

## METAL DERIVATIVES OF CONJUGATED DIENES

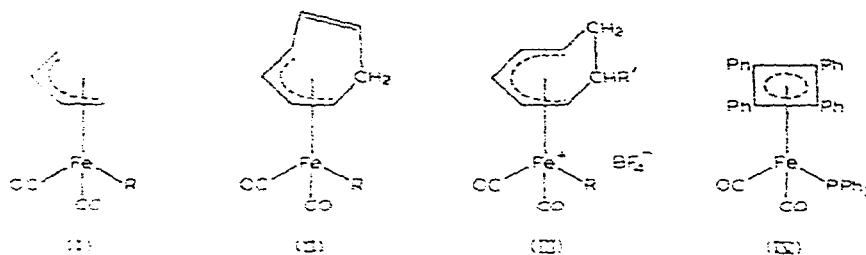
## II\*. TRIPHENYLPHOSPHINE DERIVATIVES

F. M. CHAUDHARI AND P. L. PAUSON

*Department of Pure and Applied Chemistry, Thomas Graham Building, University of Strathclyde, Glasgow, (Scotland)*

(Received June 15th, 1965)

Our re-examination<sup>1</sup> of Rheilen's tricarbonylbutadiene-iron has been followed by the preparation of a large number of related compounds in many laboratories<sup>2</sup>. Manuel and Stone<sup>3</sup> have reported that the diene ligand rather than carbon monoxide is displaced when either tricarbonylbutadiene-iron (I; R = CO) or tricarbonylcycloheptatriene-iron (II; R = CO) are heated with triphenylphosphine. On the other hand, Nesmeyanov, Anisimov and Kolobova<sup>4</sup> have shown that phosphites can displace one carbonyl group from the butadiene complex (I; R = CO).



Recently Reckziegel and Bigorgne<sup>5</sup> have reported some further examples of the replacement of carbon monoxide from such diene complexes by trimethyl phosphite, triethylphosphine and triphenylphosphine. Unfortunately these authors neither refer to the prior Russian work<sup>4</sup>, nor give melting points, analyses or adequate preparative details for any of the new compounds mentioned. Indeed several of their claims are based solely on the examination of infrared maxima in the carbonyl-stretching region of mixture of products<sup>\*\*</sup>. These deficiencies make comparison with other work virtually

\* Part I, see ref. 1.

\*\* In their reactions with the cycloheptatriene complex (II; R = CO) the French authors<sup>5</sup> show that prolonged reaction at elevated temperature leads not to the product [II; R = P(Et)<sub>3</sub> or P(OMe)<sub>3</sub>] obtained under milder conditions but to another "Fe(CO)<sub>2</sub>(diene)L". As they attribute this to an unspecified transformation of the C<sub>7</sub>H<sub>8</sub> ring, it is necessary to point out that in the light of Dauben's work<sup>6</sup>, the "diene" ligand in the new complex is almost certainly 1,3-cycloheptadiene, C<sub>7</sub>H<sub>10</sub>. Support for this assignment comes from comparison of the infrared carbonyl shift observed<sup>5</sup> in going from the "C<sub>7</sub>H<sub>8</sub>" to the "diene" complexes [1978 → 1969 and 1920 → 1913 cm<sup>-1</sup> if L = P(Et)<sub>3</sub>; 1993 → 1982 and 1936 → 1927 cm<sup>-1</sup> if L = P(OMe)<sub>3</sub>] with the difference in the carbonyl maxima of C<sub>7</sub>H<sub>8</sub>Fe(CO)<sub>2</sub>PPh<sub>3</sub> (1973, 1920 cm<sup>-1</sup>) and C<sub>7</sub>H<sub>10</sub>Fe(CO)<sub>2</sub>PPh<sub>3</sub> (1965, 1905 cm<sup>-1</sup>) prepared in the present work.

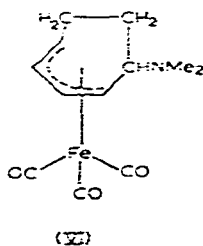
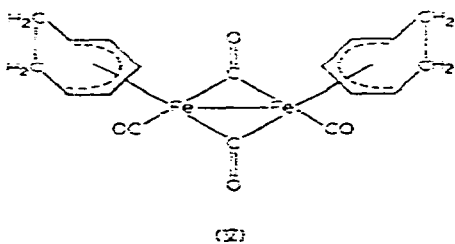
impossible. Nevertheless, this work<sup>5</sup> appears to show that whereas displacement of one CO group is possible (though inefficient) with phosphines as well as phosphites, a second phosphine or phosphite group enters only with displacement of the hydrocarbon ligand under thermal reaction conditions.

The value of photolysis in promoting the replacement of carbon monoxide has been intensively explored by Strohmeier and others<sup>6</sup> in *e.g.* the tricarbonylbenzene-chromium<sup>6a</sup> and tricarbonylcyclopentadienylmanganese<sup>6b</sup> series. As in the latter case, we now find that either one or two carbonyls can be displaced from tricarbonyldiene-irons by triphenylphosphine on irradiation. We have subjected the products to a number of reactions known to occur with the corresponding tricarbonyls and report the results.

Both dicarbonyl(triphenylphosphine) and carbonylbis(triphenylphosphine) derivatives have been obtained from the irradiation experiments when using the butadiene complex (I; R = CO) or its cyclohexadiene or cycloheptadiene analogues. By contrast tricarbonyl(tetraphenyl cyclobutadiene)iron and the triene complex (II; R = CO) gave exclusively the monosubstitution products (IV) and (II; R = PPh<sub>3</sub>) respectively. The latter, like the parent tricarbonyl complex<sup>7</sup> (II; R = CO) undergoes addition of a tritylcarbonium ion on treatment with trityl fluoroborate, giving the substituted cycloheptadienyliron complex (III; R = PPh<sub>3</sub>; R' = CPh<sub>3</sub>); in contrast to the parent complex<sup>7,9</sup> it failed to add a proton from fluoroboric acid. The dicarbonyl-(triphenylphosphine)cycloheptadienyliron fluoroborate (III; R = PPh<sub>3</sub>; R' = H) expected from the latter reaction was however produced quite readily by hydride abstraction<sup>7,9</sup> from dicarbonyl(triphenylphosphine)cycloheptadiene-iron. This reaction proceeded equally smoothly with dicarbonyl(triphenylphosphine)cyclohexadiene-iron.

Whereas tricarbonylbutadiene-iron (I; R = CO) adds hydrogen chloride to give tricarbonylcrotylchloro-iron<sup>10</sup> as a stable product, its triphenylphosphine derivative (I; R = PPh<sub>3</sub>) gave a presumably analogous compound as a yellow crystalline product, too unstable to permit adequate characterisation. Dicarbonyl(triphenylphosphine)-cycloheptenylchloro-iron proved similarly unstable.

The conversion of the cationic complex (III; R = CO; R' = H) back to the cycloheptatriene complex (II; R = CO) has not previously been described. We now find that it occurs by simple loss of fluoroboric acid when the salt (III; R = CO; R' = H) is treated with tertiary amines. Quantitative conversion can be achieved with trimethylamine or with dicyclohexylethylamine, but pyridine is less effective. When the second amine was used in acetone solution, the dimeric complex (V) was a by-product. It is a known<sup>11</sup> reduction product of the salt (III; R = CO; R' = H). Secondary amines add to this salt, as is shown using dimethylamine which gives the amino-substituted diene complex (VI). When tricarbonylcyclohexadienyliron fluoro-



borate was treated, like its homologue (III; R = CO; R' = H), with dicyclohexylethylamine, no stable benzene-iron complex could be isolated.

#### EXPERIMENTAL

All infrared spectra were determined as KCl discs unless otherwise stated.

##### *Irradiation experiments*

The carbonyls and an equimolar quantity of triphenylphosphine were dissolved in benzene and placed in an annular apparatus with a 500 W medium pressure mercury arc lamp (Hanovia 509/12) contained in a water-cooled quartz tube in the centre. Following irradiation for 18 h the solutions were filtered, evaporated under vacuum and the residues chromatographed on alumina:

(a) *Tricarbonylbutadiene-iron* (3.9 g, 20 mmole) gave *dicarbonyl(triphenylphosphine)butadiene-iron* (I; R = PPh<sub>3</sub>) (0.95 g; 11%) on elution with ligroin. After recrystallisation from ether-pentane it formed yellow crystals, m.p. 142°, showing metal-carbonyl stretching peaks at  $\nu_{\max}$  1973 and 1910 cm<sup>-1</sup>; its NMR spectrum showed complex peaks at 2.7, 5.15, 8.25 and 10.25  $\tau$  of relative intensities 15:2:2:2. (Found: C, 67.5; H, 5.0. C<sub>24</sub>H<sub>21</sub>FeO<sub>2</sub>P calcd.: C, 67.3; H, 4.9%.)

Ligroin-benzene (1:4) eluted *carbonylbis(triphenylphosphine)butadiene-iron* (0.8 g, 6%) which formed yellow crystals, m.p. 156° (from ether-pentane). The presence of a single metal-carbonyl peak at 1887 cm<sup>-1</sup> is strong evidence for the structure assigned. (Found: C, 73.8; H, 5.5. C<sub>11</sub>H<sub>26</sub>FeOP<sub>2</sub> calcd.: C, 74.2; H, 5.5%.) These products were preceded by unchanged starting materials: iron complex (I; R = CO) (trace) and triphenylphosphine (3.0 g), both eluted with ligroin, and followed by traces of tricarbonylbis(triphenylphosphine)iron, eluted with ligroin-benzene (3:2) and finally an unidentified red compound, m.p. 170°. The latter was eluted with benzene and showed metal-carbonyl peaks at  $\nu_{\max}$  2020, 1969, 1953 and 1905 cm<sup>-1</sup> (in CCl<sub>4</sub> solution). Similar byproducts were isolated in (b)-(d).

(b) *Tricarbonylcyclohexadiene-iron* (2.2 g, 10 mmole) gave *dicarbonyl(triphenylphosphine)cyclohexadiene-iron* (1.1 g, 25%) which formed yellow crystals, m.p. 117°, from ether-pentane; it showed carbonyl stretching peaks at  $\nu_{\max}$  1960 and 1894 cm<sup>-1</sup> and complex proton resonance peaks at 2.5, 5.15, 7.5 and 8.4  $\tau$  of relative intensity 15:2:2:4. (Found: C, 69.1; H, 5.3. C<sub>26</sub>H<sub>23</sub>FeO<sub>2</sub>P calcd.: C, 68.7; H, 5.1%.) This was accompanied by *carbonylbis(triphenylphosphine)cyclohexadiene-iron* (0.6 g, 9%) which formed yellow crystals, m.p. 159° (decomp.) from methylene chloride-pentane and had a single C-O stretch at 1869 cm<sup>-1</sup>. Its low stability prevented accurate analysis.

(c) *Tricarbonylcycloheptadiene-iron* (4.68 g, 20 mmole) gave *dicarbonyl(triphenylphosphine)cycloheptadiene-iron* (5.2 g; 55.6%) forming yellow crystals, m.p. 128° from ether-pentane, which had carbonyl peaks at  $\nu_{\max}$  1965 and 1905 cm<sup>-1</sup> and complex proton-resonance peaks at 2.6, 5.45, 7.64, 8.17 and 8.75  $\tau$  of relative intensity 15:2:2:4:2. (Found: C, 68.7; H, 5.3; C<sub>27</sub>H<sub>25</sub>FeO<sub>2</sub>P calcd.: C, 69.2; H, 5.4%.) Also formed was *carbonylbis(triphenylphosphine)cycloheptadiene-iron* (2 g, 14%) which crystallised from methylene chloride-pentane as yellow crystals, m.p. 138° (decomp.) with a single carbonyl peak at 1872 cm<sup>-1</sup>. Its low stability prevented accurate analysis.

(d) *Tricarbonylcycloheptatriene-iron* (5.34 g, 20 mmole) yielded only *dicarbonyl-*

(*triphenylphosphine*)cycloheptatriene-iron (II; R = PPh<sub>3</sub>) (2.5 g, 27%) as yellow crystals, m.p. 137°, from ether-pentane; carbonyl stretching peaks occurred at 1973 and 1920 cm<sup>-1</sup> and complex proton resonance peaks at 2.65, 5.3 and 7.2-9.0 τ (relative intensity 15:2:6). (Found: C, 69.6; H, 5.1. C<sub>27</sub>H<sub>23</sub>FeO<sub>2</sub>P calcd.: C, 69.5; H, 5.0%.) This product was accompanied by unchanged tricarbonyl (II; R = CO) (2 g) and no trace of bis(triphenylphosphine) complex could be isolated even after prolonged irradiation (36 h) using an excess of triphenylphosphine.

(e) *Tricarbonyl(tetraphenylcyclobutadiene)iron* (0.5 g, 1 mmole) gave *dicarbonyl(triphenylphosphine)(tetraphenylcyclobutadiene)iron* (IV) (0.18 g, 25%) as yellow crystals, m.p. 245°, from methylene chloride-pentane. It showed carbonyl stretching peaks at  $\nu$  1955 and 1904 cm<sup>-1</sup>. (Found: C, 79.0; H, 5.1; P, 4.0. C<sub>43</sub>H<sub>35</sub>FeO<sub>2</sub>P calcd.: C, 78.9; H, 4.8; P, 4.25%.) Elution of the chromatogram with benzene gave traces of a second yellow compound with both metal carbonyl and "ketonic" peaks at 1992, 1946, 1695 and 1653 cm<sup>-1</sup>.

#### Reactions with triphenylmethyl fluoroborate

These were carried out by mixing the complex dissolved in methylene chloride (5 ml) with an equimolar quantity of trityl fluoroborate in the same solvent (5 ml). After a few minutes stirring the solutions were concentrated and the products precipitated with ether.

(a) *Dicarbonyl(triphenylphosphine)cyclohexadiene-iron* (0.26 g, 0.6 mmole) gave *dicarbonyl(triphenylphosphine)cyclohexadienyliron fluoroborate* (0.31 g, 100%) after recrystallisation from methylene chloride-pentane it had m.p. 190° and  $\nu_{max}$  2028 and 1992 cm<sup>-1</sup> in the carbonyl stretching region (Found: C, 56.9; H, 4.1; P, 5.8. C<sub>26</sub>H<sub>22</sub>BF<sub>4</sub>Fe<sub>2</sub>O<sub>2</sub>P calcd.: C, 57.8; H, 4.1; P, 5.75%.)

(b) *Dicarbonyl(triphenylphosphine)cycloheptadiene-iron* (0.94 g, 2 mmole) gave the *salt* (III; R = PPh<sub>3</sub>; R' = H) (1.03 g, 93%) as a yellow powder. After recrystallisation from acetone-ether it had m.p. 178° and  $\nu_{max}$  2028, 1996 and 1980 cm<sup>-1</sup> in the carbonyl stretching region. (Found: C, 58.0; H, 4.3; F, 13.9; P, 5.6. C<sub>27</sub>H<sub>24</sub>BF<sub>4</sub>Fe<sub>2</sub>O<sub>2</sub>P calcd.: C, 58.5; H, 4.4; F, 13.7; P, 5.6%.)

In an attempt to obtain this complex from the triene derivative (II; R = PPh<sub>3</sub>) a solution of the latter in propionic anhydride was treated with 40% aqueous fluoroboric acid. No salt could be isolated and addition of water and extraction with methylene chloride led to recovery of the starting material (80%).

(c) *Dicarbonyl(triphenylphosphine)cycloheptatriene-iron* (0.47 g, 1 mmole) reacted to give the *trityl-substituted salt* (III; R = PPh<sub>3</sub>; R' = CPh<sub>3</sub>) (0.74 g, 100%) as yellow crystals, m.p. 145°, from acetone-ether; it had  $\nu_{max}$  2037, 1980 and 1912 cm<sup>-1</sup> in the carbonyl stretching region. (Found: C, 69.0; H, 4.7; F, 9.1; P, 3.8. C<sub>46</sub>H<sub>28</sub>BF<sub>4</sub>FeO<sub>2</sub>P calcd.: C, 69.3; H, 4.8; F, 9.5; P, 3.9%.)

#### Reactions with hydrogen chloride

These were carried out by passing a dry stream of this gas through the solution of the complex for 2 h.

(a) *Dicarbonyl(triphenylphosphine)butadiene-iron* (1.5 g, 3.6 mmole) was employed as a solution in benzene (100 ml). This solution turned red and then reddish yellow within the first 15 min. After filtration it was evaporated under vacuum and the residue chromatographed on alumina. Traces of the unreacted complex (I; R =

$\text{PPh}_3$ ) were eluted with ligroin. Then benzene eluted *dicarbonyl(triphenylphosphine)- $\pi$ -crotylchloro-iron* (1 g, 61 %); it formed yellow crystals from methylene chloride-pentane, m.p. 100–105° (decomp.), with  $\nu_{\text{max}}$  2016 and 1934  $\text{cm}^{-1}$  in the carbonyl stretching region, but proved too unstable to be obtained analytically pure.

(b) *Dicarbonyl(triphenylphosphine)cycloheptadiene-iron* (1 g, 2 mmole) was used in benzene (60 ml). This solution initially turned greenish-blue and then reddish-yellow within 15 min. The filtered solution was evaporated under vacuum and washed with ether to remove starting material. The remaining yellow solid, m.p. 119°,  $\nu_{\text{max}}$  2041 and 1992  $\text{cm}^{-1}$ , presumably *dicarbonyl(triphenylphosphine)cycloheptenylchloro-iron* largely decomposed during attempted crystallisation from methylene chloride-pentane.

#### *Reaction of tricarbonylcycloheptadienyliron tetrafluoroborate with tertiary amines*

The salt (III; R = CO; R' = H) (10 g, 31 mmole) and dicyclohexylethylamine (6.5 g, 31 mmole) were refluxed for 3 h in acetone (100 ml). After evaporation under vacuum the residue was extracted first with ligroin and then with methylene chloride. Evaporation of the ligroin solution gave tricarbonylcycloheptatriene-iron (II; R = CO) (6 g, 83 %) and the methylene chloride solution gave the dimeric complex (IV) (1 g, 8 %) both identical with authentic samples.

Replacement of acetone as solvent by isopropanol gave quantitative conversion to the triene complexes (II; R = CO), accompanied only by traces of tricarbonylcycloheptadiene-iron. Use of trimethylamine in acetone (2 h reflux) also gave quantitative conversion, but pyridine in the same solvent (3 h) gave only 25 % of the triene complex (II; R = CO).

A similar experiment using tricarbonylcyclohexadienyliron tetrafluoroborate gave a small quantity of tricarbonylcyclohexadiene-iron as the only identifiable product.

*Tricarbonyl-5-(dimethylamino)-1,3-cycloheptadiene-iron (VI)*. The salt (III; R = CO; R' = H) (1 g, 3 mmole) was added to aqueous dimethylamine (10 ml, 25 %) and the mixture shaken for a few minutes, then extracted with ligroin. The dried ( $\text{Na}_2\text{SO}_4$ ) ligroin solution was evaporated under vacuum and the residue chromatographed on alumina. Elution of the yellow band with ligroin-benzene (4:1) gave the *amine* (VI) (0.8 g, 92 %), b.p. 75°/0.01 mm. Carbonyl stretching peaks occur at 2041 and 1961  $\text{cm}^{-1}$  and complex proton resonance peaks at 4.6, 7.1, 7.95, 7.8 (singlet) and 8.65  $\tau$  (relative intensity 2:3:2:6:2). (Found: C, 52.0; H, 5.5; N, 5.2.  $\text{C}_{12}\text{H}_{15}\text{FeNO}_3$  calcd.: C, 52.0; H, 5.5; N, 5.1 %.) This amine reacted vigorously with methyl iodide, but the precipitated solid proved too unstable to be recrystallised.

#### ACKNOWLEDGEMENTS

We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work, and the International Nickel Company (Mond) Ltd., for generous supplies of iron carbonyl.

#### SUMMARY

The tricarbonyliron complexes of butadiene, cyclohexadiene, cycloheptadiene, cycloheptatriene and tetraphenylcyclobutadiene have been irradiated in the presence

of triphenylphosphine. This ligand can replace one carbonyl group in all cases and a second one in the first three. The products in the cyclohexa- and heptadiene cases have been converted to the corresponding dienyliiron fluoroborates with trityl fluoroborate. Addition of the latter reagent to the cycloheptatriene and of hydrogen chloride to the monophosphinebutadiene and cycloheptadiene complexes is also described. Tricarbonylcycloheptadienyliiron tetrafluoroborate is converted by tertiary amines to tricarbonylcycloheptatriene-iron, but dimethylamine adds to give tricarbonyl- $\eta^5$ -(dimethylamino)cycloheptadieneiron.

## REFERENCES

- 1 B. F. HALLAM AND P. L. PAUSON, *J. Chem. Soc.*, (1958) 642.
- 2 M. A. BENNETT, *Chem. Rev.*, 62 (1962) 611; R. PETTIT AND G. F. EMERSON, in F. G. A. STONE AND R. WEST, *Advances in Organometallic Chemistry*, Vol. 1, Academic Press, 1964.
- 3 T. A. MANUEL AND F. G. A. STONE, *J. Am. Chem. Soc.*, 82 (1960) 366.
- 4 A. N. NESMEYANOV, K. N. ANISIMOV AND N. E. KOLOBOVA, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1962) 722.
- 5 A. RECKZIEGEL AND M. BIGORGNE, *J. Organometal. Chem.*, 3 (1965) 341.
- 6 (a) W. STROHMEIER AND H. HELLMANN, *Chem. Ber.*, 96 (1963) 2859.  
(b) W. STROHMEIER AND C. BARBEAU, *Z. Naturforsch.*, 17b (1962) 848; J. LEWIS *et al.*, *Chem. Ind. (London)*, (1963) 1398.
- 7 H. J. DAUBEN AND D. J. BERTELLI, *J. Am. Chem. Soc.*, 83 (1961) 497.
- 8 A. DAVISON, W. MCFARLANE, L. PRATT AND G. WILKINSON, *Chem. Ind. (London)*, (1961) 553.
- 9 E. O. FISCHER AND R. D. FISCHER, *Angew. Chem.*, 72 (1960) 919.
- 10 F. J. IMPASTATO AND K. G. IHRMAN, *J. Am. Chem. Soc.*, 83 (1961) 3726; H. D. MURDOCH AND E. WEISS, *Helv. Chim. Acta*, 45 (1962) 1927.
- 11 M. HASHMI, P. L. PAUSON AND J. WILLIAMSON, unpublished results.

*J. Organometal. Chem.*, 5 (1966) 73-78