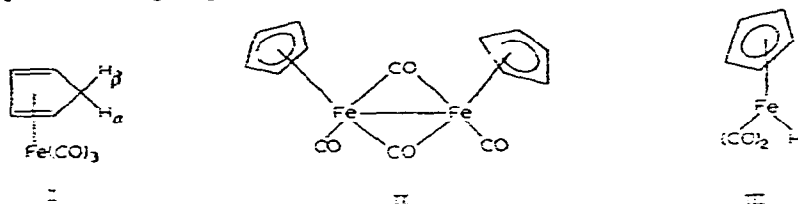# CYCLOPENTADIENEIRON TRICARBONYL

R. K. KOCHHAR AND R. PETTIT

*Department of Chemistry, University of Texas, Austin, Texas (U.S.A.)*

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Although iron tricarbonyl complexes of cycloheptadiene, cyclohexadiene, and cyclobutadiene are well characterized and found to be thermally stable materials, the corresponding complex of cyclopentadiene (I) has hitherto eluded characterization*. The most common method used for the preparation of dieneiron tricarbonyl complexes involves the direct reaction between the diene and iron pentacarbonyl. However, in the case of cyclopentadiene this reaction leads to the formation of the binuclear complex (II) in which the organic ligands are cyclopentadienyl rather than cyclopentadiene groups[2].

I   II   III

It has been suggested that one possible mode of formation of the binuclear complex in this reaction involves first the formation of cyclopentadiene iron tricarbonyl (I) which then rearranges, with loss of carbon monoxide, to cyclopentadienyliron dicarbonyl hydride (III); the latter system is then supposed to transfer a hydrogen atom to an acceptor and then dimerize to produce (II)[3].

The strong tendency for cyclopentadiene derivatives to react with Fe(CO)$_5$ to produce complexes possessing cyclopentadienyl ligands is graphically illustrated in the reaction of the spiro diene (IV). Upon reaction with Fe(CO)$_5$ this material produces the binuclear complex (V) in which a carbon skeleton rearrangement must have occurred[4].

IV   V
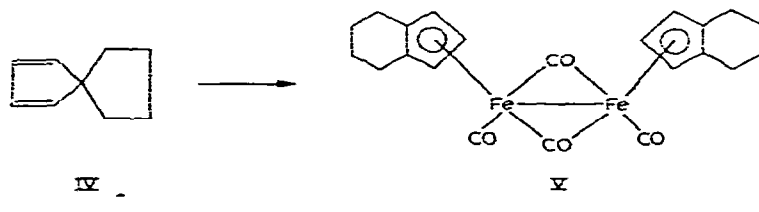
* A brief mention[1] of the preparation of cyclopentadieneiron tricarbonyl through reaction of biscyclopentadienenickel with Fe(CO)$_5$ has been made. However, from the scant properties reported, it is not clear whether this material is the same substance as is reported in the present paper.

Another reaction which might have reasonably been expected to produce cyclopentadieneiron tricarbonyl is that of the cyclopentadienyliron tricarbonyl cation (VI) with sodium borohydride. However, even when conducted at low temperature this reaction gave cyclopentadienyliron dicarbonyl hydride (III) as the first identifiable product[5].

It was considered to be of interest then to further pursue the isolation of cyclopentadieneiron tricarbonyl to determine whether it is indeed thermodynamically unstable with respect to the carbonyl hydride (III) and, if possible, to determine whether it is an intermediate in the formation of the binuclear complex (II) from cyclopentadiene and $Fe(CO)_5$.

The suggestion for the present synthesis of cyclopentadieneiron tricarbonyl originated with the report that butadiene reacts with diiron nonacarbonyl to produce butadieneiron tetracarbonyl which, also under mild conditions, loses carbon monoxide to give, together with other products, butadieneiron tricarbonyl[6]. We now find that cyclopentadiene when treated with $Fe_2(CO)_9$ at 40° gives fair yields (30 %) of cyclopentadieneiron tricarbonyl; no evidence can be seen for the formation of cyclopentadieneiron tetracarbonyl but it is presumably involved as an intermediate.

The structure of the complex is indicated by the elemental analysis and by its spectral properties. In the infrared spectrum there is a strong absorption at 2805 cm^{-1} which is assigned to the C–H stretching mode. Similar absorption bands appear in the region 2750–2765 cm^{-1} in the compounds π-C_5H_5-M-π-C_5H_6 (M = Co, Rh) and π-$C_5H_6Fe(CO)_2PPh_3$. This unusually intense and low frequency C–H stretching mode has been attributed to a methylene H_2 interaction with the metal atom[5,7]. A medium intensity band at 3076 cm^{-1} is indicative of olefinic hydrogens while the lack of absorption in the range 3100–3150 cm^{-1} points against a σ-cyclopentadienyl ring system. Finally, the three absorption bands at 1974, 1981 and 2048 cm^{-1} are typical of carbonyl absorptions in dieneiron tricarbonyl complexes[8].

The NMR spectrum of the compound is also consistent with the formulation (I). The two protons H_3 and H_4 appear as a triplet at 4.38 τ while the protons H_2 and H_5 appear as a multiplet at 7.15 τ. Proton H_β is coupled strongly with H_α ($J = 11.7$ cps) and appears as a doublet centered at 7.31 τ; proton H_α is likewise a doublet centered at 7.71 τ though the lower field peak of the $H_\alpha H_\beta$ quartet coincides with the absorptions of H_2 and H_5. These chemical shift values are entirely in accord with those of other dieneiron tricarbonyl complexes[8]. No absorptions beyond 10 τ could be detected indicating the absence of protons directly attached to a metal atom.

The isolation of cyclopentadieneiron tricarbonyl demonstrates that this material is thermodynamically stable with respect to the carbonyl hydride (III), however, its thermal decomposition is of interest in connection with the proposed scheme for the formation of the binuclear complex (II). In agreement with the suggestion made by the earlier workers[3] it is found that cyclopentadienyl decomposes to the binuclear complex (II) when heated at 140° for four hours in methylcyclohexane, with dicyclopentadiene added as a hydrogen acceptor. Under these conditions the yield of the complex (II) is 90 %, lesser yields are obtained when shorter reaction times and lower temperatures are used.

Another interesting reaction of cyclopentadieneiron tricarbonyl is that with the triphenylmethyl cation; as indicated this reaction affords the cyclopentadienyliron tricarbonyl cation identical with that reported by Wilkinson et al.[5].

In agreement with Wilkinson and coworkers[5] we find that attack of the cyclo-pentadienyl-Fe(CO)$_3$ cation (VI) with hydride ion donors (NaBH$_4$) does not give rise to cyclopentadiene-Fe(CO)$_3$ but instead affords the binuclear complex (II), presumably via the carbonyl hydride (III). Since cyclopentadiene-Fe(CO)$_3$ is stable under the conditions of the reaction then the formation of (II) must involve the direct attack

(II)

of hydride at the iron atom rather than initial attack on the C$_5$H$_5$ ligand and sub-sequent transfer to the iron atom. It is interesting to note in the case of the cyclo-pentadienyl-Fe(CO)$_2$P(C$_6$H$_5$)$_3$ cation that hydride attack occurs on the ring to give the cyclopentadiene-Fe(CO)$_2$P(C$_6$H$_5$)$_3$ complex[5].

Direct nucleophilic attack on the iron atom in (VI) is also indicated in reaction of the cation with halide ions. These reactions lead to the formation of the cor-responding cyclopentadienyliron dicarbonyl halide complexes (VII) (X = Br, Cl, I); in each case the properties agree with those reported for the same compounds produced by an alternative route[9].

(VII)

The use of Fe$_2$(CO)$_9$ for the preparation of dieneiron tricarbonyl complexes which are inaccessible through the direct reaction of the diene with either Fe(CO)$_5$ or Fe$_3$(CO)$_{12}$ is further illustrated in the following reactions.

(VIII)   (IX)

(X)   (XI)

The reaction of *cis*-piperylene with iron pentacarbonyl leads to the formation of *trans*-piperyleneiron tricarbonyl (VIII) and hitherto the only path to *cis*-piperylene-

iron tricarbonyl (IX) was by an indirect route involving reduction of the pentadienyl-Fe(CO)₃ cation with LiAlH₄[11]. We have now found that *cis*-piperylene reacts with Fe₂(CO)₉ to produce *cis*-piperyleneiron tricarbonyl with no detectable amount of the *trans* isomer (VIII) being formed.

Similarly the reaction of 4-methyl-1,3-pentadiene with Fe(CO)₅ gives rise to 2-methylpentadieneiron tricarbonyl (X); however, when Fe₂(CO)₉ is employed, then 4-methylpentadieneiron tricarbonyl (XI) is produced.

EXPERIMENTAL

Cyclopentadiene-Fe(CO)₃

Cyclopentadiene (50.0 g, 0.76 mole) (freshly prepared by thermal cracking of dicyclopentadiene) was mixed with 100.0 g (0.27 moles) of iron nonacarbonyl and 500 ml anhydrous ether in a 1-l round-bottom flask fitted with an ice-water cooled condenser. The flask was heated in an oil bath at 40–45° for one and a half hours by which time the nonacarbonyl had all dissolved to give a dark brown solution. The solution was filtered, allowed to cool in the ice box, and filtered again to remove a dark brown crystalline substance (identified as dicyclopentadienyldiiron tetracarbonyl). Removal of the solvent under partial pressure (30 mm) followed by distillation *in vacuo* afforded 16.0 g [27 % yield on Fe₂(CO)₉] of light yellow oil which slowly became dark brown upon standing in air. The oil was purified by repeated crystallizations from pentane at −20 to −30°, b.p. 30–35° (0.2 mm), n_D^{29} 1.5920. (Found: C, 47.29; H, 3.38. C₈H₆FeO₃ calcd.: C, 46.60; H, 3.10 %.)

An infrared spectrum of the compound in hexane solution showed carbonyl absorptions at 1974, 1981 and 2048 cm⁻¹. A liquid film spectrum had the following absorptions; 3070 (m), 2980 (m), 2912 (m), 2805 (s), 2350–2700 (w), 1850–2050 (broad absorptions), 1471 (m), 1393 (m), 1345 (m) 1248 (m), 1080 (m), 1008 (m), 935 (m), 928 (m), 892 (m), 840 (m), 733 (m). The nuclear magnetic resonance spectrum of the compound is discussed in the text.

Thermal decompositions

Cyclopentadieneiron tricarbonyl (1.25 g) was heated with 2.75 g of dicyclopentadiene and 5 ml of methylcyclohexane at 130° for 4 h in a flask fitted with a condenser and a bunsen valve. Upon cooling to 0° there separated 1.0 g of violet crystals of the binuclear complex (90 % yield); m.p. 196–198° with no depression upon admixture with an authentic sample. The NMR and infrared spectra were also identical to those of the authentic material.

In a similar experiment conducted at 115° for only two hours the yield of binuclear complex was 23 %. In another case 75 % of cyclopentadieneiron tricarbonyl was recovered after a sample was heated for 4 h in refluxing pentane with pentene added as a hydrogen acceptor, only trace amounts of the binuclear complex were obtained in this instance.

Preparation of the fluoroborate salt of cyclopentadieneiron tricarbonyl

A solution of 3.5 g of cyclopentadieneiron tricarbonyl in 2.5 ml methylene chloride was slowly added to a solution of 6.0 g triphenylmethyl fluoroborate in 40 ml of the same solvent contained in a 250-ml erlenmeyer flask. There was an immediate

yellow precipitation which was completed by stirring with 50 ml of ether for a period of 15 minutes. On filtration and drying, 4.6 g (70 % yield) of a light yellow crystalline powder was obtained. (Found: C, 33.12; H, 1.74. $C_8H_5BF_4FeO_3$ calcd.: C, 32.87; H, 1.71 %.)

The NMR spectrum of the salt taken in sulfur dioxide solution showed only one absorption at 4.16 τ. The infrared spectrum in hexachlorobutadiene mull showed absorptions at 3130 (vs), 1432 (vs), 1370 (m), 1286 (s), and 1232 (w) cm^{-1}, while a Nujol mull of the compound showed absorptions at 2127 (vs), 2070 (s), 1432 (s) and 1375 (m) cm^{-1}.

Attempted reduction of the cyclopentadienyliron tricarbonyl tetrafluoroborate

A suspension of the salt (2.4 g) in 50 ml tetrahydrofuran at −10° was treated with 0.4 g (50 % excess) of sodium borohydride and stirred for 15 minutes. The mixture was allowed to warm to room temperature and then shaken with 150 ml of cold water and 50 ml pentane. The organic layer was separated and washed with water three times, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure (30 mm); the residue was dissolved in 25 ml chloroform and the solution cooled whereupon 0.36 g of violet crystals separated. Another 0.16 g of the compound was obtained by passing the filtrate through alumina column and evaporating off the ether eluate to give a total of 0.52 g (37 %) of the binuclear complex, m.p. 195–196°.

Treatment of the cyclopentadienyl-iron tetrafluoroborate with potassium iodide

The salt (0.309 g) in 20 ml acetone was stirred with 0.7 g of potassium iodide for 3 h at 20–25°. After filtering from the insoluble products, the solvent was removed under reduced pressure (30 mm). The residue was taken up in 10 ml chloroform; filtration followed by concentration to a volume of 5 ml and subsequent cooling afforded 0.16 g (50 % yield) of cyclopentadienyliron dicarbonyl iodide, m.p. and mixed m.p. 118–119° (dec.). (Found: C, 27.63; H, 1.78; I, 41.88. $C_7H_5FeIO_2$ calcd.: C, 27.63; H, 1.64; I, 41.77 %.)

The NMR spectrum of the compound in carbon tetrachloride solution showed a single proton absorption at 4.95 τ.

In a similar manner the reaction with KCl and KBr produced the $C_5H_5Fe(CO)_2Cl$ and $C_5H_5Fe(CO)_2Br$ complexes respectively each in yields of 80 %. These materials were identical to those prepared through reaction of the binuclear complex with air and the appropriate hydrogen halide[9].

4-Methyl-1,3-pentadieneiron tricarbonyl

A mixture of 5.5 g of 4-methyl-1,3-pentadiene, 33.0 g of iron nonacarbonyl and 300 ml of ether was heated, with stirring, at 40° for two and a half hours. At the end of the reaction the green solution was filtered through celite and the solvent was removed under reduced pressure. The liquid was chromatographed on a 6″ × 5/8″ alumina column using Skelly "B" as the solvent. The yellow eluent on distillation *in vacuo* gave 5.0 g of an orange-red liquid, b.p. 43–40° (0.15 mm), n_D^{25} 1.5700. (Found: C, 48.85; H, 4.66. $C_9H_{10}FeO_3$ calcd.: C, 48.64; H, 4.50 %.)

A nuclear magnetic resonance spectrum of the compound showed absorptions at 4.73–5.02 τ (multiplet); 8.17 8.7 τ (complex multiplet with a sharp peak at 8.56 τ)

and a single sharp peak at 8.97 τ with areas approximately in the ratio 2:5:3. An infrared spectrum in carbon tetrachloride showed carbonyl absorptions at 1967, 1975 and 2041 cm^{-1}.

Reaction of cis-piperylene with iron nonacarbonyl

Treatment of commercial piperylene with maleic anhydride according to the method of Frank, Emmick and Johnson[12] gave a fraction which analysed by VPC to be a mixture of *trans*- and *cis*-piperylenes and cyclopentene in the ratio 5:55:40 respectively. A second treatment with maleic anhydride gave a fraction which was completely free from *trans*-piperylene. A VPC analysis showed it to contain *cis*-piperylene and cyclopentene in the ratio 55:45. To 27.0 g of iron nonacarbonyl was added 15.5 g of a 55:45 mixture of *cis*-piperylene and cyclopentene and 300 ml of dry ether. The mixture was heated in an oil bath at 45° for 1.5 h at which point the nonacarbonyl had disappeared. The solution was filtered and the solvent removed under reduced pressure (30 mm). On distillation *in vacuo* 9.2 g (60 % yield based on iron nonacarbonyl) of a dark yellow oil, b.p. 40°. (0.4 mm), n_D^{29} 1.5732, was obtained. (Found: C, 46.64; H, 3.94. $C_8H_8FeO_3$ calcd.: C, 46.15; H, 3.85 %.)

A liquid film infrared spectrum of the complex showed absorptions, besides the carbonyl, at 3110 (w), 3035 (m), 3005 (m), 2922 (m), 2880 (m), 1486 (m), 1446 (m), 1420 (m), 1382 (m), 1220 (m), 1180 (m), 1060 (m), 1038 (m), 991 (w), 932 (w), 881 (m), 857 (m), and 717 (w) cm^{-1}. The carbonyl group appeared at 1973, 1980 and 2048 cm^{-1}. A nuclear magnetic resonance spectrum in carbon tetrachloride solution showed proton absorptions at 4.72 τ (doublet), 7.33 τ (triplet), 8.23 τ (doublet), 8.53 τ (a set of two doublets) and 8.97 τ (doublet), approximately in the ratio 2:1:1:1:3.

SUMMARY

Cyclopentadieneiron tricarbonyl has been prepared through the reaction of cyclopentadiene and diiron nonacarbonyl. The complex undergoes slow decomposition at 140° to afford the dimer of cyclopentadienyliron dicarbonyl. Abstraction of a hydride ion from cyclopentadieneiron tricarbonyl yields the cyclopentadienyliron tricarbonyl cation.

cis-Piperylene reacts with diiron nonacarbonyl to give *cis*-piperyleneiron tricarbonyl.

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SHORT COMMUNICATIONS

Complexes of organometallic compounds

XIV. The coordination of tin and lead atoms in triphenyltin (IV) and triphenyllead (IV) oxinates

In an earlier paper[1] we investigated the absorption spectrum of triphenyltin (IV) oxinate in 95% aqueous ethanol, and showed it to correspond with that of 8-quinolinol in the same solvent. Then we suggested that triphenyltin (IV) oxinate was not a chelate complex in 95% ethanol, so that the tin atom in the undissociated molecule should be tetra-coordinated, bound only to the oxygen atom of the 8-quinolinol.

Our conclusions have recently been commented on as follows:

(1) Lack of chelation in 95% ethanol does not preclude chelation at the solid state[2]. Solid triphenyltin (IV) oxinate has a yellow colour, which is inconsistent with a lack of chelation[3].

(2) From the absorption spectra of triphenyltin (IV) oxinate in cyclohexane it is inferred that the compound is a chelate complex both in this solvent and (probably) in the solid state[3].

(3) The correspondence between triphenyltin (IV) oxinate and 8-quinolinol spectra in 95% aqueous ethanol may be due to the hydrolysis of the organotin compound[3]; the species $(C_6H_5)_3SnOH$ and C_9H_6NOH may be formed[2].

We did not infer anything about the solid state from solution data. On the other hand, the yellow colour of a solid oxinate is not a definite evidence of chelation: sodium oxinate is yellow too, but can hardly be considered to be chelated.

As to the formation of a chelate triphenyltin (IV) oxinate in cyclohexane[3], we had earlier reported that the absorption spectrum in benzene solution of triphenyllead (IV) oxinate (a compound which shows properties very similar to those of the corresponding organotin derivative) corresponds to the presence of a chelate complex[4].

The hypothesis that the spectrum in 95% aq. ethanol corresponds to that of 8-quinolinol, owing to complete hydrolysis of the organotin complex, implies that the tetra-coordinated species does not exist under these conditions. We carried out the investigations described below in order to elucidate the nature of the triorganometal