

*Anal.* Calcd. for  $C_9H_5F_2OCOI$ : C, 24.1; H, 1.1; F, 29.7; Co, 13.2; I, 28.4; mol. wt., 448. Found: C, 24.0, 24.2; H, 1.2, 1.7; F, 29.3, 29.5; Co, 12.9, 12.8; I, 28.0, 28.4; mol. wt., 445.

(b) **Pentafluoroethyl Iodide.**—To a mixture of cyclopentadienylcobalt dicarbonyl (3.0 g., 17 mmoles) and 50 ml. of benzene was added pentafluoroethyl iodide (10 g., 40.6 mmoles) and the reaction mixture was maintained at 45° for 17 hr., a Dry-Ice cooled condenser being used to prevent escape of the pentafluoroethyl iodide. Removal of solvent at 20 mm. (25°) and sublimation of the residue at 85° (0.1 mm.) for 12 hr. gave 4.77 g. (72% yield) of black crystalline  $C_5H_5Co(CO)(C_2F_5)I$ , m.p. 138°. The analytical sample was resublimed at 75° (0.1 mm.). The infrared spectrum of the compound (carbon disulfide solution) showed a strong carbonyl band at 2080  $cm^{-1}$ . Other bands occur at 1286(m), 1186(s), 1065(s), 1055(s), 1028(s), 905(w), 896(m), 842(w), 831(w) and 729(m)  $cm^{-1}$ .

*Anal.* Calcd. for  $C_9H_5F_2OCOI$ : C, 24.1; H, 1.3; F, 23.8; Co, 14.8; I, 31.9; mol. wt., 398. Found: C, 24.4; H, 1.4; F, 23.4; Co, 14.9; I, 32.0; mol. wt., 378.

(c) **Trifluoromethyl Iodide.**—The preparation of  $C_5H_5Co(CO)(CF_3)I$  was entirely analogous to the preparation of the  $C_2F_5$  derivative described above. The yield was much lower, due probably to loss of trifluoromethyl iodide past the -78° condenser. Thus cyclopentadienylcobalt dicarbonyl (2.0 g., 11 mmoles) and trifluoromethyl iodide (13.4 mmoles, measured as gas) in 50 ml. of benzene gave only 0.3 g. (7.5% yield) of black crystalline  $C_5H_5Co(CO)(CF_3)I$ , decomp. without melting at ~145°, subliming at 100° (0.1 mm.). The infrared spectrum of the compound (carbon disulfide solution) shows a strong carbonyl stretch at 2073  $cm^{-1}$ . Other bands occur at 1067(s), 1053(s), 1019(s), 838(m), 830(m) and 709(w)  $cm^{-1}$ .

*Anal.* Calcd. for  $C_7H_5F_3OCOI$ : C, 24.1; H, 1.5; F, 16.4; Co, 17.0; I, 36.5. Found: C, 24.2; H, 1.5; F, 16.2; Co, 17.2; I, 36.0.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

## Chemistry of the Metal Carbonyls. XIII. Iron Complexes of Divinylbenzenes<sup>1</sup>

BY T. A. MANUEL,<sup>2</sup> S. L. STAFFORD<sup>3</sup> AND F. G. A. STONE

RECEIVED NOVEMBER 3, 1960

Diiron hexacarbonyl complexes of *meta*- and *para*-divinylbenzenes are described, representing the first reported examples of substances wherein iron carbonyl groups are bonded to benzene rings. The diene complex 1,4-diphenylbutadiene-iron tricarbonyl and the arene complex 1,4-diphenylbutadiene-chromium tricarbonyl have been prepared. The latter compound reacts with triiron dodecacarbonyl to afford a complex in which 1,4-diphenylbutadiene is bonded both to chromium tricarbonyl and iron tricarbonyl groups.

Many aromatic hydrocarbons react with the hexacarbonyls of the sub-group VI metals to give arene-metal tricarbonyl complexes.<sup>4</sup> In contrast arene-iron dicarbonyl complexes have never been reported as products of reactions between aromatic hydrocarbons and iron carbonyls, even though  $\pi$ -complexes of iron of many types have been obtained by treating olefinic hydrocarbons with iron carbonyls.<sup>5</sup>

Although arene-iron dicarbonyl complexes have not been reported, benzene and other aromatic hydrocarbons can be bonded to iron atoms under certain circumstances, for example, in the complexes cyclopentadienebenzene-iron,<sup>6</sup> acenaphthylene-diiron hexacarbonyl,<sup>4e</sup> azulene-diiron pentacarbonyl<sup>7</sup> and the cyclopentadienylmesitylene iron (I) cation.<sup>8</sup> In view of the existence of these iron complexes there would appear at present to be no valid reason why suitably chosen substituents should not be able to activate a benzene ring so that it could form  $\pi$ -complexes of one type or an-

other with iron carbonyl groups. Accordingly, reactions between triiron dodecacarbonyl and alkylbenzenes, mesitylene, hexamethylbenzene, naphthalene, anthracene, styrene, 2,4-dimethylstyrene, vinyltoluene and 2,4,6-trimethylstyrene were studied. No  $\pi$ -complexes of iron were isolated from any of these reactions. However, reaction between *p*-divinylbenzene and triiron dodecacarbonyl in refluxing benzene afforded the compound *p*-divinylbenzene-diiron hexacarbonyl (I), a yellow solid melting with decomposition at 110°.

The reaction between triiron dodecacarbonyl and an excess of a commercial mixture of *meta*- and *para*-divinylbenzenes was next investigated. An orange crystalline complex (m.p. 135–136° with decomp.) was obtained. This complex (II) was isomeric with I and shown to be *m*-divinylbenzene-diiron hexacarbonyl by partial oxidation to isophthalic acid. The results of the competitive reaction between triiron dodecacarbonyl and excess of the two divinylbenzene isomers indicate that the *m*-divinylbenzene-diiron hexacarbonyl (II) is more stable than its *para*-isomer (I). Both iron complexes are stable in air and soluble in organic solvents.

The divinylbenzenes are ten  $\pi$ -electron systems. Because of this, and from a consideration of the "inert gas configuration" formalism, it was possible that the divinylbenzenes would form complexes of type divinylbenzene-diiron pentacarbonyl rather than divinylbenzene-diiron hexacarbonyl. Nevertheless, it was found that the divinylbenzene-iron carbonyl complexes contain two  $Fe(CO)_3$  groups rather than an  $Fe(CO)_5$  group and an  $Fe(CO)_2$  group, since reaction of the compounds

(1) Previous paper in this series, R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3593 (1961).

(2) National Science Foundation predoctoral fellow, 1958–1961.

(3) Natvar Corporation Fellow at Harvard University, 1959–1961.

(4) (a) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959);

(b) E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen and W. Semmlinger, *Ber.*, **91**, 2763 (1958); (c) E. O. Fischer, N. Kriebitzsch and R. D. Fischer, *ibid.*, **92**, 3214 (1959); (d) G. Natta, R. Ercoli and F. Calderazzo, *Chim. e ind. (Milano)*, **40**, 287 (1958);

(e) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4557 (1960).

(5) P. L. Pauson, *Proc. Chem. Soc.*, 297 (1960).

(6) M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 989 (1960).

(7) (a) R. Burton, M. L. H. Green, E. W. Abel and G. Wilkinson, *Chem. and Ind.*, 1592 (1958). (b) R. Burton, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

(8) T. H. Coffield, V. Sandel and R. D. Closson, *J. Am. Chem. Soc.*, **79**, 5826 (1957).

with iodine afforded six moles of carbon monoxide per mole of complex rather than five. Furthermore, reaction of I or II with triphenylphosphine gave exclusively *trans*-bis-(triphenylphosphine)-iron tricarbonyl. The presence of two  $\text{Fe}(\text{CO})_3$  groups in each complex is further confirmed by spectral studies. Both complexes show just two carbonyl stretching bands in their infrared spectra. More than two carbonyl stretching bands would be expected in the spectrum of a compound containing an iron dicarbonyl and an iron tricarbonyl group. Iron atoms of iron tricarbonyl groups formally require four electrons to complete the inert gas configuration. Formation of diiron hexacarbonyl complexes of the divinylbenzenes suggests that unsaturation equivalent to two  $\pi$ -electrons resides in the divinylbenzene moieties. It is interesting, therefore, that in the infrared spectra of I and II there is an absorption at  $1600\text{ cm}^{-1}$ , in the region expected for carbon-carbon double bonds of the aromatic type. This suggests that in the two divinylbenzene complexes the vinylic double bonds are involved in bonding to iron tricarbonyl groups. Furthermore, the spectra of both iron compounds lack the strong bands in the regions  $990\text{--}1005\text{ cm}^{-1}$  and  $905\text{--}920\text{ cm}^{-1}$ , characteristic of carbon-hydrogen deformation modes of a free vinyl group. However, since it is not possible to say definitely what effect the formation of an iron-to- $\text{C}_6$ -ring bond would have upon the location and intensity of absorptions due to a vinylic double bond, the spectra do not positively exclude the possibility of one of the vinyl groups in the iron derivatives not being bonded to the metal.

In contrast to the divinylbenzenes, phenylbutadienes react with iron carbonyls to give complexes of the iron tricarbonyl group analogous to butadiene-iron tricarbonyl.<sup>9</sup> Other workers<sup>10</sup> have reported the compound tetraphenylbutadiene-iron tricarbonyl and as described in the Experimental section 1,4-diphenylbutadiene-iron tricarbonyl may be prepared by a two-stage reaction from the hydrocarbon and triiron dodecacarbonyl. On the other hand, treatment of chromium hexacarbonyl with diphenylbutadiene at elevated temperatures affords the arene complex diphenylbutadiene-chromium tricarbonyl. Formation from 1,4-diphenylbutadiene of a diene-iron and an arene-chromium complex shows that the phenyl and diene parts of the ligand are able to act independently of each other to form metal tricarbonyl complexes of the type most common for each metal.

Although a study<sup>11a</sup> of acid strengths shows that a chromium tricarbonyl group exerts a strong electron-withdrawing effect on a benzene ring bonded to it, in the case of diphenylbutadiene-chromium tricarbonyl this effect does not diminish the  $\pi$ -complexing ability of the butadiene system. This reaction of diphenylbutadiene-chromium tricarbonyl with triiron dodecacarbonyl afforded a complex of diphenylbutadiene containing both chromium tricarbonyl and iron tricarbonyl groups. This complex shows carbonyl stretching bands in

the infrared at 2045, 1970, 1905, 1895 and  $1845\text{ cm}^{-1}$ . Shift of some of the carbonyl frequencies almost into the bridging region is notable and perhaps indicates a diminished acceptor ability of the organic ligand. Diphenylbutadiene-chromium tricarbonyl-iron tricarbonyl is the first compound to be reported in which a single hydrocarbon ligand is bonded to metal tricarbonyl moieties of different metals.

### Experimental<sup>11</sup>

Infrared spectra were taken using a Perkin-Elmer Model 21 double-beam spectrophotometer equipped with sodium chloride optics. N.m.r. spectra were obtained at 60 mc. by a Varian Model 4300B high resolution spectrometer fitted with a super stabilizer. Saturated solutions in carbon disulfide were employed. 1,4-Diphenylbutadiene was prepared by the method described elsewhere.<sup>12</sup> *p*-Divinylbenzene was prepared by bromination of commercial divinylbenzenes and separation of the tetrabromides,<sup>13</sup> followed by debromination of *p*-tetrabromodivinylbenzene with zinc dust. Molecular weight determinations were made by the isopiestic method.

**Reaction between *p*-Divinylbenzene and Triiron Dodecacarbonyl.**—A 2.5 g. sample of "*p*-divinylbenzene" (shown by chromatography to contain about 80% (15 mmoles) *p*-divinylbenzene, plus ethylvinylbenzenes and benzene) was refluxed in benzene under nitrogen for 18 hr. with triiron dodecacarbonyl (3.4 g., 6.7 mmoles). Cooling and filtration gave a brown solution, which was evaporated under reduced pressure to leave a yellow solid. The solid was dissolved in a pentane-dichloromethane mixture and chromatographed on alumina. Pentane eluted nothing, but a 4:1 pentane:dichloromethane mixture eluted an orange solution, which was evaporated under reduced pressure to afford 1.21 g. (29% yield) of orange crystals containing a trace of an oil. Sublimation ( $90\text{--}100^\circ$  ( $10^{-1}\text{ mm.}$ )) gave *p*-divinylbenzene-diiron hexacarbonyl as a yellow solid.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{10}\text{O}_6\text{Fe}_2$ : C, 46.8; H, 2.5; Fe, 27.3; mol. wt., 410. Found: C, 47.0; H, 2.5; Fe, 26.9; mol. wt., 420.

The compound has carbonyl stretching bands in its infrared spectrum at  $2035$  and  $1975\text{ cm}^{-1}$  (carbon disulfide solution).

**Reaction between Practical Grade Divinylbenzenes and Triiron Dodecacarbonyl.**—A mixture of triiron dodecacarbonyl (4.7 g., 9.3 mmoles) and 10 ml. of practical grade<sup>14</sup> divinylbenzenes in 40 ml. of benzene was refluxed for 6 hr. under nitrogen. Cooling and filtration gave a red-brown solution, which was evaporated under reduced pressure. The red solid residue was dissolved in dichloromethane; upon addition of pentane 250 mg. of orange crystals settled out of solution and were filtered off. Chromatography of the remaining solution on alumina with pentane followed by a 4:1 pentane:dichloromethane mixture yielded orange solutions which were evaporated to dryness under reduced pressure to yield an additional 950 mg. of orange crystals. After washing all the product with cold pentane and drying, *m*-divinylbenzene-diiron hexacarbonyl (1.15 g., 20% yield) was obtained.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{10}\text{O}_6\text{Fe}_2$ : C, 46.8; H, 2.5; Fe, 27.3; mol. wt., 410. Found: C, 46.7, 47.1; H, 2.7, 2.7; Fe, 27.0; mol. wt., 413.

*m*-Divinylbenzene-diiron hexacarbonyl may be sublimed at  $100^\circ$  ( $10^{-1}\text{ mm.}$ ) and shows carbonyl stretching bands in its infrared spectrum at  $2045$  and  $1985\text{ cm}^{-1}$  (carbon disulfide solution). The spectrum particularly in the  $1600\text{--}1250\text{ cm}^{-1}$  region is different from that of *p*-divinylbenzene-diiron hexacarbonyl. In an experiment representative of those used to determine the number of CO groups in the divinylbenzene complexes a 47.9 mg. (0.117 mmole) sample

(11) Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institut für Kohlenforschung, and by Schwarzkopf Micro-analytical Laboratory, Woodside, New York.

(12) "Organic Syntheses," Coll. Vol. II, p. 229.

(13) A. S. Hay, *J. Org. Chem.*, **25**, 637 (1960).

(14) Supplied by the Borden Chemical Co., Philadelphia, and containing 36% *m*-divinylbenzene, 18% *p*-divinylbenzene, 37% ethylvinylbenzenes and the remainder diethylbenzenes.

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

(10) (a) W. Hübel and E. H. Braye, *J. Inorg. & Nuclear Chem.*, **10**, 250 (1959); (b) G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5307 (1959).

of *m*-divinylbenzene-diiron hexacarbonyl was dissolved in 8 ml. of toluene and heated at 60° with 0.6 g. (2.4 mmoles) of iodine and 3 g. of potassium iodide in 7 ml. of water. This treatment afforded 15.6 cc. (S.T.P.) of carbon monoxide, 99% of the theoretical for 6 carbon monoxide groups per mole of complex.

A 1.0 g. (2.4 mmoles) sample of *m*-divinylbenzene-diiron hexacarbonyl was refluxed for 22 hr. in basic potassium permanganate solution. The iron complex was largely unattacked, but after removal of excess of permanganate with sodium bisulfite solution a white solid having an infrared spectrum (Nujol mull) identical with that of isophthalic acid was obtained.

**1,4-Diphenylbutadiene-chromium Tricarbonyl.**—Chromium hexacarbonyl (5.5 g., 25 mmoles) was refluxed under nitrogen for 48 hr. with 1,4-diphenylbutadiene (5.5 g., 27 mmoles) in 180 ml. of ethylcyclohexane. The mixture was cooled to -78° and filtered, giving an orange solid. After recrystallization from benzene the orange solid was dissolved in dichloromethane and chromatographed on alumina. Elution with chloroform gave a solution from which was crystallized 4.83 g. of orange solid. Sublimation (80-120° (10<sup>-1</sup> mm.)) gave diphenylbutadiene. Continued sublimation above 140° (10<sup>-1</sup> mm.) afforded 2.4 g. (28% yield) of red-orange 1,4-diphenylbutadiene-chromium tricarbonyl (m.p. 156-160°).

*Anal.* Calcd. for C<sub>19</sub>H<sub>14</sub>O<sub>3</sub>Cr: C, 66.7; H, 4.1; Cr, 15.2; mol. wt., 342. Found: C, 65.9; H, 4.0; Cr, 15.3; mol. wt., 350.

The compound (carbon disulfide solution) has carbonyl bands at 1970 and 1905 cm.<sup>-1</sup>.

**Reaction between 1,4-Diphenylbutadiene and Triiron Dodecacarbonyl.**—A mixture of 1.7 g. (3.3 mmoles) of triiron dodecacarbonyl and 1.0 g. (4.9 mmoles) of diphenylbutadiene in 35 ml. of benzene was refluxed under nitrogen for 6 hr. Filtration of the mixture at room temperature gave an orange solution, which was concentrated under reduced pressure. Chromatography on alumina with pentane, followed by chloroform, indicated that only one iron complex was present. Crystallization from the orange eluate gave 1.02 g. of orange crystals, m.p. 156°. Analysis of the product at this stage gave results in accord with a composition "C<sub>18</sub>H<sub>14</sub>Fe(CO)<sub>3</sub>·1/2 C<sub>18</sub>H<sub>14</sub>" (Calcd. for C<sub>27</sub>H<sub>21</sub>O<sub>3</sub>Fe: C, 72.1; H, 4.7. Found: C, 72.0; H, 4.5). The infrared spectrum of the crystals (carbon disulfide solution) showed a band at 976 cm.<sup>-1</sup>, characteristic of 1,4-diphenylbutadiene. Further purification was attempted by recrystallization, chromatography and sublimation but without effect on the analytical results. Repeat reactions between 1,4-diphenylbutadiene and triiron dodecacarbonyl in benzene or with iron pentacarbonyl in ethylcyclohexane consistently gave a material with composition corresponding to a ratio 1<sup>1</sup>/<sub>2</sub> diphenylbutadiene:1 iron tricarbonyl.

Subsequent experiments established that it was possible to prepare pure 1,4-diphenylbutadiene-iron tricarbonyl by heating the above mentioned crystals with triiron dodecacarbonyl. A mixture of 2.0 g. of the orange crystals, 2.5 g. (5 mmoles) of triiron dodecacarbonyl and 40 ml. of benzene was refluxed under nitrogen for 18 hr. Evaporation of the green solution gave a brown residue which was dissolved in a pen-

tane-dichloromethane mixture and chromatographed on alumina. Elution with a 2:1 pentane:dichloromethane mixture gave an orange solution, which was evaporated to afford a yellow-orange solid. Sublimation (140° (10<sup>-1</sup> mm.)) gave 2.0 g. (85% yield) of 1,4-diphenylbutadiene-iron tricarbonyl (m.p. 159°), having carbonyl bands in its infrared spectrum at 2045 and 1980 cm.<sup>-1</sup> (carbon disulfide) but no infrared band at 976 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>19</sub>H<sub>14</sub>O<sub>3</sub>Fe: C, 66.0; H, 4.0; Fe, 16.2; mol. wt., 346. Found: C, 66.2; H, 3.8; Fe, 16.0; mol. wt., 320.

**Reaction between 1,4-Diphenylbutadiene-chromium Tricarbonyl and Triiron Dodecacarbonyl.**—A mixture of 0.92 g. (2.7 mmoles) of 1,4-diphenylbutadiene-chromium tricarbonyl and 1.0 g. (2.0 mmoles) of triiron dodecacarbonyl in 35 ml. of benzene was refluxed under nitrogen for 18 hr. Cooling and filtration gave a deep red solution, which was evaporated under reduced pressure to an orange solid. The solid was dissolved in a pentane-dichloromethane mixture, and the solution was chromatographed on alumina. A 1:1 pentane:dichloromethane mixture eluted a deep orange solution, which gave 1,4-diphenylbutadiene-chromium tricarbonyl on evaporation. A 3:2 dichloromethane:pentane mixture eluted a yellow solution, which afforded a yellow-orange solid on evaporation. Recrystallization of the latter solid from a dichloromethane-pentane mixture gave 200 mg. (15% yield) of 1,4-diphenylbutadiene-chromium tricarbonyl-iron tricarbonyl, a pale orange solid decomposing above 170°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>14</sub>O<sub>6</sub>CrFe: C, 54.7; H, 2.9; Cr, 10.8; Fe, 11.6; mol. wt., 482. Found: C, 54.6; H, 2.7; Cr, 10.6; Fe, 11.8; mol. wt., 460.

**Nuclear Magnetic Resonance Studies.**—The proton n.m.r. spectra of 1,4-diphenylbutadiene, 1,4-diphenylbutadiene-iron tricarbonyl and 1,4-diphenylbutadiene-chromium tricarbonyl were recorded in order to demonstrate beyond doubt the nature of the iron tricarbonyl and chromium tricarbonyl complexes of 1,4-diphenylbutadiene. Due to low solubility of the metal compounds, accurate chemical shift measurements were not possible. However, qualitatively, the spectra showed a large peak with a small shoulder for 1,4-diphenylbutadiene (attributable to the 10 phenyl protons and 4 butadiene protons respectively), a single peak for 1,4-diphenylbutadiene-iron tricarbonyl (attributable to the 10 phenyl protons, the resonances due to the butadiene protons being lost in the noise) and for 1,4-diphenylbutadiene-chromium tricarbonyl two peaks of equal intensity (attributable to the protons of two non-equivalent phenyl groups, the butadiene protons again not being observable). Since only one resonance due to phenyl-protons is observed in the spectrum of 1,4-diphenylbutadiene-iron tricarbonyl, the iron atom cannot be bonded to one of the benzene rings. For the spectrum of 1,4-diphenylbutadiene-chromium tricarbonyl the reverse is true; two resonances due to phenyl-protons are observed, showing that one of the benzene rings is bonded to a metal.

**Acknowledgment.**—We are indebted to the Union Carbide Metals Company for a gift of chromium hexacarbonyl.