

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 π -olefin complexes, salts of the $[\text{Cl}_3\text{Pt}(\text{C}_2\text{H}_4)]^-$ anion,¹ the first conjugated diene complex of a transition metal, (η^4 -1,3-butadiene)iron tricarbonyl, was prepared. Hans Reihlen (Figure 1),² 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.³ 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.⁴ 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:⁴

"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.

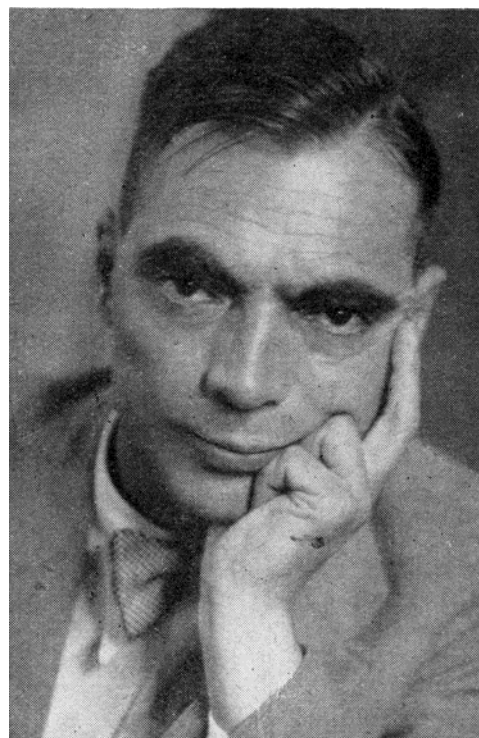
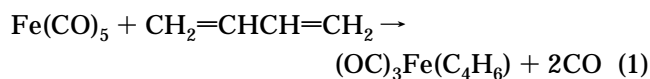


Figure 1. Hans Reihlen (from *Angew. Chem.* 1950, 62, 545; reproduced by permission of Wiley/VCH).

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-

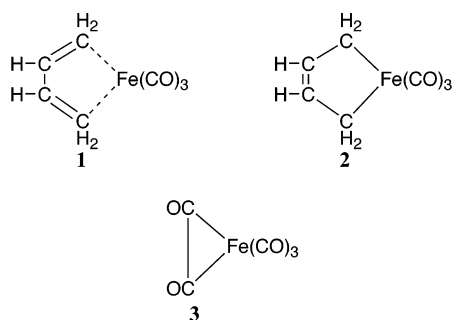


densed into a bomb tube containing $\text{Fe}(\text{CO})_5$ (1 molar equiv). The sealed (under nitrogen) tube then was heated at ~135 °C for 24 h, after which time the tube was cooled to –10 °C and opened. After evaporation of unreacted butadiene, the liquid residue was distilled between 120 and 180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

Fe(CO)₅ and then, at 29.5–30 °C under high vacuum, a light yellow liquid. When 30 cm³ 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 H₂SO₄ and with HNO₃. 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)₃Fe(C₄H₆), as was its elemental analysis (C, H, Fe).

Isoprene and 2,3-dimethyl-1,3-butadiene also reacted with Fe(CO)₅ under these conditions, but pure products of the type (OC)₃Fe(diene) could not be obtained. Instead, materials of stoichiometry (diene)_nFe(CO)₃ (*n* = 2, 3) were isolated, which apparently were inseparable mixtures of the expected (diene)Fe(CO)₃ 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)₃Fe(C₄H₆) with Fe(CO)₅ 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)₃Fe(C₄H₆), **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 monograph⁵ 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,⁶ 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)₃C₆H₁₀.” (They chose here one of the two examples that did not give a pure (diene)Fe(CO)₃, 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)₃ 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)₃ 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.⁷ 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)₃]₅[C₄H₆]₆. 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.

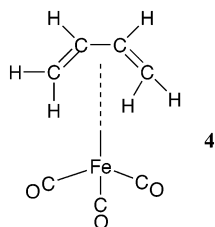
The discovery of ferrocene in 1951 and the determination of its novel sandwich structure in 1952 resulted in an explosive growth of the field of organotransition metal chemistry, and Peter Pauson, the discoverer (with Kealy) of the first laboratory synthesis of ferrocene, after having studied the reaction of iron carbonyls with cyclopentadiene, became interested in the tricarbonyl-iron derivatives of conjugated dienes.⁸ 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 C₄H₆ 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.

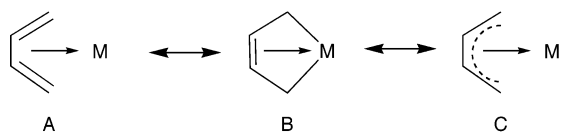
(7) Veltman, P. L. U.S. Patent 2,409,167, 1946; *Chem. Abstr.* **1947**, 41, 595.

(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 Robinson⁹ (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 π -complex", with C–C distances "in agreement with the complete delocalization of the π -electrons from the formal diene structure". A ^{13}C NMR study¹⁰ confirmed (via the ^{13}C – ^1H coupling constants) that all the C–H bonds in (butadiene)iron tricarbonyl involve essentially sp^2 -hybridized carbon atoms. However, other data suggested that there was slight rotation about the C_1 – C_2 and C_3 – C_4 bonds of the C_4H_6 ligand. Such steric distortion from planarity has as a result that the Fe– C_1 and Fe– C_4 bonds are somewhat different from the Fe– C_2 and Fe– 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 CH_2Cl_2 in the presence of AlCl_3 to give the 1-acetyl derivative.^{11a} Competition studies^{11a} 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-

(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.

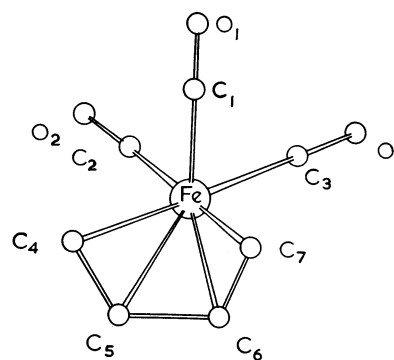


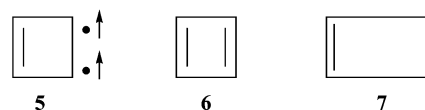
Figure 2. X-ray crystal structure of (butadiene)iron tricarbonyl (from ref 9b; reproduced by permission of the International Union of Crystallography).

iron tricarbonyl cation intermediate in which the acyl oxygen atom is coordinated to the iron atom.^{11b}

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

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- α -pyrone in noble gas matrices at 8–20 K was successful.¹³ The apparent instability of cyclobutadiene was intriguing, and theoretical treatments all agreed that the delocalization of π -electrons in this molecule was zero.¹⁴ 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. Orgel¹⁵ 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 π bonds. Thus, 5 would form two π bonds

(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.

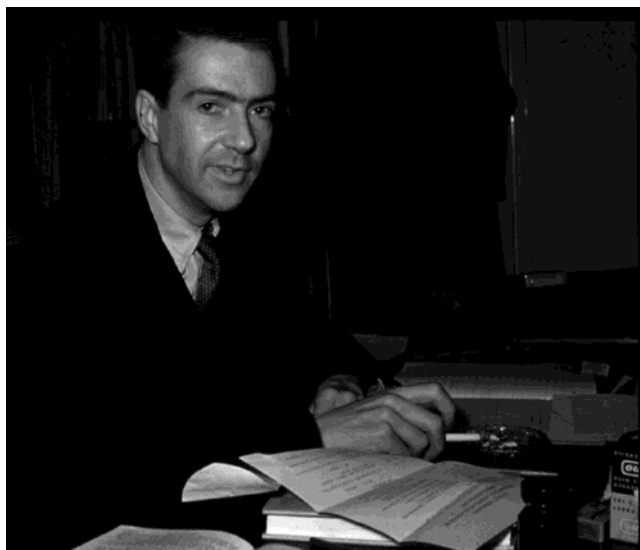
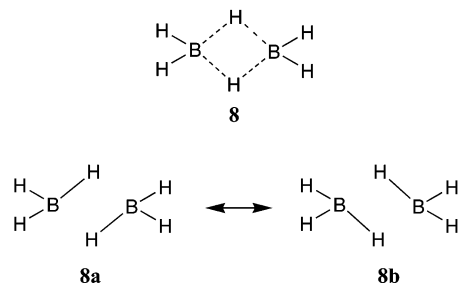


Figure 3. H. Christopher Longuet-Higgins, photograph by J. D. Roberts, at Kings College (London) in 1953 (reproduced by permission of J. D. Roberts and H. C. Longuet-Higgins).

to the metal. Furthermore, there would also be two other weak coordinate bonds: a σ bond to the metal atom from a ring orbital and a δ bond involving back-donation from the metal atom to the C_4 ring. As a consequence, it was predicted that cyclobutadiene–metal complexes might be more stable than cyclopentadienyl–metal complexes. It was suggested that formally zerovalent metals would form 18-electron complexes such as $(C_4H_4)Ni(CO)_2$, while positively charged metal species could give stable 16-electron complexes: e.g., $(C_4H_4)AuCl_2$. Some known chemistry was interpreted in terms of the intermediacy of $(\pi-C_4H_4)$ metal species: the reactions of acetylenes with Pd(II) and Au(III) chlorides and a possible $(C_4H_4)Ni(CN)_2$ in Reppe's $Ni(CN)_2$ -catalyzed synthesis of cyclooctatetraene from acetylene. In a note added in proof¹⁵ it was suggested that a complex prepared in Reppe's laboratory that was of stoichiometry $C_7H_4O_3Fe$ "is most reasonably formulated as $Fe(CO)_3(C_4H_4)$ since its reactions suggest that it is a substituted iron carbonyl. It may be an example of an 18-electron complex." However, the $C_7H_4O_3Fe$ compound, as described by Reppe and Vetter,¹⁶ red-brown prismatic needles that did not sublime in high vacuum and did not melt before they began to decompose at 170 °C, was not (cyclobutadiene)iron tricarbonyl. The identity of this compound remains unknown.

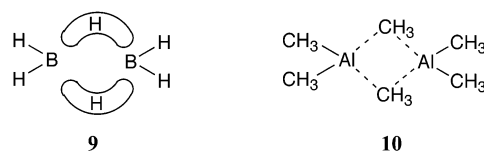
The paper of Longuet-Higgins and Orgel was indeed a remarkable one. Usually theory follows synthesis, but here theory *preceded* synthesis. But then, Christopher Longuet-Higgins (b. 1923, Figure 3) has had a remarkable career in chemistry and, more generally, in science. The prediction of the existence of stable cyclobutadiene–metal complexes was not his only coup in chemistry. Prior to that he made seminal contributions to our understanding of "electron-deficient" compounds whose constituent atoms do not contain enough valence electrons to bind them together solely by two-center, two-electron covalent bonds. Here also, he made predictions of molecules and structures which only later were

discovered by others. His studies in this area began in 1941 while he was an 18-year-old, second-year undergraduate student at Balliol College in Oxford University, when he wrote a paper in which the double-bridge structure of diborane (**8**) was suggested. This suggestion



was based on his analysis of experimental data that had been published previously by others (electron diffraction, Raman and IR spectra, and specific heat measurements). (The paper was published, together with Professor R. P. Bell as coauthor, in 1943.^{17a}) This structure had been considered and rejected earlier by S. H. Bauer (and by Linus Pauling) as a result of electron diffraction data that had been interpreted in terms of an ethane-like structure, H_3BBH_3 . In this paper, Longuet-Higgins formulated the bridge bonding in **8** in terms of a resonance hybrid between structures containing only normal electron-pair bonds (**8a,b**). He predicted that such $M\cdots H\cdots M$ bridge bonds are present in other hydride compounds.¹⁸ Noteworthy were his predictions of the polymeric H-bridged structure of beryllium hydride, the three-dimensional H-bridged structure of aluminum hydride with hexacoordinate aluminum, and the unsymmetrically H-bridged structures of beryllium and aluminum borohydrides. (At the time, the binary hydrides of beryllium and aluminum still were unknown.) In later years, the work of others showed all of these predictions to be correct.

In his first paper,^{17a} Longuet-Higgins talked about the bridge bond in B_2H_6 in terms of a "resonance link". Two years later,^{17b} he stated that such a representation is "an artificial way of representing the actual electron distribution" and suggested that a better view would be obtained by a molecular orbital approach, which, as he said, "has not yet been attempted." In 1949, the B–H–B bridge is pictured as a "banana bond" (**9**),¹⁹ and in a 1953 review it is MO theory that is applied in his discussion of the structures of the boron hydrides.



Included in Longuet-Higgins' discussion of electron-deficient compounds were the metal alkyls known to be associated (i.e., those of Al, Be, Mg, and Li) which were pictured with alkyl bridge bonding: e.g., **10**.^{18,21} Among the higher boron hydrides considered by Longuet-

(16) Reppe, W.; Vetter, H. *Liebigs Ann. Chem.* **1953**, 582, 133.

(17) (a) Longuet-Higgins, H. C.; Bell, R. P. *J. Chem. Soc.* **1943**, 250. (b) Full, detailed treatment: Bell, R. P.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1945**, A183, 357.

(18) Longuet-Higgins, H. C. *J. Chem. Soc.* **1946**, 139.

(19) Longuet-Higgins, H. C. *J. Chim. Phys.* **1949**, 46, 268.

Higgins was the unknown icosahedral $B_{12}H_{12}$, which, on the basis of MO theory, he predicted was not capable of existence.²² The anion $[B_{12}H_{12}]^{2-}$, on the other hand, his considerations showed could well be stable. Some years later, highly stable salts of this anion were reported by Pitochelli and Hawthorne and were shown by Earl Muetterties and co-workers at CRD du Pont to have a fascinating chemistry.

Longuet-Higgins' theoretical studies in chemistry included, among others, the development of a molecular orbital theory of conjugated molecules and heterocyclic compounds, statistical thermodynamics of mixtures and of polymer solutions, the electronic spectra of aromatic molecules, optical properties of helical molecules, and elements of symmetry in nonrigid molecules such as hydrazine via group theory. During the time that he was active in these areas, Longuet-Higgins, after leaving Oxford, was professor of theoretical physics at King's College, London (1952–1954), and professor of theoretical chemistry at the University of Cambridge (1954–1967). In 1967 came an abrupt change in the direction of his interests and career: he moved to the University of Edinburgh as co-founder of the Department of Machine Intelligence and Perception. Here he studied artificial intelligence and information processing systems. In 1974 he joined the Department of Experimental Psychology of the University of Sussex (where he now is Emeritus Professor), where his research was devoted to aspects of perception including pose-recovery in machine vision, the mechanisms of language, and the perception of music. (A 1995 lecture that he gave was entitled "The Musical Shoe: Rhythmical Universals in the World's National Anthems"—a long way from chemistry!) Longuet-Higgins' move to other pastures was a great loss to chemistry.

Now we return to cyclobutadiene–metal complexes. Three years after the publication of the Longuet-Higgins/Orgel paper, two groups reported the synthesis of a cyclobutadiene–metal complex. One synthesis was serendipitous, and the other was by design, based on the lead given by Longuet-Higgins and Orgel.

In Brussels, in the laboratories of the European Research Associates S.A., a group headed by Walter Hübel (a former Ph.D. student of Walter Hieber at the Technische Hochschule München) had been studying the reactions of metal carbonyls, in particular iron carbonyls, with acetylenes since 1955 in a project sponsored by the Union Carbide Corp. Very interesting initial results were published in a communication (received July 18, 1958)²³ and a full paper (received Nov 4, 1958).²⁴ Among the many products obtained in these complex reactions was a very stable compound, isolated as a light yellow, crystalline solid with melting point 234 °C, that sublimed in vacuum at ~180 °C. It was obtained in only a trace amount as a byproduct of the reaction of diphenylacetylene and $Fe_3(CO)_{12}$, but the reaction of diphenylacetylene with $Fe(CO)_5$ at 200–240 °C gave this product in good yield in addition to

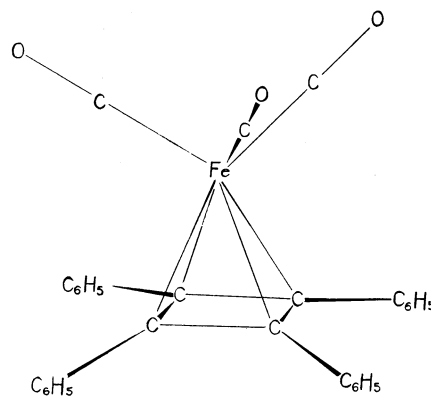
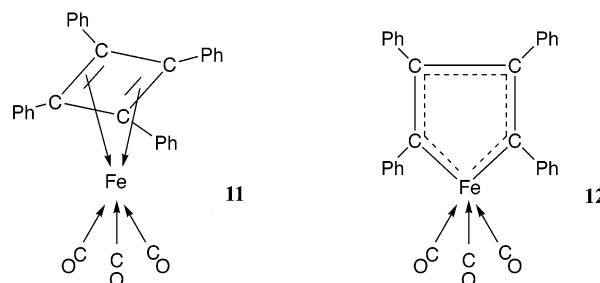


Figure 4. X-ray crystal structure of (tetraphenylcyclobutadiene)iron tricarbonyl (from ref 25, reproduced by permission of R. P. Dodge and *Nature*).

another organoiron carbonyl. The elemental analysis of the yellow crystals indicated the composition $Fe(CO)_3(C_6H_5C_2C_6H_5)_2$. The structure of $Fe(CO)_3(C_6H_5C_2C_6H_5)_2$ was not determined by Hübel and Braye, but the formation of 1,2,3,4-tetraphenylbutadiene in its reaction with $LiAlH_4$ and of 1,2,3,4-tetraphenylbutane when it was treated with sodium in liquid ammonia suggested that at least one C–C bond had been formed in the $Fe(CO)_5$ /diphenylacetylene reaction. Two possible structures were suggested by Hübel and Braye: a tetraphenylcyclobutadiene complex (**11**) and a delocalized organoiron heterocycle (**12**). The formation of the linear



tetraphenylbutadiene on reaction of the complex of possible structure **11** with $LiAlH_4$ could be rationalized in terms of reductive cleavage of a C–C bond of the C_4 ring. That $Fe(CO)_3(C_6H_5C_2C_6H_5)_2$ was the cyclobutadiene complex **11** was shown by an X-ray crystallographic structure determination (Figure 4) by Dodge and Schomaker at the Union Carbide Research Institute in Tarrytown, NY.²⁵ Interesting though this complex was, with phenyl substituents on its four ring carbon atoms, it was a dead end as far as development of further chemistry at the cyclobutadiene ring was concerned. What was needed was the unsubstituted (cyclobutadiene)iron tricarbonyl, $(C_4H_4)Fe(CO)_3$.

At the University of Karlsruhe in Germany, Rudolf Criegee (Figure 5)²⁶ had been interested in the cyclobutadiene problem. His attempts to prepare and isolate tetramethylcyclobutadiene by dehalogenation of dichloride **13** with lithium amalgam in diethyl ether were unsuccessful, giving instead the dimer **14** in excellent yield.²⁷ Longuet-Higgins and Orgel's prediction that cyclobutadiene might be stabilized as a nickel complex, together with a report that nickel tetracarbonyl could

(20) Longuet-Higgins, H. C. *Q. Rev. Chem. Soc.* **1957**, *11*, 121.

(21) Longuet-Higgins, H. C. *J. R. Inst. Chem.* **1953**, *77*, 179.

(22) Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1955**, *A230*, 110.

(23) Hübel, W.; Braye, E. H.; Clauss, A.; Weiss, E.; Krüerke, U.; Brown, D. A.; King, G. S. D.; Hoogzand, C. *J. Inorg. Nucl. Chem.* **1959**, *9*, 204.

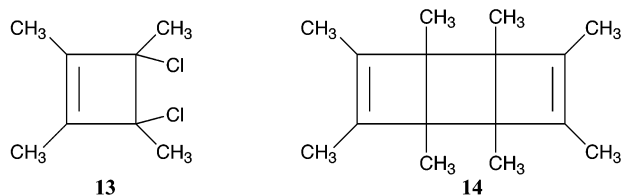
(24) Hübel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959**, *10*, 250.

(25) Dodge, R. P.; Schomaker, V. *Nature* **1960**, *186*, 798.



Figure 5. Rudolf Criegee (reproduced by permission of Deutsche Akademie der Naturforscher Leopoldina, Erna Lämmel, Director of Archive, and Gesellschaft Deutscher Chemiker, e.V. (Dr. K. Begitt)).

dehalogenate substituted allylic chlorides,²⁸ led Criegee to try a reaction of dichloride **13** with $\text{Ni}(\text{CO})_4$.^{29,30} When



the reaction was carried out under nitrogen in refluxing benzene for 10–12 h, a red-brown solution resulted. Appropriate workup gave black-violet needles in 70% yield whose total elemental analysis indicated the empirical formula $\text{C}_8\text{H}_{12}\text{NiCl}_2$. Reactions carried out in refluxing diethyl ether and acetone gave better yields (92% and 86%, respectively). The nickel complex was found to be thermally quite stable, decomposing above

(26) Rudolf Criegee (1902–1975), one of the leading German organic chemists of the last century. Chemistry studies at the Universities of Tübingen and Greifswald (where Hans Reihlen was his laboratory instructor in inorganic chemistry) and Würzburg (Ph.D. with Otto Dimroth on acridinium salt reactions, and *Habilitation*). Professorships at the Universities of Marburg (1932) and Karlsruhe (1937). Interruption by military service in Russia during World War II, badly wounded and return to Karlsruhe in 1943; interruption again due to destruction of the Chemical Institute in a bombing raid in 1944. At Karlsruhe for the rest of his career; emeritus 1969, but active in research until the end. Research highlights (synthetic and mechanistic studies): (1) oxidation chemistry: 1,2-glycol cleavage with $\text{Pb}(\text{OAc})_4$, cis-hydroxylation of olefins with OsO_4 , allylic hydroperoxides by autoxidation, peresters and peroxide rearrangements, ozonolysis; (2) small rings, mainly cyclobutene, chemistry; (3) valence isomers of benzene. Biography: Maier, G. *Chem. Ber.* **1977**, *110*, XXVII.

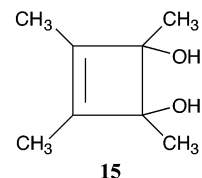
(27) Criegee, R.; Louis, G. *Chem. Ber.* **1957**, *90*, 417.

(28) Prichard, W. W.; Whitman, G. M. U.S. Patent 2,524,833, 1949 (to E. I. du Pont de Nemours & Co.); *Chem. Abstr.* **1952**, *46*, 1404.

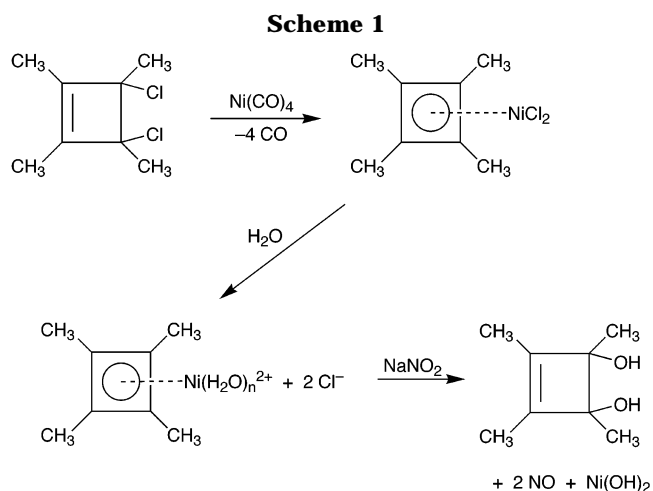
(29) (a) Criegee, R.; Schröder, G. *Angew. Chem.* **1959**, *71*, 70 (communication, received Dec 12, 1958). (b) *Liebigs Ann. Chem.* **1959**, *623*, 1.

(30) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 519 (review).

120 °C at 12 mmHg. It dissolved in chlorinated organic solvents (CH_2Cl_2 , CHCl_3), giving violet solutions, but was poorly soluble in benzene and acetone and even less so in diethyl ether, petroleum ether, and carbon tetrachloride. It dissolved readily in water; its aqueous solutions were blood red and had an electrical conductivity indicative of a strong electrolyte. A proton NMR spectrum of the aqueous solution showed only a single C–H resonance. Mild oxidation of a cold aqueous solution of the $\text{C}_8\text{H}_{12}\text{NiCl}_2$ product with sodium nitrite resulted in a color change to brown, with subsequent evolution of nitric oxide and precipitation of $\text{Ni}(\text{OH})_2$. The organic product, extracted with ether, was identified as **15**. Catalytic hydrogenation (Pd/C) in aqueous



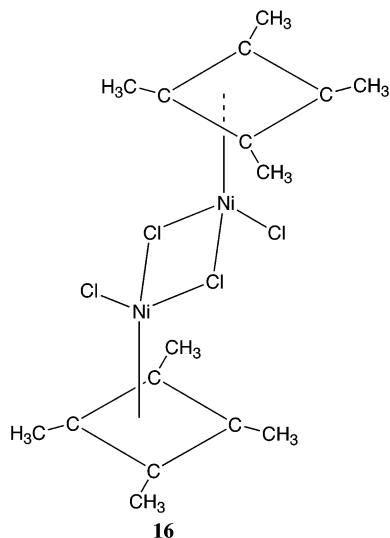
solution destroyed the nickel complex. Two molar equivalents of H_2 per Ni were consumed. The products were metallic nickel and tetramethylcyclobutane (90% of which was in the all-cis form). On the basis of the available experimental evidence, it was concluded that the organic ligand in $\text{C}_8\text{H}_{12}\text{NiCl}_2$ was tetramethylcyclobutadiene. The chemistry involved is summarized in Scheme 1.



Confirmation of this conclusion was provided by an X-ray structure determination of the (tetramethylcyclobutadiene)nickel dichloride–benzene adduct by Dunitz, Mez, Mills, and Shearer.³¹ The molecule is dimeric, $[(\text{CH}_3)_4\text{C}_4\text{NiCl}_2]_2 \cdot \text{C}_6\text{H}_6$, with two Cl ligands bridging the nickel atoms to form a four-membered NiCl_2Ni ring. The other two Cl ligands are monodentate. On the outside of the NiCl_2Ni ring, each Ni has the $(\text{CH}_3)_4\text{C}_4$ cyclobutadiene ligand ($\text{Ni}-\text{C} = 2.00\text{--}2.05 \text{ \AA}$). The C_4 ring is planar and square (or very nearly square) with $d(\text{C}-\text{C}) = 1.40\text{--}1.45 \text{ \AA}$. The CH_3 substituents are displaced away from the Ni atoms by $0.12\text{--}0.19 \text{ \AA}$, probably due to steric interference with the Cl ligands.

(31) Dunitz, J. D.; Mez, H. C.; Mills, O. S.; Shearer, H. M. M. *Helv. Chim. Acta* **1962**, *45*, 647.

The structure of the $(\text{CH}_3)_4\text{C}_4\text{Ni}(\text{Cl})\text{Cl}_2(\text{Cl})\text{NiC}_4(\text{CH}_3)_4$ molecule is shown in **16**.



Criegee and Schröder's procedure was applied by Brune et al. to the synthesis of (di-, tri-, and tetraalkylcyclobutadiene)nickel dichloride complexes with 1,2-dimethyl-, trimethyl-, trimethylethyl-, trimethylisopropyl-, 1,2-dimethyl-3,4-diethyl-, and 1,2-dimethyl-3,4-diisopropylcyclobutadiene as the organic ligands. More interesting, however, is the rapid and quantitative synthesis of (tetramethylcyclobutadiene)nickel dibromide by the reaction of zerovalent, naphthalene-complexed nickel, obtained by the action of lithium naphthalenide in THF on NiBr_2 , with 3,4-dibromotetramethylcyclobutene.³²

As in the case of (tetraphenylcyclobutadiene)iron tricarbonyl, the four ring carbon atoms of (tetramethylcyclobutadiene)nickel dichloride are blocked from attack by external reagents by the four organic substituents. The only possible reactions are nucleophilic displacement of chloride ion and tetraorganocyclobutadiene ligand displacement processes. Both have been observed.

In the hope of preparing $(\text{CH}_3)_4\text{C}_4\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2$, Criegee and Ludwig treated the dichloride with 2 molar equiv of sodium cyclopentadienide in THF.³³ They obtained a red crystalline product in good yield which had the correct elemental composition, $\text{C}_{18}\text{H}_{22}\text{Ni}$. However, on the basis of mostly chemical evidence, Criegee and Ludwig concluded that it was **17** rather than the expected complex. Two years later, R. B. King interpreted the ^1H NMR spectrum of the Criegee/Ludwig product as indicative of structure **18**.³⁴ An X-ray crystal structure study of Oberhansli and Dahl³⁵ showed neither structure to be correct: the Criegee/Ludwig complex was **19**.

Several tetramethylcyclobutadiene ligand transfer reactions have been reported. Thus, the $\{[(\text{CH}_3)_4\text{C}_4]\text{-NiCl}_2\}_2$ dimer reacted with $\text{Co}_2(\text{CO})_8$ in THF at 25 °C to give $[(\text{CH}_3)_4\text{C}_4]\text{Co}(\text{CO})_2\text{-Co}(\text{CO})_4$, while $\{[(\text{CH}_3)_4\text{C}_4]\text{-NiI}_2\}_2$ reacted with $\text{Co}_2(\text{CO})_8$ to give $[(\text{CH}_3)_4\text{C}_4]\text{Co}(\text{CO})_2\text{I}$.³⁶

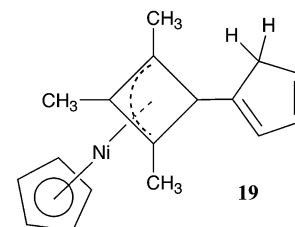
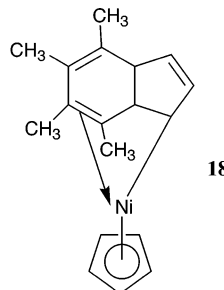
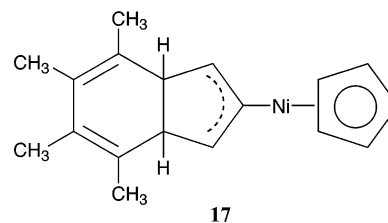
(32) Henri-Olivé, G.; Olivé, S. *Angew. Chem.* **1967**, *79*, 897.

(33) Criegee, R.; Ludwig, P. *Chem. Ber.* **1961**, *94*, 2038.

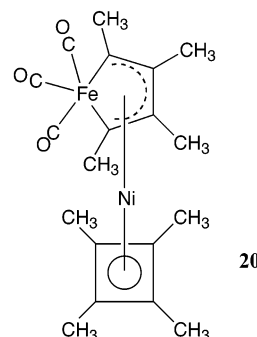
(34) King, R. B. *Inorg. Chem.* **1963**, *2*, 528.

(35) Oberhansli, W.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 150.

(36) Bruce, R.; Maitlis, P. M. *Can. J. Chem.* **1967**, *45*, 2017.



The reaction of the latter with sodium cyclopentadienide was straightforward, giving $[(\text{CH}_3)_4\text{C}_4]\text{Co}(\eta^5\text{-C}_5\text{H}_5)$. (Tetramethylcyclobutadiene)iron tricarbonyl was obtained in fair yield in a reaction of $\text{Fe}_3(\text{CO})_{12}$ with $\{[(\text{CH}_3)_4\text{C}_4]\text{-NiCl}_2\}_2$ in refluxing THF.³⁷ A minor byproduct of this reaction was found in an X-ray crystallographic study³⁸ to be **20**. Unexpectedly, the reaction of $\{[(\text{C}_6\text{H}_5)_4\text{C}_4]\text{-NiCl}_2\}_2$ with $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ or $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ gave $\{[(\text{C}_6\text{H}_5)_4\text{C}_4]\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\}^+\text{FeBr}_4^-$: ligand transfer, but from iron to nickel.³⁹ Such (tetraphenylbutadiene)-nickel dihalides (and other tetrakis-substituted-phenylbutadiene nickel complexes) can be prepared by ligand transfer from $[(\text{Ar}_4\text{C}_4)\text{PdX}_2]_2$ complexes (eq 2).^{40a} The latter are easily prepared by reaction in 2:1 ratio of a diarylacetylene with a Pd(II) halide.^{40b}



$[\text{Ar}_4\text{C}_4\text{PdX}_2]_2 + 2(\text{Bu}_3\text{P})_2\text{NiX}_2 \rightarrow$
 $[\text{Ar}_4\text{C}_4\text{NiX}_2]_2 + 2(\text{Bu}_3\text{P})_2\text{PdX}_2$ (1)

A Ni(I) tetraphenylcyclobutadiene complex, $[(\text{C}_6\text{H}_5)_4\text{C}_4]\text{Ni}[(\text{C}_6\text{H}_5)_3\text{P}]\text{Br}$, has been prepared by reduction in

(37) Bruce, R.; Moseley, K.; Maitlis, P. M. *Can. J. Chem.* **1967**, *45*, 2011.

(38) Epstein, E. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 502.

(39) Maitlis, P. M.; Efraty, A.; Games, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 719.

(40) (a) Pollock, D. F.; Maitlis, P. M. *Can. J. Chem.* **1966**, *44*, 2673.

(b) Blomquist, A. T.; Maitlis, P. M. *J. Am. Chem. Soc.* **1962**, *84*, 2329.

(c) Maitlis, P. M.; Games, M. L. *Can. J. Chem.* **1964**, *42*, 183. (d)

Maitlis, P. M.; Pollock, D.; Games, M. L.; Pryde, W. J. *Can. J. Chem.* **1965**, *43*, 470.

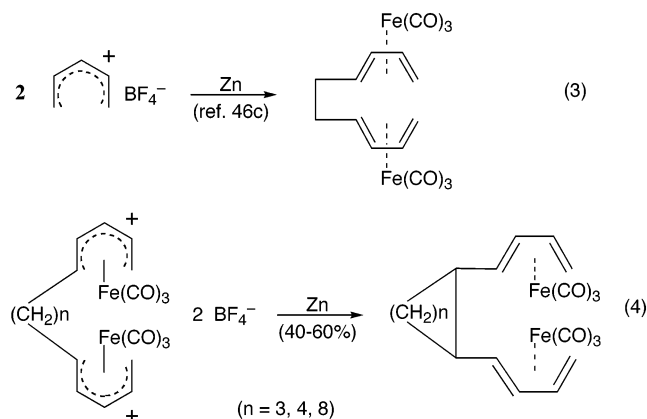
THF of the NiBr₂ complex with sodium in the presence of triphenylphosphine.⁴¹

III. (Cyclobutadiene)iron Tricarbonyl, an Unsubstituted Cyclobutadiene Ligand at Last! Rowland Pettit at the University of Texas in Austin

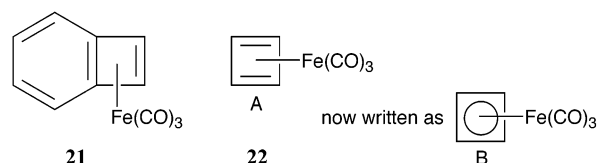
Rowland Pettit (1927–1981) (Figure 6) was an outstandingly creative and productive organic/organometallic chemist.⁴² During the course of his all-too-short career, he made significant contributions to organometallic chemistry, working not only on cyclobutadiene–metal complexes, whose story we tell here, but also on the role of orbital symmetry in metal-catalyzed isomerization reactions of strained hydrocarbons and the mechanisms of the water-gas shift and Fischer–Tropsch reactions, both industrially important processes. Pettit was born in Port Lincoln, Australia in 1927. After his chemistry studies at the University of Adelaide (B.Sc., 1949; Ph.D., 1953, dissertation on natural products and polynuclear heterocyclic chemistry), he obtained an Exhibition of 1851 Overseas Fellowship, which enabled him to continue his studies in England with Michael J. S. Dewar, the newly appointed professor of chemistry at Queen Mary College (University of London). There he not only carried on with synthetic projects (first rational synthesis of tropylium salts, aromatic borazaro compounds in which a >B=N< unit replaces a –CH=CH– grouping in an aromatic hydrocarbon) but also became acquainted with (and active in) molecular orbital theory and its applications in organic chemistry. Pettit stayed at Queen Mary College for 4 years, and during that time he obtained a second Ph.D., this time from the University of London. Two professors were present at his Ph.D. oral examination: Dewar and, by coincidence, H. C. Longuet-Higgins. (Did they talk about cyclobutadiene–metal complexes, on the possibility of whose existence Longuet-Higgins published a year earlier? Professor Longuet-Higgins does not recall such a conversation.)

In 1957, Pettit accepted an appointment as assistant professor of chemistry at the University of Texas in Austin. Promotion to associate professor (1960) and full professor (1963) followed. At UT Austin he continued studies in straight organic chemistry but soon became interested and active in organoiron chemistry, initially in acyclic diene–iron complexes. The Fe(CO)₃ complex of the nonconjugated bicyclo[2.2.1]heptadiene was published in 1959.⁴³ Further studies on Fe(CO)₃ complexes of acyclic conjugated dienes followed: protonation of butadiene–iron tricarbonyl (and of substituted diene complexes) with strong acids to give π -allyl–iron tricarbonyl salts,⁴⁴ π -pentadienyl– and π -hexadienyl–iron

tricarbonyl cations and other studies based on substituted conjugated diene–Fe(CO)₃ complexes,⁴⁵ substituted 1,3-diene rearrangements on reaction with Fe(CO)₅,^{46a,b} and, later, an interesting synthesis of cyclic hydrocarbon complexes via reactions of pentadienyl–iron tricarbonyl cations with zinc (eqs 3 and 4).^{46c} Two reviews on diene–iron carbonyl complexes were written.⁴⁷



How extension of this research to cyclobutadiene–iron carbonyl complexes occurred is told by John Gilbert in his biographical memoir of Pettit.⁴⁸ It seems that Nathan Bauld, a colleague of Pettit's at UT Austin, was interested in preparing the nickel dibromide complex of benzocyclobutadiene, a compound in which he was interested, using Criegee's procedure: i.e., the reaction of nickel tetracarbonyl with *trans*-dibromobenzocyclobutene. This attempted reaction was unsuccessful. The story continues: "Bauld, knowing that one of Pettit's students, George Emerson, was having great success making diene–iron tricarbonyl complexes, provided Emerson with a sample of the dibromide; the rest is history." After Emerson's successful preparation of (benzocyclobutadiene)iron tricarbonyl (**21**), which was



the result of this generous gift, *cis*-3,4-dichlorocyclobutene was prepared and reacted with a suspension of Fe₂(CO)₉ in pentane at 30 °C for about 2 h. Filtration, removal of pentane, and vacuum distillation gave a yellow liquid, with boiling point 68–70 °C at 30 mmHg, that crystallized as pale yellow prisms from pentane with melting point 26 °C. The elemental analysis (C,

(41) Hoberg, H.; Richter, W.; Fröhlich, C. *J. Organomet. Chem.* **1981**, *213*, C49.

(42) Biographical sketches: (a) Gilbert, J. C. *Biographical Memoirs*; Scientific Memoirs series; National Academy of Sciences, National Academy Press: Washington, DC, 1995; Vol. 67, p 293 (a warm and amusing biography which makes enjoyable reading, especially for all who knew Rolly). (b) Nicholas, K. M. *Organometallics* **1982**, *1*, 1557.

(43) Pettit, R. *J. Am. Chem. Soc.* **1959**, *81*, 1266.

(44) Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 4591. The protonation of (1,3-diene)iron tricarbonyl complexes is, however, more complicated, giving either a neutral (π -allyl)iron tricarbonyl or a (π -allyl)iron tricarbonyl cation, depending on the strength of the acid used: Olah, G. A.; Liang, G.; Yu, S. H. *J. Org. Chem.* **1976**, *41*, 2227 and references therein.

(45) (a) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 1511. (b) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3955. (c) Mahler, J. E.; Gibson, D. H.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3959. (d) Emerson, G. F.; Mahler, J. E.; Pettit, R. *Chem. Ind. (London)* **1964**, 836. (e) Holmes, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 2531.

(46) (a) Arnet, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1961**, *83*, 2955. (b) Emerson, G. F.; Mahler, J. E.; Kochhar, R.; Pettit, R. *J. Org. Chem.* **1964**, *29*, 3620. (c) Sapienza, R. S.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Organomet. Chem.* **1976**, *121*, C35.

(47) (a) Pettit, R.; Emerson, G. F.; Mahler, J. *J. Chem. Educ.* **1963**, *40*, 175. (b) Pettit, R.; Emerson, G. F. *Adv. Organomet. Chem.* **1964**, *1*, 1.

(48) Reference 42a, footnote 4.

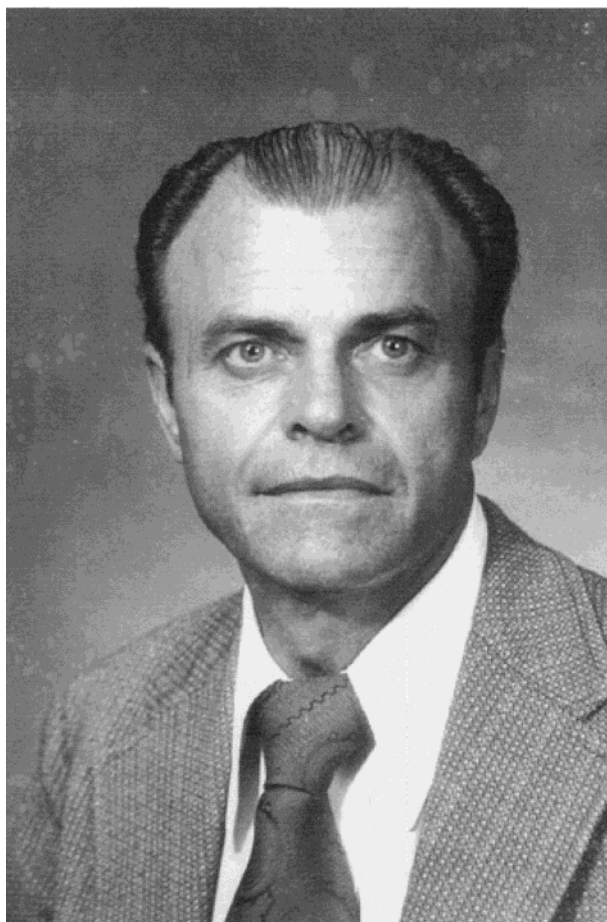
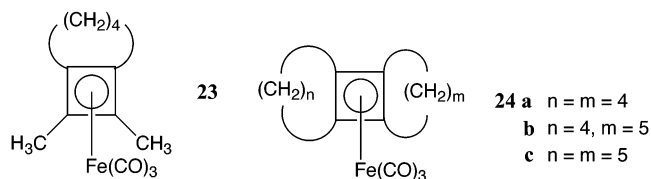


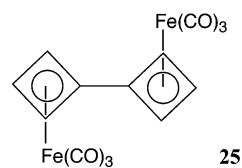
Figure 6. Rowland Pettit (reproduced by permission of Prof. J. A. Holcombe, Chairman, Department of Chemistry, University of Texas at Austin).

H, Fe, CO) agreed with the $(C_4H_4)Fe(CO)_3$ formulation. The 1H NMR spectrum showed a single sharp resonance at δ 3.91, and the IR spectrum showed CO bands at 1985 and 2055 cm^{-1} . Oxidation of the product with $FeCl_3$ in ethanol, or with ceric ammonium nitrate in acetone saturated with lithium chloride, gave *trans*-3,4-dichlorocyclobutene, good evidence for the presence in the product of a four-membered ring. (Cyclobutadiene)iron tricarbonyl (**22**) had been prepared,⁴⁹ the first metal complex of unsubstituted cyclobutadiene. (In the initial publications the diene representation A was used. After it was discovered that $(C_4H_4)Fe(CO)_3$ had the reactivity of an aromatic system, representation B gradually came into use. However, A is still used.) Once it was known that (cyclobutadiene)iron tricarbonyl was stable and that it could be prepared by halogen elimination from vicinal dihalocyclobutenes with $Fe_2(CO)_9$, others used this procedure to prepare diverse alkyl-substituted cyclobutadiene-iron carbonyl complexes: 1,2-dimethyl-3,4-diethyl-, trimethylethyl-,⁵⁰ 1-ethyl-2,3-dimethyl-,⁵¹ isopropyl-2,3-dimethyl-,⁵² 1,2-dimethyl-3,4-diisopropyl-,⁵³ trimethylisopropyl-,⁵³ 1,2-dimethyl-,⁵⁴ tet-

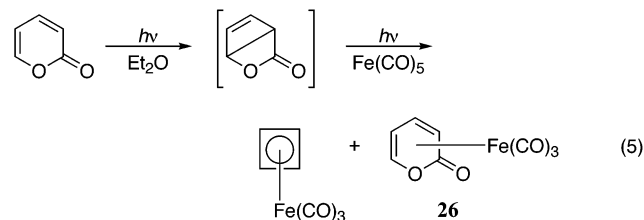
ramethyl-, trimethyl-, and 1,3-dimethylcyclobutadiene-iron tricarbonyl,⁵⁵ as well as **23** and **24**.⁵⁵



Attempted preparation of (bromocyclobutadiene)iron tricarbonyl by reaction of 3,4-dichloro-1-bromocyclobutene with $Fe_2(CO)_9$ was not successful. Instead of the expected product, bis[(cyclobutadiene)iron tricarbonyl] (**25**) was obtained.⁵⁶ However, the reaction of 1,3,4-tribromocyclobutene with $Fe_2(CO)_9$ was successful, giving (bromocyclobutadiene)iron tricarbonyl.⁵⁷



An alternate one-pot synthesis of (cyclobutadiene)iron tricarbonyl, the reaction of photo- α -pyrone with iron pentacarbonyl (eq 5), was reported by Michael Rosenblum (who in Woodward's laboratory explored the organic chemistry of ferrocene in 1952 and found it to be a highly reactive aromatic system) and Gatsonis.⁵⁸



The yield of (cyclobutadiene)iron tricarbonyl, however, was not high and (α -pyrone)iron tricarbonyl (**26**) also was formed in the reaction. The latter could be separated from the cyclobutadiene complex by crystallization from pentane solution or by fractional sublimation of $(C_4H_4)Fe(CO)_3$ (room temperature/0.1 mmHg). Unfortunately, both products are photolabile; thus, they are decomposed in part during the course of the reaction in which they are produced.

This procedure has been used to prepare (cyclobutadiene)(cyclopentadienyl)cobalt (eq 6).⁵⁹ Here also two other products, identified as shown in eq 6, were formed. The photo- α -pyrone route also has served in the preparation of (cyclobutadiene)(cyclopentadienyl)rhodium (from

(49) (a) Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131. (b) Pettit, R.; Henry, J. *Org. Synth.* **1970**, *50*, 21.

(50) Brune, H. A.; Wolff, H. P. *Tetrahedron* **1971**, *27*, 3949.

(51) Brune, H. A.; Wolff, H. P. *Tetrahedron* **1968**, *24*, 4861.

(52) Brune, H. A.; Wolff, H. P.; Hüther, H. *Tetrahedron* **1969**, *25*, 1089.

(53) Brune, H. A.; Wolff, H. P.; Hüther, H. *Z. Naturforsch., B* **1971**, *26b*, 765.

(54) Brune, H. A.; Wolff, H. P.; Klein, W.; Záhorszky, U.-I. *Z. Naturforsch., B* **1972**, *27b*, 639.

(55) Fongers, K. S.; Hogeveen, H.; Kingma, R. F. *Synthesis* **1982**, 839.

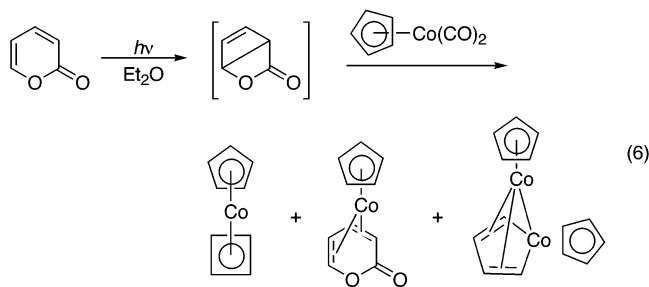
(56) Brune, H. A.; Horlbeck, G.; Záhorszky, U.-I. *Z. Naturforsch., B* **1971**, *26b*, 222.

(57) Brune, H. A.; Horlbeck, G.; Böttle, H. *Z. Naturforsch., B* **1972**, *27b*, 505.

(58) Rosenblum, M.; Gatsonis, C. *J. Am. Chem. Soc.* **1967**, *89*, 5074.

(59) (a) Rosenblum, M.; North, B. *J. Am. Chem. Soc.* **1968**, *90*, 1060.

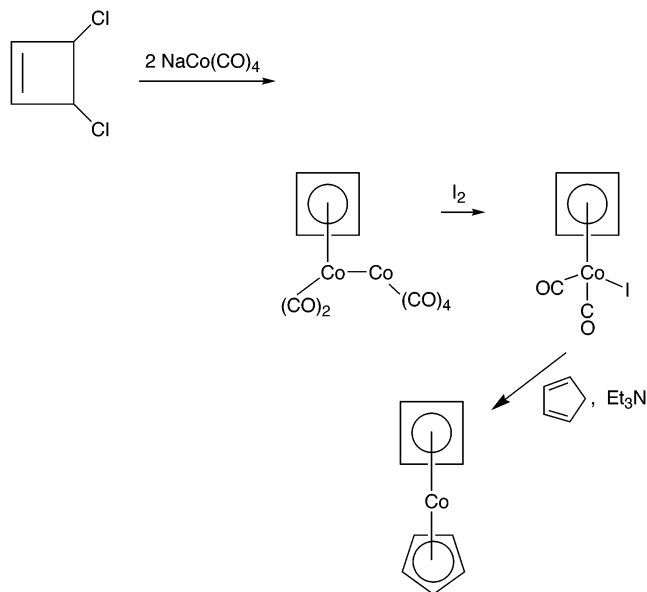
(b) Rosenblum, M.; North, B.; Wells, D.; Giering, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 1239.



CpRh(CO)₂⁶⁰ and (cyclobutadiene)(cyclopentadienyl)dicarbonylvandium (from CpV(CO)₄),⁶¹

The 3,4-dihalocyclobutene/metal carbonyl procedure was not found applicable to metal carbonyls other than Ni(CO)₄ and Fe₂(CO)₉, but Amiet, Reeves, and Pettit discovered a third procedure that served in such syntheses: the reaction of 3,4-dihalocyclobutenes with the sodium salts of metal carbonyl anions.⁶² Thus, 3,4-dichlorocyclobutene reacted with Na₂Fe(CO)₄ to give (cyclobutadiene)iron tricarbonyl. Reactions of the respective metal carbonyl anion with 3,4-dichlorocyclobutene and 3,4-dichlorotetramethylcyclobutene gave (C₄H₄)Ru(CO)₃, (C₄H₄)Mo(CO)₄ (orange-red solid, mp 17 °C, 35% yield), (C₄H₄)W(CO)₄, [(CH₃)₄C₄]Fe(CO)₃, and [(CH₃)₄C₄]M(CO)₄ (M = Cr, Mo, W). Apparently, many product yields were poor. This procedure also was applicable to the preparation of (cyclobutadiene)(cyclopentadienyl)cobalt, but since the initial product was (cyclobutadiene)cobalt hexacarbonyl, further reactions were required (Scheme 2).⁶³

Scheme 2



We return now to our cover molecule, (cyclobutadiene)iron tricarbonyl. Its X-ray crystal structure was determined at -45 °C by Harvey et al. (Figure 7).⁶⁴ The

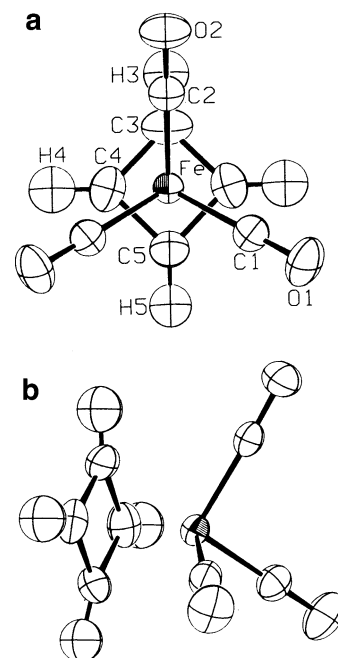


Figure 7. X-ray crystal structure of (cyclobutadiene)iron tricarbonyl at -45 °C: (a) ORTEP drawing projected perpendicular to the cyclobutadiene ring plane; (b) ORTEP view of the molecule showing the displacement of the H atoms from the cyclobutadiene plane (from ref 64).

C₄H₄ ring is square planar with two independent C–C distances of 1.420(3) and 1.430(3) Å (i.e., within 2σ of their average of 1.425(7) Å). The C–H hydrogen atoms are bent away from the carbonyl groups, ~0.1 Å out of the C₄ plane. (This paper also includes a reinterpretation of the low-temperature Raman spectrum⁶⁵ of (C₄H₄)Fe(CO)₃ in the solid state.) A single-crystal X-ray diffraction study at -35 °C of (C₄H₄)Fe(Ph₂PCH₂-CH₂PPh₂)CO has been reported.⁶⁶ (For a listing of crystallographic bond lengths of many substituted (cyclobutadiene)iron tricarbonyl complexes known in 1982, see ref 67.) Riley and Davis, by X-ray diffraction, determined the structures of (cyclobutadiene)(cyclopentadienyl)cobalt⁶⁸ and (cyclobutadiene)dicobalt hexacarbonyl.⁶⁹

The structure of (cyclobutadiene)iron tricarbonyl, determined by gas-phase electron diffraction,^{70,71} is the same as in the solid state. It was not possible to establish definitely if there was free rotation of the Fe(CO)₃ unit, but it was considered “highly probable”. The microwave spectrum of (cyclobutadiene)iron tricarbonyl is essentially that of a symmetric top molecule: i.e., the cyclobutadiene ring is square and perpendicular to the *a*-inertial axis. Hindered internal rotation effects were not observed.^{72,73} Measurement of the proton direct dipole coupling constants in the partially oriented ¹H

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(70) Oberhammer, H.; Brune, H. A. *Z. Naturforsch., A* **1969**, *24a*, 607.

(71) Davis, M. I.; Speed, C. S. *J. Organomet. Chem.* **1970**, *21*, 401.

(72) Roehrig, M. A.; Wikrent, P.; Huber, S. R.; Wigley, D. E.; Kukulich, S. G. *J. Mol. Spectrosc.* **1992**, *154*, 355.

(73) Lucken, E. A. C.; Pozzi, R.; Ramaprasad, K. R. *J. Mol. Struct.* **1973**, *18*, 377.

(60) Gardner, S. A.; Rausch, M. D. *J. Organomet. Chem.* **1973**, *56*, 365.

(61) Rausch, M. D.; Grossi, A. V. *J. Chem. Soc., Chem. Commun.* **1978**, 401.

(62) Amiet, R. G.; Reeves, P. C.; Pettit, R. *Chem. Commun.* **1967**, 1208.

(63) Amiet, R. G.; Pettit, R. *J. Am. Chem. Soc.* **1968**, *90*, 1059.

(64) Harvey, P. D.; Schaefer, W. P.; Gray, H. B.; Gilson, D. F. R.; Butler, I. S. *Inorg. Chem.* **1988**, *27*, 57.

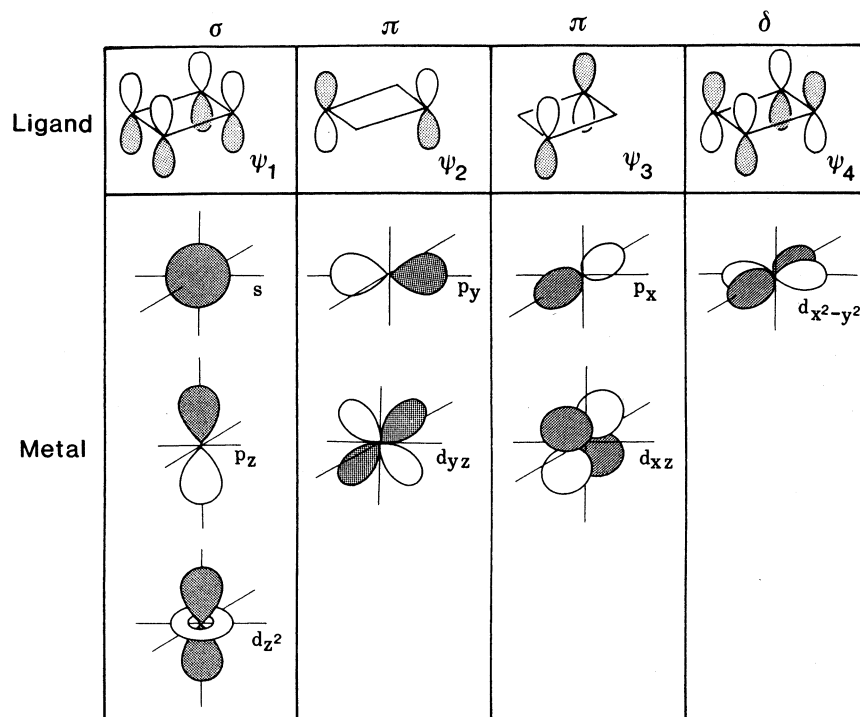


Figure 8. Metal–cyclobutadiene interactions in cyclobutadiene–metal complexes (from: Elschenbroich, C.; Salzer, A. *Organometallics—A Concise Introduction*, 2nd ed.; VCH: Weinheim, Germany, 1992; reproduced by permission, B. G. Teubner GmbH).

and ^2H NMR spectra of $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ and $(\text{C}_4\text{H}_3\text{D})\text{Fe}(\text{CO})_3$ in liquid crystal solvents at different temperatures suggested a very small departure from square symmetry of the cyclobutadiene ring, possibly caused by interaction with the solvent.^{74–76}

The electronic structure of (cyclobutadiene)iron tricarbonyl has been the subject of many papers. He I and He II low-energy photoelectron spectra provided useful information.^{77,78} The eight observed bands in the low-energy PE spectrum of (cyclobutadiene)iron tricarbonyl in the range 7.65–20.31 eV all were assigned.⁷⁸ The calculations (ab initio SCF MO) showed that there is a net negative charge on the cyclobutadiene ligand that results from π back-bonding from the iron atom into an antibonding MO of the ligand (δ bond). Better agreement between the experimental assignments and theoretical calculations was obtained by Chinn and Hall using generalized MO calculations with configuration interaction.⁷⁹ A simple textbook approach to the bonding is shown in Figure 8.⁸⁰ It is assumed that it is triplet state cyclobutadiene that is involved with unpaired electrons in the two degenerate ψ_2 and ψ_3 molecular orbitals. These interact with two singly occupied iron orbitals, generating two covalent bonds.

Brune and co-workers investigated the bonding in (substituted-cyclobutadiene)iron tricarbonyls by measuring the long-range ^{13}C – ^1H coupling constants in

their proton NMR spectra.^{81,82} The main conclusion agreed with the results of the other structural and spectroscopic studies: the ligand has a square geometry with all C–C bonds of equal length. The results of a similar NMR study of ((para-substituted phenyl)cyclobutadiene)iron tricarbonyl complexes, $(\text{Z}-\text{C}_6\text{H}_4\text{C}_4\text{H}_3)\text{Fe}(\text{CO})_3$; Z = H, CH₃, F, Cl, Br (^{13}C – ^1H and ^1H – ^1H coupling constants and $\nu(\text{CO})$ in the IR spectra) suggested there is no conjugative π interaction between the phenyl and cyclobutadiene rings.⁸³

After this discussion of structure and bonding we come to the chemical reactivity of our cover molecule.

IV. After the Breakthrough Synthesis: Rapid Development of the Chemistry of (Cyclobutadiene)iron Tricarbonyl by Pettit and Others

Pettit and his students very quickly discovered that (cyclobutadiene)iron tricarbonyl was quite reactive. In their first communication on its reactivity,⁸⁴ it is stated “We now wish to report data which indicate that this complex is aromatic in the sense that it undergoes electrophilic substitution reactions to yield a series of new cyclobutadiene complexes.” The close similarity to the reactivity of ferrocene was pointed out. The reaction most often used first to assess the reactivity of a new compound with potential aromatic character is the Friedel–Crafts reaction, and this worked well in the

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(75) Diehl, P.; Moia, F.; Boesiger, H.; Wirz, J. *J. Mol. Spectrosc.* **1983**, *98*, 297.

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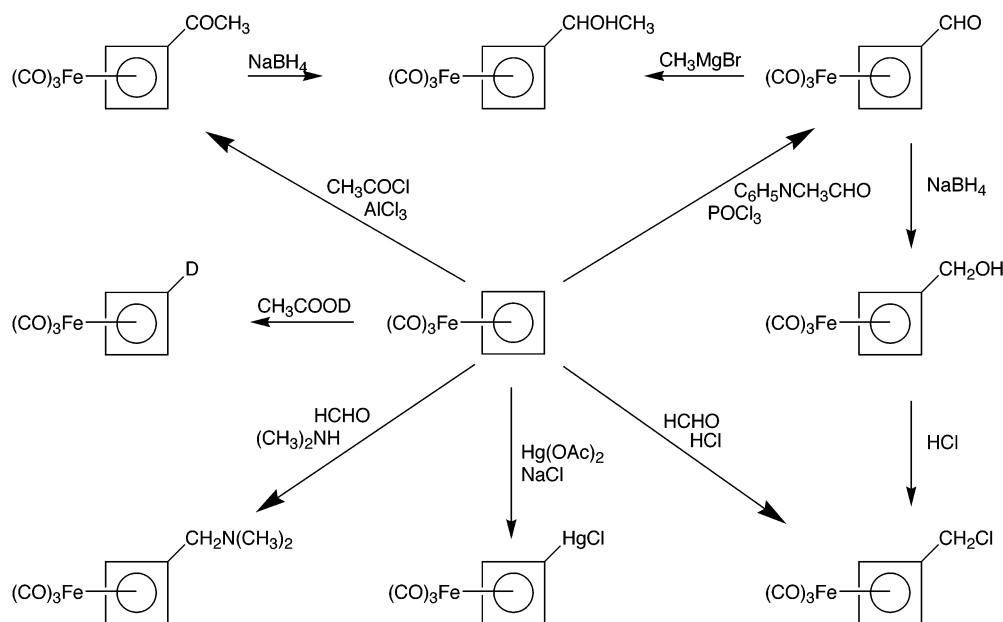
(81) (a) Brune, H. A.; Wolff, H. P.; Hüther, H. *Z. Naturforsch.*, **B** **1968**, *23b*, 1185. (b) *Chem. Ber.* **1968**, *101*, 1485.

(82) Brune, H. A.; Hanebeck, H.; Hüther, H. *Tetrahedron* **1970**, *26*, 3099.

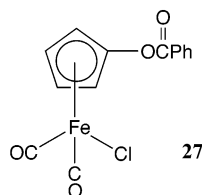
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(84) Fitzpatrick, J. D.; Watts, L.; Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3254.

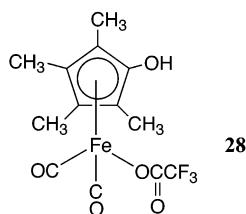
Scheme 3



case of (cyclobutadiene)iron tricarbonyl. It reacted with acetyl chloride in the presence of aluminum chloride in CS_2 at 20°C within 45 min to give $(\text{CH}_3\text{C}(\text{O})\text{C}_4\text{H}_3)\text{Fe}(\text{CO})_3$ in 60% yield. Benzoyl chloride reacted in similar fashion. The other reactions studied were summarized in a scheme (see Scheme 3) and included Vilsmeier formylation to give $(\text{C}_4\text{H}_3\text{CHO})\text{Fe}(\text{CO})_3$, chloromethylation which produced $(\text{C}_4\text{H}_3\text{CH}_2\text{Cl})\text{Fe}(\text{CO})_3$, aminomethylation which gave $(\text{C}_4\text{H}_3\text{CH}_2\text{NMe}_2)\text{Fe}(\text{CO})_3$, and monodeuteration with $\text{CF}_3\text{CO}_2\text{D}$. Details of these reactions and of the characterization of the products were not given. A full follow-up paper was promised but, apparently, never written. A review⁸⁵ tells of a novel byproduct isolated in the Friedel–Crafts benzoylation of (cyclobutadiene)iron tricarbonyl, **27**. The suggested



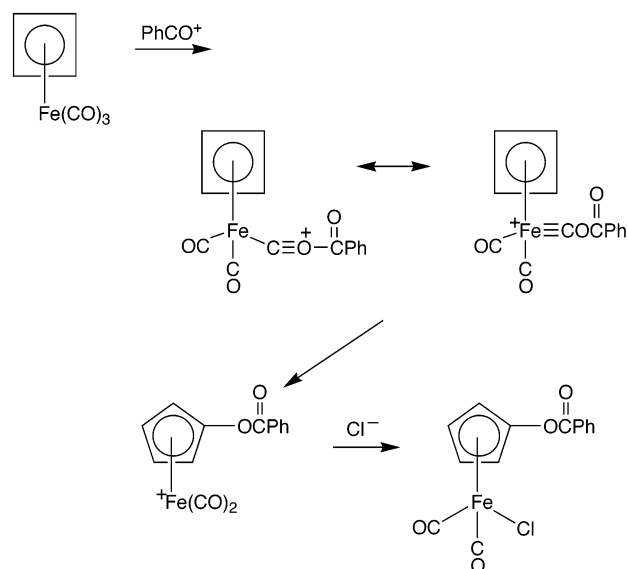
reaction course is shown in Scheme 4. Similar C_4 ring expansions were encountered in the reaction of (cyclobutadiene)molybdenum tetracarbonyl with $\text{CH}_3\text{C}(\text{O})\text{Cl}/\text{AlCl}_3$ and in the reaction of $[(\text{CH}_3)_4\text{C}_4]\text{Fe}(\text{CO})_3$ with $\text{CF}_3\text{CO}_2\text{H}$, in which **28** was formed.⁸⁵



The mercuriation of $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ is a very facile reaction. A 30 min reaction with an equimolar quantity

(85) Pettit, R. *J. Organomet. Chem.* **1975**, *100*, 205.

Scheme 4

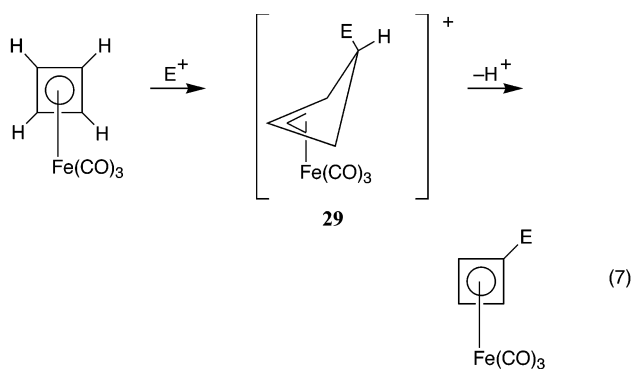


of mercuric acetate in acetic acid gave a mixture in 5.5:2.0:0.5:1:1 molar ratio of the mono-, 1,2-di-, 1,3-di-, tri-, and tetraacetoxymercury derivatives, respectively.⁸⁶ These ratios were determined by conversion of the mercuriation products to the respective iodo derivatives by treatment with KI_3 . This is a reversible process: when either $(\text{C}_4\text{H}_3\text{HgOAc})\text{Fe}(\text{CO})_3$ or $[\text{C}_4(\text{HgOAc})_4]\text{Fe}(\text{CO})_3$ was dissolved in acetic acid, a mixture of all possible mercurated derivatives was formed. Both $(\text{C}_4\text{H}_3\text{HgCl})\text{Fe}(\text{CO})_3$ and $(\text{C}_4\text{H}_3\text{I})\text{Fe}(\text{CO})_3$ served as precursors for the useful (monolithiocyclobutadiene)iron tricarbonyl, $(\text{C}_4\text{H}_3\text{Li})\text{Fe}(\text{CO})_3$, in reactions with methyl- or phenyllithium at -78°C .⁸⁷

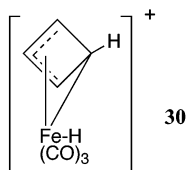
(86) Amiet, G.; Nicholas, K.; Pettit, R. *Chem. Commun.* **1970**, 161.

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The reactivity of (cyclobutadiene)iron tricarbonyl with electrophiles is quite similar to that of ferrocene. The reaction course is believed to be that shown in eq 7.⁸⁴



Studies by C. M. Adams et al.⁸⁸ provided evidence for exo attack on the C₄H₄ ligand as shown. While intermediates of type **29** have not been isolated in Friedel–Crafts acylation of (cyclobutadiene)iron tricarbonyl, Olah and Liang⁸⁹ have reported ¹H and ¹³C NMR studies of the protonation product of (C₄H₄)Fe(CO)₃ in FSO₃H/SO₂ solution at -78 °C which showed (via observation of the *gem* ¹H–Fe–¹H_x and ¹³C–Fe–H_x coupling) it to be the static σ–π-bonded cation **30**, the



thermodynamically favored species. This, however, does not exclude **29** (E = H) as the cation formed under kinetically controlled conditions. Functionally substituted (cyclobutadiene)iron tricarbonyl complexes also can be prepared directly by the reaction of the appropriate substituted dihalocyclobutene with Fe₂(CO)₉ or Na₂Fe(CO)₄: e.g., Scheme 5.⁹⁰ 1,2-Disubstituted (cyclobutadiene)iron complexes such as those shown in Scheme 5 are chiral and, in appropriate cases, may be resolved.^{90c} Once some key functional groups have been introduced into (cyclobutadienyl)iron tricarbonyl, standard functional group conversions are possible (as in the case of ferrocene) and many such reactions have been reported. It is beyond the scope of this essay to provide details of this more routine chemistry. What was done up to 1977 is summarized very thoroughly in the lengthy *Chemical Reviews* article by Avi Efraty.⁹¹ (See also later reviews in which (cyclobutadiene)iron tricarbonyl complexes are covered.⁹²) However, some of the other chemistry of (cyclobutadiene)iron tricarbonyl is very interesting and worth discussing.

The photolytic ejection of a CO ligand from metal carbonyls is a well-known process, in many cases of

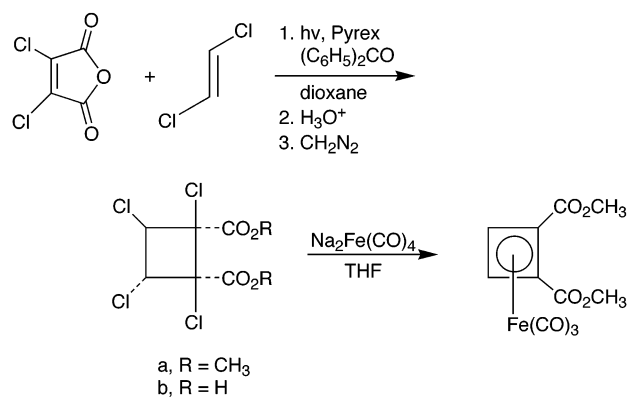
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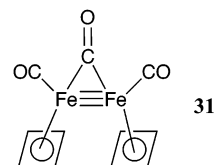
(90) (a) Berens, G.; Kaplan, F.; Rimerman, R.; Roberts, B. W.; Wissner, A. *J. Am. Chem. Soc.* **1975**, *97*, 7076. (b) Roberts, B. W.; Wissner, A.; Rimerman, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 6208. See also: (c) Schmidt, E. K. G. *Chem. Ber.* **1974**, *107*, 2440. (d) Adams, C. M.; Joslin, S. A.; Crawford, E. S.; Schemenaur, J. E. *Organometallics* **1993**, *12*, 656.

(91) Efraty, A. *Chem. Rev.* **1977**, *77*, 691–744.

Scheme 5



synthetic utility. The formation of (C₄H₄)Fe(CO)₂(N₂) and (C₄H₄)Fe(CO)(N₂)₂ during photolysis in low-temperature matrices has been reported.⁹³ Dinitrogen and dihydrogen are completely miscible with supercritical xenon (scXe); therefore, it is advantageous to carry out the photolysis of (C₄H₄)Fe(CO)₃ in this medium. Experiments in which (C₄H₄)Fe(CO)₃ was photolyzed in a high-pressure IR cell in scXe under a N₂ pressure of 1200 psi showed that both N₂ complexes had been formed.⁹⁴ A similar experiment with H₂ in place of N₂ led to the formation of the nonclassical dihydrogen complex (C₄H₄)Fe(CO)₂(H₂). This product is not very stable, decomposing under 1500 psi of H₂ at room temperature with a *t*_{1/2} value of ~10 min. Koerner von Gustorf and co-workers⁹⁵ found that UV irradiation of (C₄H₄)Fe(CO)₃ in THF at -40 °C in a stream of nitrogen gave, after removal of THF at -20 °C, a dark red, extremely sensitive solid believed to be **31** on the basis of spec-



troscopic and chemical evidence. Its reactions with CO and with trimethyl phosphite gave (C₄H₄)Fe(CO)₃ and a mixture of (C₄H₄)Fe(CO)₂[P(OMe)₃] and (C₄H₄)Fe(CO)-[P(OMe)₃]₂, respectively.

The action of NO⁺PF₆⁻ in acetonitrile on (C₄H₄)Fe(CO)₃ produced [(C₄H₄)Fe(CO)(NO)]PF₆, an air-stable, yellow-orange solid. The latter reacted with group 15 triphenyl compounds in refluxing acetone to give [(C₄H₄)Fe(CO)(NO)(Ph₃E)]PF₆ (E = P, As, Sb).⁹⁶ Olefin complexes **32** and **33** also were prepared by photolysis of (C₄H₄)Fe(CO)₃

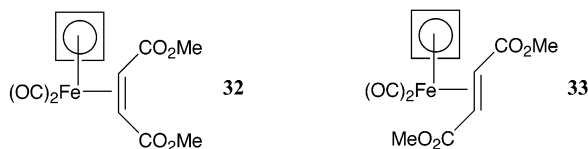
(92) (a) Black, D. St.; Jackson, W. R.; Swan, J. M. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, U.K., 1979; Vol. 3, Chapter 15.6, pp 1297–1302. (b) Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1982; Vol. 4, Chapter 31.3, pp 444–447, 459–461, 471–474. (c) Donaldson, W. A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, Chapter 6.2, pp 623–636. (d) Pearson, A. In ref 92c, pp 637–683.

(93) (a) Rest, A. J.; Sodeau, J. R.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1978**, 652. (b) Fitzpatrick, N. J.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1979**, 351.

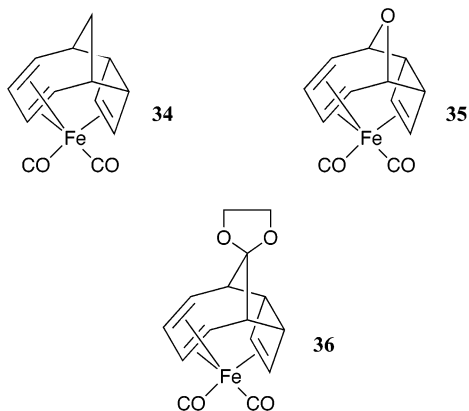
(94) Howdle, S. M.; Healy, M. A.; Poliakov, M. *J. Am. Chem. Soc.* **1990**, *112*, 4804.

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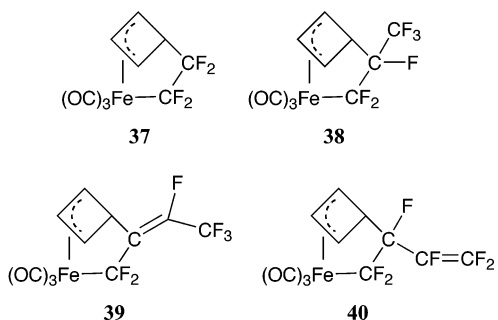
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in the presence of the respective olefin.⁹⁷ In contrast, similar photolytic reaction of $(C_4H_4)Fe(CO)_3$ with cyclohexatriene gave an orange, crystalline solid whose X-ray crystal structure determination showed it to be **34**.⁹⁸

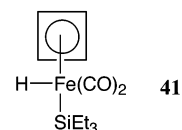


Presumably, $(C_4H_4)Fe(CO)_2$ (cycloheptatriene) is the initially formed product. The two hydrocarbon ligands then undergo intramolecular cycloaddition to give **34**. Similar reactions giving **35** and **36** were observed with oxepin and the ethylene ketal of tropone. A similar reaction path appears to be followed in the reactions of $(C_4H_4)Fe(CO)_3$ with tetrafluoroethylene, hexafluoropropene, and hexafluorobuta-1,3-diene, which produced **37–39**, respec-

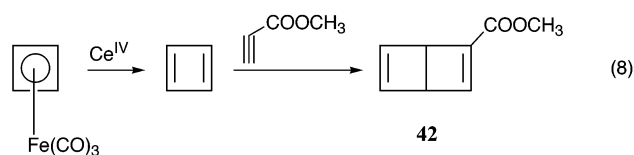


tively.⁹⁹ In the case of **39**, it was suggested that **40** was formed first, which then underwent a fluoride-anion catalyzed 1,3-fluorine shift.

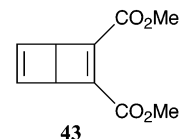
Photoinduced oxidative addition to the iron atom of (cyclobutadiene)iron tricarbonyl also is possible. When Hill and Wrighton¹⁰⁰ photolyzed $(C_4H_4)Fe(CO)_3$ in a hydrocarbon glass at ~ 100 K, IR spectroscopic evidence for the formation of free carbon monoxide and the unsaturated $16e$ d^6 species $(C_4H_4)Fe(CO)_2$ was obtained. When this intermediate was generated in a glass containing triethylsilane (Et_3SiH), complex **41** was formed and characterized by IR spectroscopy.



Of greater interest and utility are those reactions in which free, transient cyclobutadiene is generated by appropriate oxidation of (cyclobutadiene)iron tricarbonyl. Emerson, Watts, and Pettit had found that oxidation of (cyclobutadiene)iron tricarbonyl with ceric ammonium nitrate produced a mixture of organic products which included a dimer of cyclobutadiene.⁴⁹ In an effort to trap the putative intermediate cyclobutadiene, the oxidation of $(C_4H_4)Fe(CO)_3$ was carried out in the presence of methyl propiolate in cold ethanol solution. The expected product, **42**, was isolated and identified (eq 8).¹⁰¹ When dimethyl acetylenedicarboxy-



late was used as a trapping agent, **43** was obtained,



which was completely isomerized to dimethyl phthalate when heated at $90^\circ C$ for 30 min. These reactions were interpreted in terms of the liberation and bimolecular trapping of free cyclobutadiene. In an attempt to test this hypothesis, Pettit and co-workers carried out the following experiment,¹⁰¹ as described in their own words:

“A solution of the complex $[(C_4H_4)Fe(CO)_3]$ in alcohol was slowly added to a flask containing a stirred aqueous solution of ceric ammonium nitrate maintained at 0° . The gases which evolved were passed through a short tube and led into a second flask immersed in liquid nitrogen. A water aspirator was attached to the second flask and a pressure of 100 mm. was maintained in the system. After completion of the addition, the apparatus was disconnected and a cold ethereal solution of methyl propiolate was added to the material which had collected in the receiver flask. The ether solution was then heated and analyzed by vapor phase chromatography. The experiment was repeated several times, and in each case small amounts of methyl benzoate were detected in the product.

We interpret this to mean that free cyclobutadiene is liberated in the reaction between the complex and ceric ions and that this hydrocarbon, although obviously extremely reactive, nonetheless possesses a finite lifetime.”

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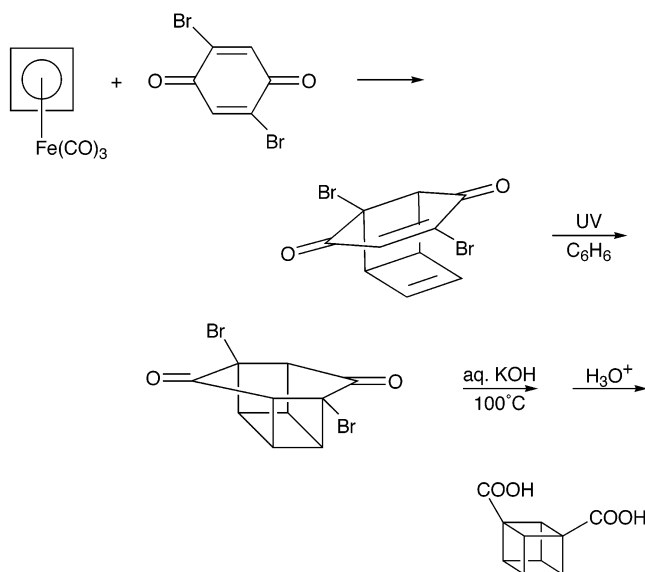
(98) Ward, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1971**, *93*, 262.

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(100) Hill, R. H.; Wrighton, M. S. *Organometallics* **1987**, *6*, 632.

(101) Watts, L.; Fitzpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253.

Scheme 6

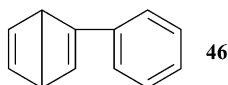


(The initially formed bicyclic product, **42**, obviously underwent thermal rearrangement to $C_6H_5CO_2Me$.) Subsequent work in the Pettit group was devoted to an understanding of the nature of the ground state of free cyclobutadiene.¹⁰² In the initial report^{102a} cyclobutadiene acted as expected for a singlet diene. On oxidative degradation of $(C_4H_4)Fe(CO)_3$ in the presence of dimethyl maleate *endo,cis*-dicarbomethoxybicyclohexene (**44**)



was the sole product. With dimethyl fumarate exclusive formation of *trans*-dicarbomethoxybicyclohexene (**45**) was observed. Such stereospecific addition would not be expected if cyclobutadiene were to be a triplet species. Further support for this conclusion was provided by later work. The possibility of a direct reaction of $(C_4H_4)Fe(CO)_3$ with the trapping agent as an alternative mechanism was excluded.⁹⁷ Further studies^{102b} suggested that cyclobutadiene is rectangular (rather than square) in its ground state.

Reactions of free cyclobutadiene as generated by ceric ammonium nitrate oxidation at 0 °C of (cyclobutadiene)iron tricarbonyl are of general synthetic utility, as shown by a few examples. Thus, reaction of cyclobutadiene with phenylacetylene gave hemi-Dewar biphenyl (**46**).¹⁰³ Cubane 1,3-dicarboxylic acid was prepared

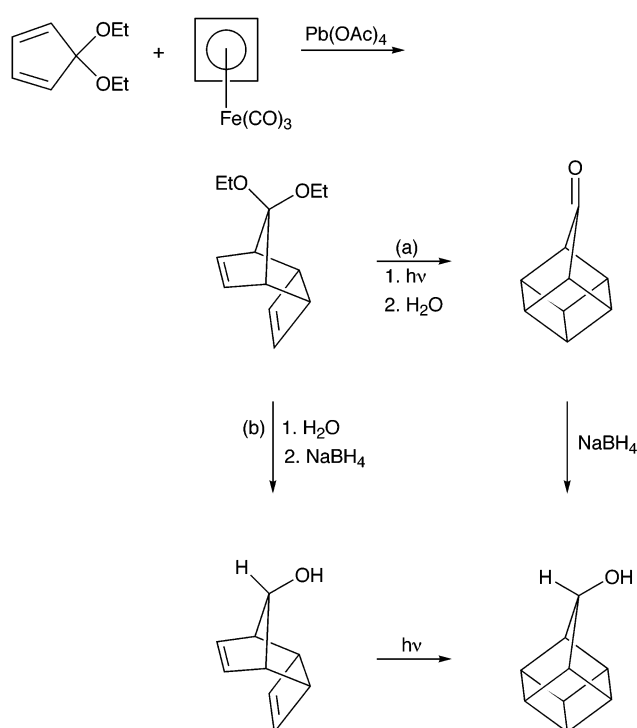


in a several-step procedure (Scheme 6), the first one of which was trapping of cyclobutadiene by 2,5-dibromobenzoquinone.¹⁰⁴ Also accessible was the homocubyl system (Scheme 7).¹⁰⁵

(102) (a) Watts, L.; Fitzpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 623. (b) Reeves, P.; Devon, T.; Pettit, R. *J. Am. Chem. Soc.* **1969**, *91*, 5890.

(103) Burt, G. D.; Pettit, R. *Chem. Commun.* **1965**, 517.

Scheme 7



Two cyclobutadiene molecules can add to an activated acetylene (eq 9).¹⁰⁶ Intramolecular trapping of cyclobutadiene (eq 10) also has been reported.¹⁰⁷ In addition to acetylenes and olefins, diazenes have been used as trapping agents (eq 11).¹⁰⁸

Substituted (cyclobutadiene)iron tricarbonyl complexes of the type $(C_4H_3CH_2X)Fe(CO)_3$ ($X = OH, Cl$) were of special interest.¹⁰⁹ Thus, only a brief treatment of $(C_4H_3CH_2OH)Fe(CO)_3$ with concentrated HCl served to convert it to the chloride, $(C_4H_3CH_2Cl)Fe(CO)_3$. The latter underwent rapid solvolysis in water to regenerate the alcohol; in methanol, the methyl ether $(C_4H_3CH_2OCH_3)Fe(CO)_3$ was obtained. These conversions suggested the intermediacy of a stable cationic species. A crystalline, yellow salt, $[(C_4H_3CH_2)Fe(CO)_3]^+[SbCl_6]^-$, which was stable in the cold, was formed on treatment of the chloromethyl derivative with $SbCl_5$. The same cation was generated when $(C_4H_3CH_2OH)Fe(CO)_3$ was dissolved in concentrated H_2SO_4 . The 1H NMR spectrum of the cation derived from $(C_4H_3CH(OH)CH_3)Fe(CO)_3$ in concentrated H_2SO_4 was interpreted by the authors as indicative of two possible stabilized structures for the cation, **47** and **48**, with the latter preferred. The structural question also was addressed by the determination of the X-ray crystal structures of several (cyclobutadiene)iron tricarbonyl-substituted carbenium ions, **49–51** (deep red) and **52** (yellow), as the BF_4^- salts.^{109b} The structure of **51** is shown in Figure 9. In **49–51** the cyclobutadiene rings and the carbenium center are

(104) Barborak, J. C.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 1328.

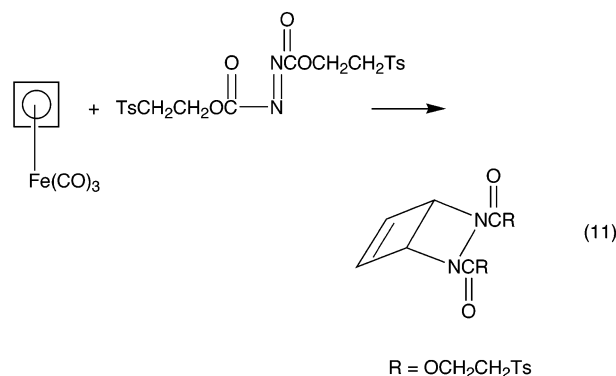
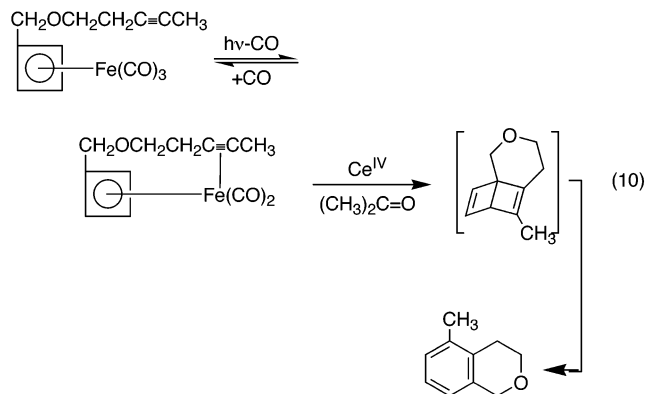
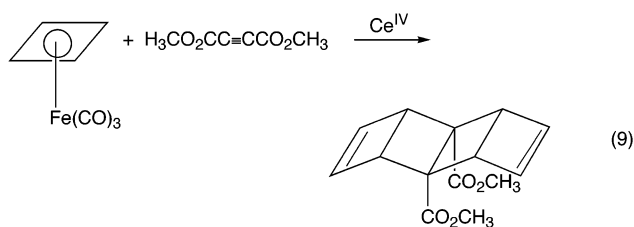
(105) Barborak, J. C.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 3080.

(106) Meinwald, J.; Mioduski, J. *Tetrahedron Lett.* **1974**, 3839.

(107) Grubbs, R. H.; Pancoast, T. A.; Grey, R. A. *Tetrahedron Lett.* **1974**, 2425.

(108) Masamune, S.; Nakamura, N.; Spadaro, J. *J. Am. Chem. Soc.* **1975**, *97*, 918.

(109) (a) Fitzpatrick, J. D.; Watts, L.; Pettit, R. *Tetrahedron Lett.* **1966**, 1299. (b) Davis, R. E.; Simpson, H. D.; Grice, N.; Pettit, R. *J. Am. Chem. Soc.* **1971**, *93*, 6688.



essentially coplanar and there appears to be no direct bonding interaction between the iron atom and the carbenium center. It was concluded "that the major interaction leading to stabilization of the cation involves interaction of a filled metal orbital with the four carbon atoms of the cyclobutadiene ring and, through π - π carbon-carbon interaction, electrons are transmitted to the electron-deficient exocyclic carbon atoms". Thus, the stabilization of $[(C_4H_3CR_2)^+]$ carbenium ions appears to be different in nature from the stabilization of ferrocenyl-substituted α -carbenium ions in which there is an Fe-C(α)⁺ interaction.

A later ¹³C NMR study of the alcohols (C₄H₃CH₂OH)-Fe(CO)₃ and (C₄H₃CH(OH)R)Fe(CO)₃ (R = CH₃, C₆H₅)

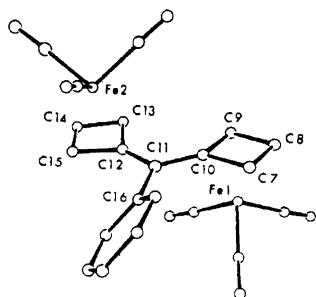
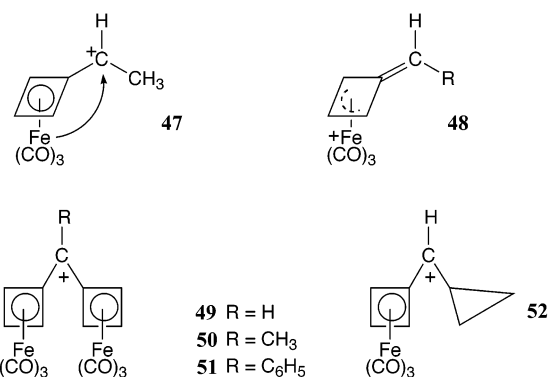


Figure 9. X-ray crystal structure of $\{C_6H_5C[C_4H_3Fe(CO)_3]_2\}^+$ (from ref 109b).

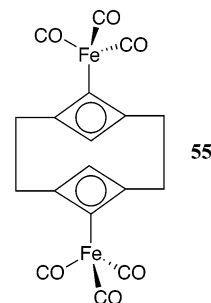
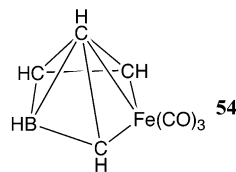
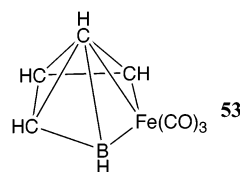
in CDCl₃ and of the derived carbenium ions $[(C_4H_3CH_2)^+$



Fe(CO)₃⁺ and $[(C_4H_3CHR)Fe(CO)_3]^+$ (R = CH₃, C₆H₅) in concentrated H₂SO₄ gave results which also were interpreted in terms of stabilization of the carbenium center via the interaction shown in formula **48**.¹¹⁰

There is much more chemistry of (cyclobutadiene)iron tricarbonyl and its diverse derivatives, and the reader is referred to the reviews noted earlier. There are, however, a few areas of (cyclobutadiene)iron tricarbonyl and (cyclobutadiene)(η^5 -cyclopentadienyl)cobalt chemistry which merit special mention.

Fehlner has reported a very interesting reaction of (cyclobutadiene)iron tricarbonyl with pentaborane(9) which proceeded when the reactants were irradiated in diethyl ether.¹¹¹ A low yield of a product of empirical formula BC₄H₅Fe(CO)₃ was isolated. On the basis of its ¹H and ¹¹B NMR spectra, it could be either **53** or **54**, with the boron atom in the basal plane. Since the three observed C-H chemical shifts were nearly equal, structure **53** was preferred.



Of interest also is the synthesis of **55**, the smallest cyclophane containing two metalloaromatic (cyclobutadiene)iron tricarbonyl units held cofacially by two C₂H₄ bridges.¹¹²

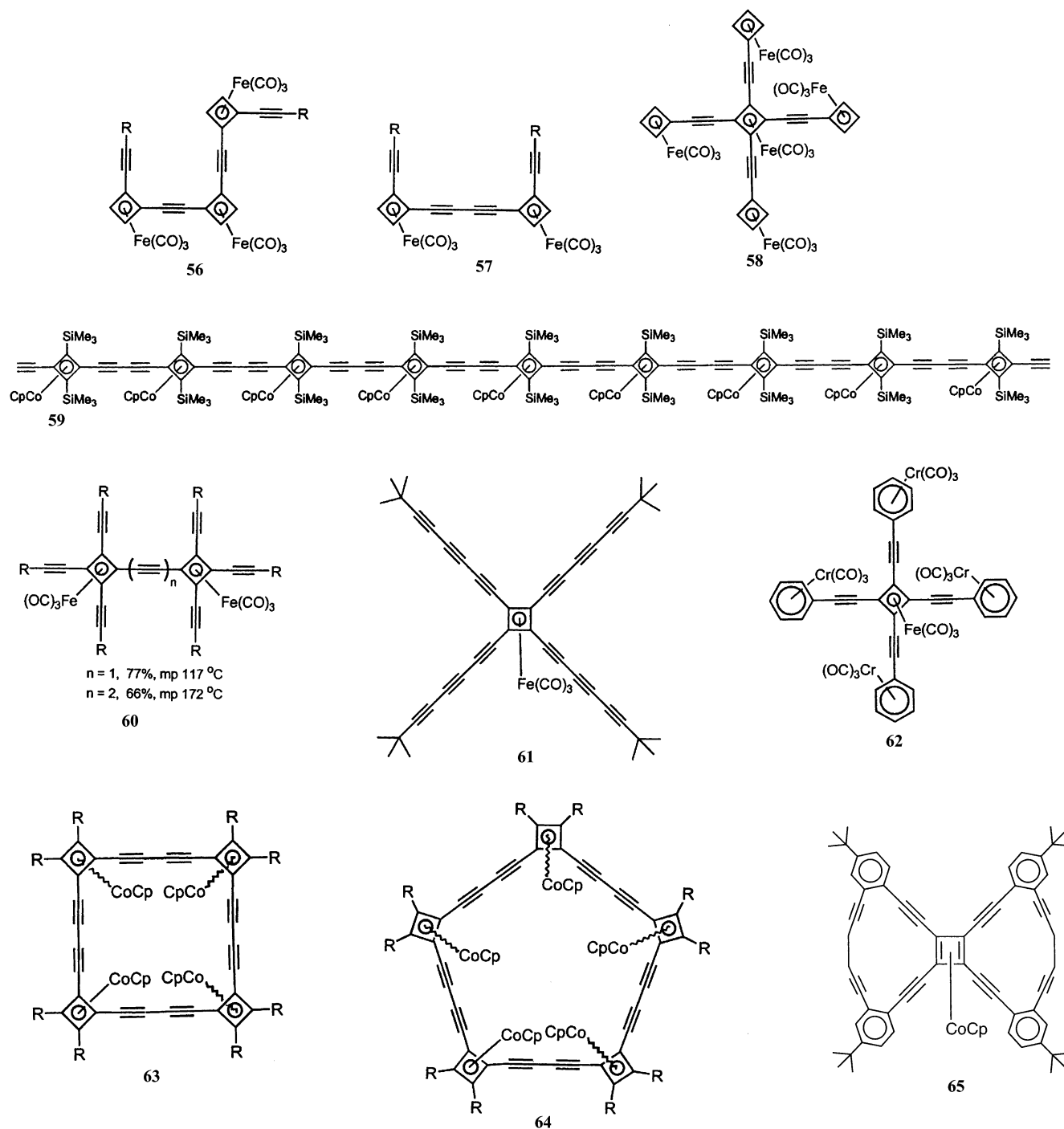
A large body of very interesting work by Uwe Bunz, begun at the Max Planck Institut für Polymerforschung in Mainz and continued at the University of South Carolina, on multiply ethynylated (cyclobutadiene)iron

(110) Eschbach, C. S.; Seyferth, D.; Reeves, P. C. *J. Organomet. Chem.* **1976**, *104*, 363.

(111) Fehlner, T. P. *J. Am. Chem. Soc.* **1978**, *100*, 3250.

(112) Adams, C. M.; Holt, E. M. *Organometallics* **1990**, *9*, 980.

Chart 1



tricarbonyl and (cyclobutadiene)(η^5 -cyclopentadienyl)-cobalt complexes has been summarized in a review.¹¹³ These were used as building blocks for the construction of organoiron and -cobalt carbon-rich materials of higher molecular weight of some interest. Complexes such as **56–58** (Chart 1) were prepared, also fascinating linear

oligomers such as **59** and **60**, star-shaped molecules such as **61** and **62**, cyclics such as **63** and **64**, and butterfly-shaped molecules, **65**. Bunz has continued his studies in this area.¹¹⁴

V. Concluding Remarks

In conclusion, we return to Rowland Pettit. Rolly, as he was called by his many friends, was dedicated to his research. He approached it with drive and enthusiasm. His interests were broad—ranging from theoretical aspects to the development of new organometallic systems and a study of their reactivity and to catalytic processes both of basic and industrial interest. However, he was not one-sided. He had a great capacity for

(113) Bunz, U. H. E. *Top. Curr. Chem.* **1999**, *201*, 131.

(114) Some examples: (a) Laskoski, M.; Morton, J. G. M.; Smith, M. D.; Bunz, U. H. F. *Chem. Commun.* **2001**, 2590. (b) Laskoski, M.; Smith, M. D.; Morton, J. G. M.; Bunz, U. H. F. *J. Org. Chem.* **2001**, *66*, 5174. (c) Steffen, W.; Köhler, B.; Altmann, M.; Scherf, U.; Stitzer, K.; zur Loye, H. C.; Bunz, U. H. F. *Chem. Eur. J.* **2001**, *7*, 117. (d) Laskoski, M.; Morton, J. G. M.; Smith, M. D.; Bunz, U. H. F. *J. Organomet. Chem.* **2002**, *652*, 21. (e) Waybright, S. M.; McAlpine, K.; Laskoski, M.; Smith, M. D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2002**, *124*, 8661.

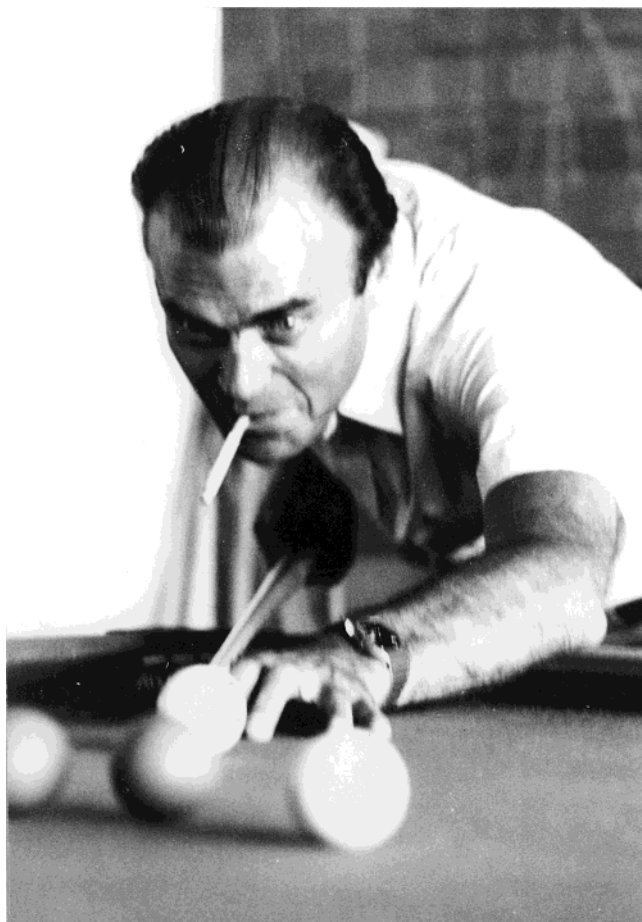


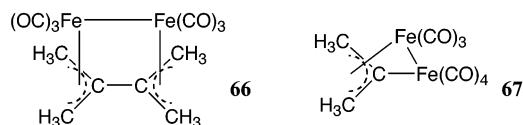
Figure 10. Rowland Pettit in a typically relaxed mood after giving his Plenary Lecture at the Tenth Sheffield-Leeds International Symposium on Organometallic Chemistry, University of Sheffield, July 1979 (reproduced by permission of Professor Peter Maitlis, University of Sheffield).

enjoying life and had a fine sense of humor. He liked to play pool (Figure 10) and, unfortunately, enjoyed smoking, which no doubt contributed to his early death at the age of 54 from lung cancer. He loved to travel, and it was during a trip in India that I came to know him well and to admire and esteem him, both as a great chemist and a wonderful person. The American Chemical Society, on my recommendation, appointed him a member of the first Editorial Advisory Board of *Organometallics*, but sadly, he did not live to see the first issue of our journal, which was dedicated to his memory.

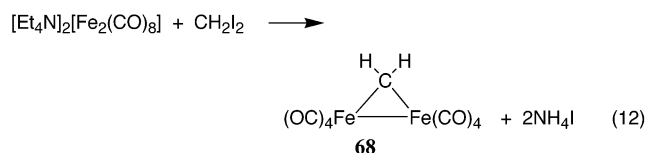
While Pettit's research in the 1965–1975 period was focused mainly on (cyclobutadiene)iron tricarbonyl chemistry, he was active in other areas of organometallic chemistry as well:

- The in situ preparation of the cationic methylene complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{Fe-CH}_2]^+$ by reaction of $(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{FeCH}_2\text{OCH}_3$ with HBF_4 . When carried out in the presence of an olefin, the reaction resulted in stereospecific formation of a cyclopropane.¹¹⁵
- The preparation of cyclopentadieneiron tricarbonyl by reaction of cyclopentadiene with $\text{Fe}_2(\text{CO})_9$ in refluxing diethyl ether.¹¹⁶
- Valence tautomerism in (cyclooctatetraene)iron tricarbonyl.¹¹⁷

- Degenerate valence tautomerism in $(\text{Me}_2\text{-C=C=CMe}_2)\text{Fe}(\text{CO})_3$, in which the allene–iron interaction alternates between the two orthogonal π MOs of the allene.¹¹⁸
- Reaction of allene with $\text{Fe}_2(\text{CO})_9$, which gave **66** and **67**.¹¹⁹



- New trimethylenemethane complexes of iron, molybdenum, and chromium.¹²⁰
- Bond localization in aromatic iron carbonyl complexes (an X-ray structural study of a series of $\text{Fe}(\text{CO})_3$ complexes of vinylbenzenes and -naphthalenes).¹²¹
- The $\text{Co}_2(\text{CO})_6$ unit as an alkyne protecting group.¹²²
- A complex containing an $\text{Fe}=\text{Fe}$ double bond, tetracarbonylbis(μ -2,2,5,5-tetramethylhex-3-yne)diiron, prepared by reaction of di-*tert*-butylacetylene with $\text{Fe}_3(\text{CO})_{12}$.¹²³
- Preparation of (α -alkynyl)dicobalt hexacarbonyl carbenium ions that are stable in solution and useful in organic synthesis.¹²⁴
- $[2\pi + 6\pi]$ cycloaddition reactions between ligands coordinated to an iron atom.¹²⁵
- Chemistry of octacarbonyl(μ -methylene)diiron (**68**) and its derivatives (eq 12).¹²⁶



This impressive body of research in organometallic chemistry (and more) was produced in less than 20 years. Pettit was going strong at the time that his health deteriorated. Another 15 years no doubt would have brought many more interesting and important contributions. His early death was a great loss for organometallic chemistry (and to his family and many friends throughout the world).

This has, I think, been an interesting story. It started in 1930 with the discovery of (butadiene)iron tricarbonyl, a novel but completely unappreciated organometallic complex. After a hiatus of nearly 30 years, it was rediscovered and led to a new, very active area of

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 (116) Kochhar, R. K.; Pettit, R. *J. Organomet. Chem.* **1966**, *6*, 279.
 (117) Keller, C. E.; Shoulders, B. A.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 4760.
 (118) Ben-Shoshan, R.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 2231.
 (119) Ben-Shoshan, R.; Pettit, R. *Chem. Commun.* **1968**, 247.
 (120) Ward, J. S.; Pettit, R. *Chem. Commun.* **1970**, 1419.
 (121) Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1970**, *92*, 716.
 (122) Nicholas, K. M.; Pettit, R. *Tetrahedron Lett.* **1971**, 3475.
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 (124) Nicholas, K. M.; Pettit, R. *J. Organomet. Chem.* **1972**, *44*, C21.
 (125) Davis, R. E.; Dodds, T. A.; Hsen, T.-H.; Wagnon, J. C.; Devon, T.; Tancrede, J.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7562.
 (126) (a) Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752. (b) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350.

research—that of conjugated diene–metal complexes. The extension to (cyclobutadiene)metal complexes resulted from theoretical considerations of Longuet-Higgins and Orgel, who predicted that metal complexes of the unstable ligand should be stable enough to permit their isolation. Only 3 years later an iron and a nickel complex were isolated, but the ligands in these were tetraphenyl- and tetramethylcyclobutadiene, respectively, both dead ends as far as an exploitation of C₄-ring reactivity was concerned. Six years later, in an extension of Pettit's investigation of (conjugated, acyclic diene)iron tricarbonyl complexes, Emerson, Watts, and Pettit reported the preparation and isolation of our cover molecule, (cyclobutadiene)iron tricarbonyl, (C₄H₄)Fe(CO)₃, which allowed the development of an extensive and exciting new chemistry, not only of the complex itself but also, for the first time, of *free cyclobutadiene*. This new organometallic chemistry has indeed borne unexpected organic fruit.

This essay has been concerned in the main with cyclobutadiene–iron complexes. Some (cyclobutadi-

ene)(cyclopentadienyl)cobalt complexes have been mentioned as well (and, in fact, (tetramethylcyclobutadiene)cobalt complexes have been the subject of a flurry of studies in recent years).¹²⁷ However, the field by now is even broader: cyclobutadiene complexes of many other metals—vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, ruthenium, osmium, rhodium, iridium, nickel, palladium, and platinum—have been reported.¹²⁸ After an almost explosive growth during the 1965–1975 period, the field has matured, but today, new contributions still are being reported.

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(128) For a recent, short review see: Baker, P. K.; Silgram, H. *Trends Organomet. Chem.* **1999**, *3*, 21.