1$  and Fe– $\text{C}_4$  bonds are somewhat different from the Fe– $\text{C}_2$  and Fe– $\text{C}_3$  bonds, although in each case p orbitals on the carbon atoms are involved. As discussions of other authors have indicated, the bonding situation in (1,3-diene)metal complexes is complex and it has been pictured as shown in A–C. (Butadiene)iron tricarbonyl is better described by hybrid A, the consensus seems to be.



Since the time of the work by Hallam and Pauson, the chemistry of acyclic and cyclic (1,3-diene)iron tricarbonyl complexes has become an active research area and some interesting reactions of (butadiene)iron tricarbonyl itself and of many new substituted (butadiene)iron tricarbonyl complexes have been reported. For instance, (butadiene)iron tricarbonyl reacted with acetic anhydride in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{AlCl}_3$  to give the 1-acetyl derivative.<sup>11a</sup> Competition studies<sup>11a</sup> showed  $(\text{C}_4\text{H}_6)\text{Fe}(\text{CO})_3$  to have a Friedel–Crafts reactivity similar to that of ferrocene (which Woodward and Rosenblum had shown to be a superelectrophile). Later work showed that Friedel–Crafts acylation of (butadiene)iron tricarbonyl proceeds via a substituted allyl-



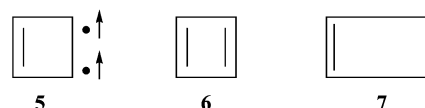
**Figure 2.** X-ray crystal structure of (butadiene)iron tricarbonyl (from ref 9b; reproduced by permission of the International Union of Crystallography).

iron tricarbonyl cation intermediate in which the acyl oxygen atom is coordinated to the iron atom.<sup>11b</sup>

For accounts of the extensive chemistry of (conjugated diene)iron tricarbonyls, the reader is referred to some reviews.<sup>12</sup>

## II. Prediction and First Synthesis of Cyclobutadiene–Metal Complexes: Serendipity and Design

A more interesting 1,3-diene is *cyclobutadiene*, a molecule of theoretical interest that has not been isolated in substance, although its matrix isolation by irradiation of photo- $\alpha$ -pyrone in noble gas matrices at 8–20 K was successful.<sup>13</sup> The apparent instability of cyclobutadiene was intriguing, and theoretical treatments all agreed that the delocalization of  $\pi$ -electrons in this molecule was zero.<sup>14</sup> The three possibilities for its electronic and geometric structure were a square triplet (5), a square singlet (6), and a rectangular singlet (7).



It was a theoretical paper in 1956 entitled "The Possible Existence of Transition Metal Complexes of *cyclo* Butadiene" by H. C. Longuet-Higgins and L. E. Orgel<sup>15</sup> that provided the stimulus which led to the experimental work directed toward the synthesis of cyclobutadiene–metal complexes, including our cover molecule. It was pointed out that the two unpaired electrons in 5, in a doubly degenerate orbital, could be used to form  $\pi$  bonds. Thus, 5 would form two  $\pi$  bonds

(9) (a) Mills, O. S.; Robinson, G. *Proc. Chem. Soc.* **1960**, 921. (b) *Acta Crystallogr.* **1963**, 16, 758.

(10) (a) Retcofsky, H. L.; Frankel, E. N.; Gutowsky, H. S. *J. Am. Chem. Soc.* **1966**, 88, 2710. (b) For the low- and high-energy photoelectron spectra of (butadiene)iron tricarbonyl and ab initio self-consistent field MO calculations, see: Connor, J. A.; Derrick, L. M. R.; Hall, M. B.; Hillier, I. H.; Guest, M. L.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1974**, 28, 1193.

(11) (a) Anisimov, K. N.; Magomedov, G. K.; Kolobova, N. E.; Trufanov, A. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 2533; *Bull. Acad. Sci. USSR, Div. Chem. Ser. (Engl. Transl.)* **1970**, 2379. (b) Greaves, E. O.; Knox, G. R.; Pauson, P. L. *Chem. Commun.* **1969**, 1124. See also: Greaves, E. O.; Knox, G. R.; Pauson, P. L.; Toma, S. *Chem. Commun.* **1974**, 257.

(12) (a) Pettit, R.; Emerson, G. F. *Adv. Organomet. Chem.* **1964**, 1, 1. (b) Green, M. L. H. In *Organometallic Compounds*, Coates, G. E., Green, M. L. H., Wade, K., Eds.; Methuen: London, 1968, Vol. 2 (The Transition Elements), Chapter 3. (c) King, R. B. In *The Organic Chemistry of Iron*; Koerner von Gustorf, G., Ed.; Academic Press: New York, 1978; pp 528–625 (with 412 references).

(13) (a) Lin, C. Y.; Krantz, A. *J. Chem. Soc., Chem. Commun.* **1972**, 1111. (b) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, 95, 614.

(14) For summaries of the cyclobutadiene problem, see: (a) Pettit, R. *Pure Appl. Chem.* **1969**, 17, 253. (b) Pettit, R. *J. Organomet. Chem.* **1975**, 100, 205. (c) Efraty, A. *Chem. Rev.* **1977**, 77, 691. (d) Maitlis, P. *Adv. Organomet. Chem.* **1966**, 4, 95. (e) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1974**, 13, 425.

(15) Longuet-Higgins, H. C.; Orgel, L. E. *J. Chem. Soc.* **1956**, 1969.