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## Some Tertiary Phosphine-Iron Carbonyl Compounds

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Derivatives of iron pentacarbonyl containing 1,2-bis-(diphenylphosphino)-ethane are described, as well as related compounds containing halide and perfluoroalkyl groups. Stereoisomers of dichlorodicarbonyl-[1,2-bis-(diphenylphosphino)-ethane]-iron(II) have been observed. A modified synthesis of tertiary phosphine-iron carbonyl compounds is described.

### Introduction

Tertiary phosphine-iron carbonyls of the types  $\text{Fe}(\text{CO})_4\text{PR}_3$  and  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$  have been prepared in the past by reaction at elevated temperatures between the phosphine and an iron carbonyl<sup>1,2</sup> or diene-iron tricarbonyl complex.<sup>3</sup> Recently the direct addition of carbon monoxide under mild conditions to dihalobis-(tertiary phosphine)-iron(II) complexes has yielded dihalodicarbonylbis-(tertiary phosphine)-iron(II) compounds,  $\text{FeX}_2(\text{CO})_2(\text{PR}_3)_2$ .<sup>4</sup> Unsubstituted metal carbonyls often have been prepared by reduction of metal halides with organometallic reagents in the presence of carbon monoxide.<sup>5</sup> The circumstances suggested to us that reduction of a metal halide in the presence of carbon monoxide and a tertiary phosphine might provide a new route to mixed phosphine-metal carbonyls. Such a technique could be useful in cases in which instability of the product or side reaction makes the use of high temperatures undesirable. We have found that treatment of a dihalobis-(tertiary phosphine)-iron complex, a dihalodicarbonylbis-(tertiary phosphine)-iron complex, or a mixture of ferrous halide and tertiary phosphine with an organolithium compound, a Grignard reagent, or a complex metal hydride, in the presence of carbon monoxide at 0 to 25°, will yield a tricarbonylbis-(tertiary phosphine)-iron(0) compound.

Recent interest in mixed iron carbonyl derivatives containing perfluoroalkyl groups<sup>6-8</sup> has extended to tertiary phosphine-containing species.<sup>9</sup> We have prepared such compounds containing the bidentate tertiary phosphine, 1,2-bis-(diphenylphosphino)-ethane.<sup>10</sup>

### Experimental

**Analytical.**—Infrared spectra were taken on a Beckman IR-5 instrument, using NaCl optics, in tetrachloroethylene solution except in those cases in which relative insolubility required the

use of chloroform. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, and by the Analytical Research Division of this Company. Melting points were taken in open tubes and are uncorrected. Thermogravimetric analyses utilized the Chevenard apparatus.

**Starting Materials.**—Iron pentacarbonyl was obtained from Antara Chemical Co. Triiron dodecacarbonyl was prepared by a method based on that of Hieber.<sup>11</sup> Tricarbonyl-(cyclooctatetraene)-iron(0),<sup>8</sup> iodoperfluoropropyltetracarbonyliron(II),<sup>8,7</sup> (octafluorotetramethylene)-tetracarbonyliron(II),<sup>8</sup> and 1,2-bis-(diphenylphosphino)-ethane<sup>10,12</sup> were prepared as described in the literature. Ethyldiphenylphosphine was prepared by the Grignard method from chlorodiphenylphosphine. Ferrous chloride was dehydrated by heating *in vacuo*. Tetrahydrofuran (THF) was purified before use by distillation from lithium aluminum hydride. Phenyllithium was prepared and analyzed by standard methods.<sup>13</sup> Heptafluoropropyl iodide was obtained from Columbia Organic Chemicals. All other chemicals were reagent grade.

1. **Dichlorodicarbonyl-(diphosphine)-iron(II).**—(a) A mixture of 4.0 g. (10 mmoles) of the diphosphine and 1.3 g. (10 mmoles) of ferrous chloride in 60 ml. of benzene was refluxed under nitrogen for 16 hr. The mixture, containing much white solid, was stirred at room temperature under carbon monoxide pressure (5 p.s.i.) for 2.5 hr. Filtration gave an orange solid which was washed with benzene and pentane and dried *in vacuo*; yield 4.4 g. (75%); m.p. 135° dec. The solid had carbonyl stretching frequencies at 2000 (s) and 2062 (s)  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ). Recrystallization from dichloromethane-ether gave a sample of m.p. 150–153° dec.

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{24}\text{O}_2\text{Cl}_2\text{P}_2\text{Fe}$ : C, 57.86; H, 4.16; P, 10.65. Found: C, 57.00; H, 4.11; P, 9.82.

Evaporation of the benzene solution gave a red solid (1.1 g.) having no carbonyl stretching bands in the infrared.

(b) A mixture of 4.0 g. (10 mmoles) of the diphosphine, 1.3 g. (10 mmoles) of ferrous chloride, and 70 ml. of THF was stirred at room temperature under carbon monoxide pressure (5 p.s.i.) for 3 hr. Filtration gave an orange solid, which was washed with benzene and pentane and dried *in vacuo*; yield, 4.8 g. (81%); m.p. 139–141° dec. Evaporation of the THF solution gave a sticky, red-brown solid (0.7 g.) having carbonyl stretching bands at 2062 (m), 2000 (m), and 1949 (w)  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ). The main product had a carbonyl stretching band at 1949 (m)  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ).

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{24}\text{O}_2\text{Cl}_2\text{P}_2\text{Fe}$ : C, 57.86; H, 4.16; P, 10.65. Found: C, 58.47; H, 4.74; P, 10.07.

(c) A mixture of 4.0 g. (10 mmoles) of the diphosphine and 1.3 g. (10 mmoles) of ferrous chloride in 65 ml. of benzene was refluxed for 16 hr. under nitrogen. Solvent was removed from the mixture *in vacuo*. The white residue was stirred under carbon monoxide pressure (5 p.s.i.) in 70 ml. of THF at room temperature for 3 hr. Filtration and washing with benzene

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(9) R. A. Plowman and F. G. A. Stone, *Inorg. Chem.*, **1**, 518 (1962).

(10) For convenience we refer to 1,2-bis-(diphenylphosphino)-ethane,  $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ , as "diphosphine."

(11) W. Hieber, *Z. anorg. allgem. Chem.*, **204**, 171 (1932).

(12) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(13) H. Gilman and J. W. Morton, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter VI.

and pentane left an orange solid, m.p. 139° dec., having a carbonyl stretching frequency at 1949  $\text{cm}^{-1}$ ; yield, 3.5 g. (59%). Evaporation of the THF filtrate left a red-orange solid, having carbonyl stretching frequencies at 2062, 2000, and 1949  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ); yield, 1.1 g.

(d) A 250-mg. sample of  $\text{FeCl}_2(\text{CO})_2 \cdot (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ , showing carbonyl bands at 2062 and 2000  $\text{cm}^{-1}$ , was stirred in 35 ml. of refluxing acetone under nitrogen for 17 hr. Evaporation left an orange solid having a carbonyl stretching band only at 1949  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ). Crystallization from pentane-dichloromethane gave 130 mg. of mustard-colored solid, m.p. 139°–146° dec.

**2. Dichlorodicarbonylbis-(ethylidiphenylphosphine)-iron(II).<sup>4</sup>**—(a) A mixture of 1.3 g. (10 mmoles) of ferrous chloride, 4.5 g. (21 mmoles) of ethylidiphenylphosphine, and 70 ml. of THF was stirred under carbon monoxide pressure (5 p.s.i.) at room temperature for 3 hr. After evaporation of solvent, no carbonyl stretching frequencies were seen in the infrared spectrum of the tan residues.

(b) A mixture of 1.3 g. (10 mmoles) of ferrous chloride, 4.5 g. (21 mmoles) of ethylidiphenylphosphine, and 70 ml. of THF was placed in a glass liner in a 300-ml. Autoclave Engineers stirred autoclave. The mixture was stirred under  $\sim 1000$  p.s.i. pressure of carbon monoxide for about 12 hr. Filtration then gave an orange, crystalline solid, which was washed with benzene and pentane and dried *in vacuo*; m.p. 166–169° dec. (lit.<sup>4</sup> 160°); yield 2.7 g. (44%).

*Anal.* Calcd. for  $\text{C}_{30}\text{H}_{30}\text{O}_2\text{Cl}_2\text{P}_2\text{Fe}$ : C, 58.94; H, 4.94; P, 10.13. Found: C, 58.51; H, 4.79; P, 10.58.

The THF solution was evaporated, leaving an oil from which pentane precipitated 1.1 g. of yellow solid. Both fractions had carbonyl stretching bands at 2037 (s) and 1988 (s)  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ).

(c) A 290-mg. sample of  $\text{FeCl}_2(\text{CO})_2[(\text{C}_6\text{H}_5)_2\text{PC}_2\text{H}_5]_2$  was stirred in 35 ml. of refluxing acetone under nitrogen for 23 hr. Evaporation left a solid having carbonyl stretching frequencies only at 2037 (s) and 1988 (s)  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ).

**3. Tricarbonylbis-(ethylidiphenylphosphine)-iron(0).**—(a) A mixture of 4.0 g. (19 mmoles) of ethylidiphenylphosphine and 2.0 g. (4 mmoles) of triiron dodecacarbonyl in 60 ml. of benzene was refluxed under nitrogen for 2 hr. Filtration gave an orange solution, which was evaporated to an oil. The addition of pentane precipitated a tan solid, which was recrystallized from pentane-dichloromethane to a pale yellow powder, having a carbonyl stretching band at 1883 (s)  $\text{cm}^{-1}$ ; m.p. 151–154° dec.; yield, 1.33 g. (25%).

*Anal.* Calcd. for  $\text{C}_{31}\text{H}_{30}\text{O}_3\text{P}_2\text{Fe}$ : C, 65.50; H, 5.32; P, 10.89. Found: C, 64.25; H, 5.05; P, 11.09.

Evaporation of the filtrates gave a non-crystallizable orange oil having strong carbonyl stretching bands at 2044, 1976, 1938, and 1883  $\text{cm}^{-1}$ .

(b) A mixture of 12 g. (56 mmoles) of ethylidiphenylphosphine and 1.8 g. (14 mmoles) of ferrous chloride in 45 ml. of benzene was stirred and refluxed under nitrogen for 16 hr. The cooled mixture was placed in the glass liner of a 300-ml. Autoclave Engineers autoclave and stirred at room temperature under  $\sim 1000$  p.s.i. pressure of carbon monoxide for about 16 hr. The infrared spectrum of some of the yellow solid thus formed<sup>4</sup> showed carbonyl absorption at 2037 and 1988  $\text{cm}^{-1}$ . The entire mixture was placed in a 250-ml. flask fitted with a gas inlet, magnetic stirrer, and pressure-compensated dropping funnel. At 0°, with stirring, 55 ml. (25 mmoles) of 0.45 N phenyllithium in diethyl ether was dropped into the mixture, under carbon monoxide pressure (5 p.s.i.). After stirring for 1 hr. at 0° and 1 hr. at room temperature, the mixture was chromatographed on an alumina column; elution with dichloromethane was continued until the eluates were colorless. Evaporation of the later portions of eluate gave a yellow solid (530 mg.) having carbonyl stretching bands at 2037 and 1988  $\text{cm}^{-1}$  (those of starting material). The major portion of the eluate was evaporated and the oil thus obtained was washed with pentane. The solid residue (5.1 g.) (m.p. 138° dec.) had carbonyl stretching

bands at 2037 (vw), 1988 (vw), and 1883 (vs)  $\text{cm}^{-1}$ . A 2.1-g. sample of this material was dissolved in a pentane-dichloromethane mixture; the solution was chromatographed on a pentane-alumina column. A 3:1 pentane-dichloromethane mixture eluted a yellow solution, evaporating to a yellow solid (860 mg.), having a carbonyl absorption at 1883  $\text{cm}^{-1}$ ; m.p. 151–154° dec. In this case, as always with this type of compound, considerable decomposition and loss of material appeared to occur on the column.

**4. Tricarbonyl-(diphosphine)-iron(0).**—(a) A mixture of 1.25 g. (5 mmoles) of cyclooctatetraeneiron tricarbonyl (containing a small amount of  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$ )<sup>3</sup> and 2.0 g. (5 mmoles) of the diphosphine in 50 ml. of toluene was refluxed under nitrogen for 6 hr. The cooled mixture was evaporated to dryness. The residues were dissolved in 4:1 pentane-dichloromethane, and the solution was chromatographed. A 4:1 pentane-dichloromethane mixture eluted a red solution, giving on evaporation 280 mg. of red solid shown by its infrared spectrum to be  $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ . A 2:1 pentane-dichloromethane mixture eluted a yellow solution evaporating to a yellow solid, which was washed with pentane and dried to a powder, m.p. 135° dec.; yield, 1.95 g. (72%). The compound had carbonyl stretching bands at 1992 (s), 1923 (m, sh), and 1901 (s)  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{24}\text{O}_3\text{P}_2\text{Fe}$ : C, 64.70; H, 4.49; P, 11.50. Found: C, 63.46; H, 4.80; P, 11.79.

Elution with dichloromethane and evaporation of the eluates gave a red-brown solid having a carbonyl stretching band at 1887  $\text{cm}^{-1}$ ; m.p. 202–205° dec.; yield, 150 mg.

*Anal.* Calcd. for  $\text{C}_{29}\text{H}_{24}\text{O}_3\text{P}_2\text{Fe}$ : C, 64.70; H, 4.49. Found: C, 64.04; H, 4.78.

(b) A mixture of 4.0 g. (10 mmoles) of the diphosphine and 20 ml. (150 mmoles) of iron pentacarbonyl was placed in a 150-ml. stainless steel bomb, which then was cooled to  $-196^\circ$ , evacuated, and sealed. The bomb was heated at 130° for 6 hr. After cooling, the bomb was rinsed with about 50 ml. of dichloromethane. Evaporation of the solution left a yellow-brown residue having a very complex spectrum in the 2000  $\text{cm}^{-1}$  region. The solid was dissolved in pentane-dichloromethane; the solution was chromatographed on alumina. A 4:1 pentane-dichloromethane mixture eluted a yellow liquid. Evaporation and recrystallization (pentane-dichloromethane) gave a yellow solid, having carbonyl absorptions at 2049 (s), 1976 (s), and 1934 (s)  $\text{cm}^{-1}$ ; m.p. 170° dec.; yield, 650 mg. (9%).

*Anal.* Calcd. for  $\text{C}_{34}\text{H}_{24}\text{O}_3\text{P}_2\text{Fe}_2$ : C, 55.61; H, 3.29; P, 8.43. Found: C, 56.37; H, 3.28; P, 8.24.

Elution of the column with 1:1 pentane-dichloromethane and evaporation of the eluates gave a small amount of yellow and brown solids, having carbonyl bands at 2049, 1992, 1930, and 1893  $\text{cm}^{-1}$ , decomposing at 160°.

(c) A mixture of 2.0 g. (4 mmoles) of triiron dodecacarbonyl and 4.0 g. (10 mmoles) of diphosphine in 70 ml. of benzene was refluxed under nitrogen for 1 hr. The cooled mixture was filtered and the filtrate was evaporated *in vacuo*. The oily residue was dissolved in pentane-dichloromethane and the solution was chromatographed. A 3:2 pentane-dichloromethane mixture eluted a bright yellow solution, which was evaporated. The residue was washed with pentane and dried to a yellow solid having strong carbonyl absorptions at 2049, 1992, 1927, and 1908  $\text{cm}^{-1}$ . The absorption contours indicated the presence of unresolved bands. Recrystallization from pentane-dichloromethane showed no sign of separating the two components.

(d) A mixture of 4.0 g. (10 mmoles) of the diphosphine, 1.3 g. (10 mmoles) of ferrous chloride, and 70 ml. of THF was stirred at 0° under carbon monoxide pressure (5 p.s.i.), and 50 ml. (22 mmoles) of 0.45 N phenyllithium in diethyl ether was added dropwise. After stirring for 1 hr. the solvent was evaporated, leaving a black, oily mixture, which was treated with pentane (100 ml.). Filtration gave brown tars, which were dissolved in pentane-dichloromethane; this solution was chromatographed on alumina, eluting with  $\text{CH}_2\text{Cl}_2$ . The products were still oily, so rechromatography was required. Elution with 1:1

pentane-dichloromethane gave a solution yielding on evaporation a yellow solid, having carbonyl absorptions at 1992 (s), 1923 (sh), 1901 (s)  $\text{cm}^{-1}$ ; m.p. 135° dec.; yield, 1.0 g. (19%).

5. **Tricarbonyl-bis-(triphenylphosphine)-iron(0)**<sup>13</sup>.—(a) A mixture of 10.0 g. (38 mmoles) of triphenylphosphine and 2.0 g. (16 mmoles) of ferrous chloride in 80 ml. of benzene was refluxed under nitrogen for 17 hr. The mixture was stirred at 0° under carbon monoxide pressure (5 p.s.i.) and 125 ml. (45 mmoles) of phenyllithium (0.36 *N* in diethyl ether) was added dropwise. After stirring for 45 min. the mixture was evaporated to a black oil. Treatment with 500 ml. of pentane and filtration left a tan residue, which was dissolved in pentane-dichloromethane. The solution was chromatographed (3:1 pentane-dichloromethane) on alumina. The yellow eluates were evaporated and the residue was recrystallized from pentane-dichloromethane to give yellow crystals, having a carbonyl absorption at 1887  $\text{cm}^{-1}$ ; m.p. 249° dec.; yield, 1.73 g. (16%).

*Anal.* Calcd. for  $\text{C}_{30}\text{H}_{30}\text{O}_3\text{P}_2\text{Fe}$ : C, 70.49; H, 4.55. Found: C, 70.72; H, 4.0.

Evaporation of the pentane solution gave an orange solid showing carbonyl bands at 2049, 1976, 1937, and 1887  $\text{cm}^{-1}$ . From another run, repeated crystallization separated a solid, having carbonyl bands at 2049, 1976, and 1937  $\text{cm}^{-1}$ ; m.p. 193° dec.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{13}\text{O}_4\text{PFe}$ : C, 61.42; H, 3.51; P 7.20. Found: C, 61.47; H, 3.80; P, 7.33.

(b) In a flask were placed 1.6 g. (13 mmoles) of ferrous chloride, 5.3 g. (20 mmoles) of triphenylphosphine, and 0.20 g. (5.3 mmoles) of sodium borohydride. The mixture was stirred at room temperature under carbon monoxide pressure (5 p.s.i.), while 100 ml. of THF was added. After 1.5 hr. the mixture was chromatographed on alumina, the column being eluted with dichloromethane. From evaporation of the eluates and crystallization was obtained 540 mg. of tricarbonyl-bis-(triphenylphosphine)-iron(0), identified by its infrared spectrum and melting point.

6. **Reactions of Tricarbonyl-bis-(tertiary phosphine)-iron(0) Compounds.**—(a) A mixture of 450 mg. (0.8 mmole) of tricarbonyl-(diphosphine)-iron(0), 35 ml. of toluene, 1.0 ml. (10 mmoles) of *n*-propyl iodide, and 1.5 ml. (13 mmoles) of cyclooctatetraene was refluxed under nitrogen for 4 hr. The black mixture was filtered. Evaporation of the filtrate left solids showing in the infrared the carbonyl stretching bands only of tricarbonyl-(diphosphine)-iron(0).

(b) A mixture of 270 mg. (0.5 mmole) of tricarbonyl-(diphosphine)-iron(0) and 260 mg. (1 mmole) of triphenylphosphine in 35 ml. of toluene was stirred and refluxed under nitrogen for 21 hr. Removal of solvent left residues having the carbonyl stretching bands only of tricarbonyl-(diphosphine)-iron(0).

(c) A mixture of 270 mg. (0.5 mmole) of tricarbonyl-(diphosphine)-iron(0) and 100 mg. (6 mmoles) of  $\alpha,\alpha'$ -dipyridyl in 35 ml. of toluene was stirred and refluxed under nitrogen for 21 hr. Removal of solvent left residues having the carbonyl stretching bands only of tricarbonyl-(diphosphine)-iron(0).

(d) A mixture of 270 mg. (0.5 mmole) of tricarbonyl-(diphosphine)-iron(0) and 400 mg. (1 mmole) of the diphosphine was placed in a 150-ml. stainless steel bomb, which was evacuated and sealed. After heating at 130° for 17 hr., the bomb was opened and rinsed with eight 10-ml. portions of dichloromethane. Evaporation of the filtered and combined solutions left a yellow solid showing strong carbonyl bands at 1992, 1923, and 1901  $\text{cm}^{-1}$  (starting material) and a very, very weak band at 1845  $\text{cm}^{-1}$ .

(e) A mixture of 270 mg. (0.5 mmole) of tricarbonyl-(diphosphine)-iron(0) and 0.6 ml. (4 mmoles) of heptafluoroiodopropane in 40 ml. of diethyl ether was stirred at room temperature under nitrogen for 1 hr. Filtration left a brown residue (90 mg.) having no carbonyl stretching bands and giving a positive test for iron(II). Evaporation of the filtrate left residues washed with pentane and dried to a hygroscopic brown solid, having carbonyl stretching bands at 2037 (m) and 1988 (m)  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ );

m.p. 115° dec. The compound also shows ( $\text{CS}_2$ ) infrared bands characteristic of the  $\sigma\text{-C}_3\text{F}_7$  group.<sup>14</sup>

*Anal.* Calcd. for  $\text{C}_{31}\text{H}_{24}\text{O}_2\text{F}_7\text{IP}_2\text{Fe}$ : C, 46.18; H, 3.00; P, 7.68. Found: C, 45.76; H, 3.19; P, 6.39.

(f) A mixture of 420 mg. (0.7 mmole) of tricarbonyl-bis-(ethyldiphenylphosphine)-iron(0) and 2.5 ml. (18 mmoles) of heptafluoroiodopropane in 50 ml. of diethyl ether was stirred at room temperature under nitrogen for 3 hr. Filtration left a brown residue showing in its infrared spectrum only tricarbonyl-bis-(ethyldiphenylphosphine)-iron(0). Evaporation of the filtrate left a brown solid (430 mg.) showing in its infrared spectrum a very strong carbonyl absorption at 1883  $\text{cm}^{-1}$  and possibly very, very weak bands at 2037 and 1976  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ).

(g) A mixture of 280 mg. (0.5 mmole) of tricarbonyl-bis-(ethyldiphenylphosphine)-iron(0) and 130 mg. (0.5 mmole) of iodine in 35 ml. of acetone was stirred at room temperature under nitrogen for 2 hr. Evaporation of solvent left a sticky red-brown material which could not be induced to crystallize. This material showed carbonyl stretching frequencies at 2083 (vw), 2033 (vs), and 1976 (vs)  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ).

7. **Reaction of the Diphosphine with Perfluoroalkyliron Compounds.**—(a) A mixture of 510 mg. (1.1 mmoles) of heptafluoropropylidotetracarbonyliron(II) and 480 mg. (1.2 mmoles) of the diphosphine in 60 ml. of diethyl ether was stirred under nitrogen for 1 hr. at room temperature and then for 1 hr. at reflux. Filtration and evaporation followed by pentane washing and drying of the residues left a brown solid, having carbonyl stretching bands at 2037 and 1988  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ); m.p. 110–112° dec.; yield, 800 mg. (90%).

*Anal.* Calcd. for  $\text{C}_{31}\text{H}_{24}\text{O}_2\text{F}_7\text{IP}_2\text{Fe}$ : C, 46.18; H, 3.00; P, 7.68. Found: C, 47.28; H, 3.38; P, 7.82.

(b) A mixture of 450 mg. (1.22 mmoles) of (octafluorotetramethylene)-tetracarbonyliron(II) and 350 mg. (0.88 mmole) of the diphosphine in 50 ml. of methylcyclohexane was refluxed under nitrogen for 3 hr. On cooling to room temperature a white solid precipitated. Filtration and recrystallization (diethyl ether-pentane) gave a cream-colored solid, m.p. 224–226° dec., having carbonyl bands at 2041 and 1996  $\text{cm}^{-1}$ ; yield, 250 mg. (40%). Evaporation of the methylcyclohexane filtrate gave a white solid. Infrared examination showed this and the residues from the crystallization to contain the main product with traces of starting materials.

*Anal.*<sup>15</sup> Calcd. for  $\text{C}_{32}\text{H}_{24}\text{O}_2\text{F}_8\text{P}_2\text{Fe}$ : C, 54.10; H, 3.40; P, 8.72; F, 21.4. Found: C, 54.45; H, 3.42; P, 8.68; F, 21.1.

The  $\text{F}^{19}$  nuclear magnetic resonance spectrum<sup>16</sup> of this compound (56.4 Mc.  $\text{CH}_2\text{Cl}_2$  solution) showed resonances (upfield from the line of  $\text{CCl}_3\text{F}$ ) at 74.2 p.p.m. (triplet,  $J = 12$  c.p.s.) and 138 p.p.m. The parent compound  $\text{FeC}_4\text{F}_8(\text{CO})_4$  shows resonances at 70.6 and 136.9 p.p.m.<sup>6</sup>

## Discussion

The tertiary phosphine-iron carbonyl compounds prepared in this study are of various shades of yellow in color and moderately air-sensitive, especially in solution. Tricarbonyl-bis-(triphenylphosphine)-iron(0) has always been prepared in the *trans* configuration.<sup>2,3</sup> We hoped by avoiding the use of high temperatures to obtain *cis* isomers of this and related compounds. This was achieved, however, only with the diphosphine, which cannot form monomeric *trans*-disubstituted compounds. The compound  $\text{Fe}(\text{CO})_3(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}$

(14) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

(15) When prepared in the presence of aromatic solvents, this compound was always obtained with solvent of crystallization. We are indebted to a referee for suggesting the use of methylcyclohexane as a reaction medium.

(16) We are indebted to Dr. W. Naegle of this Company for obtaining the spectrum.

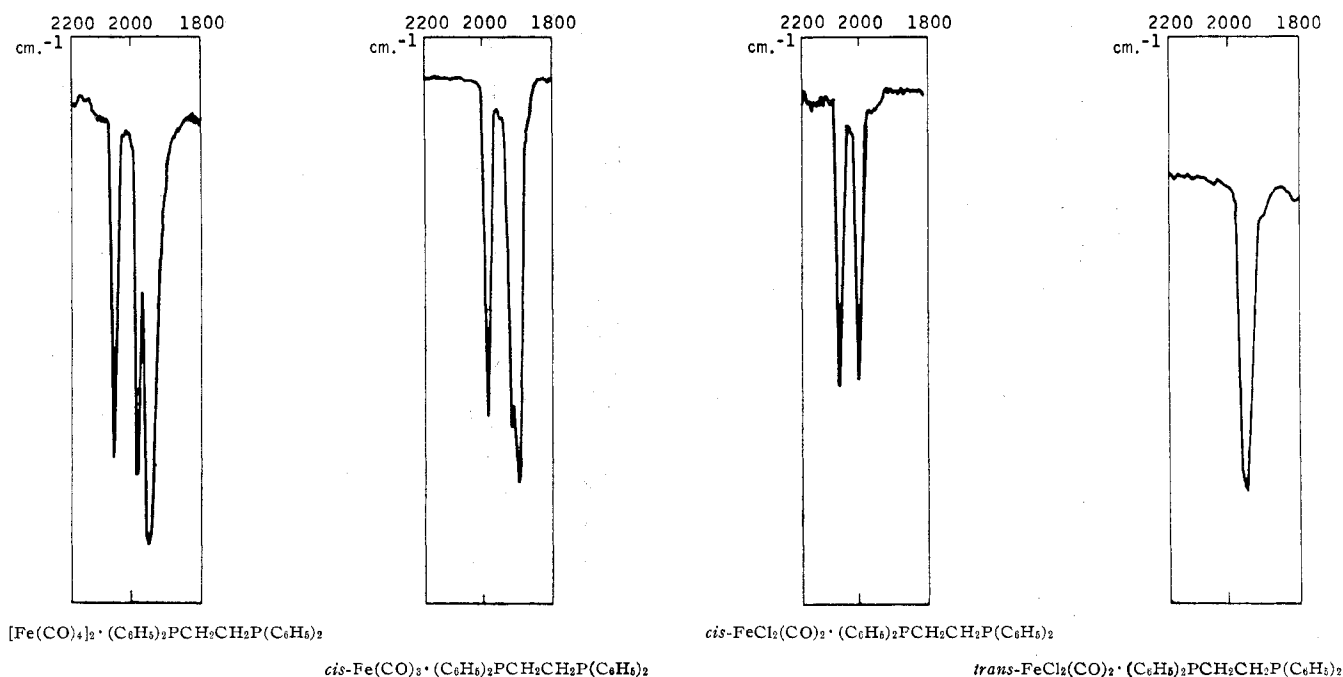
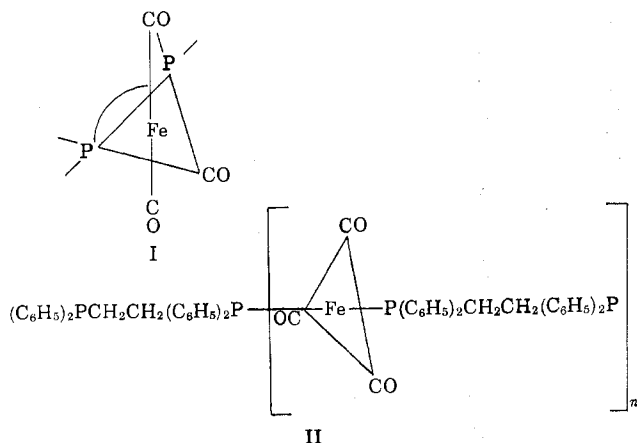


Fig. 1.—Carbonyl stretching bands of substituted iron carbonyl derivatives.

$(\text{C}_6\text{H}_5)_2$  (I)<sup>17</sup> has three carbonyl stretching bands in the infrared, as predicted by Cotton.<sup>2,18</sup> A second species of composition,  $\text{Fe}(\text{CO})_3$  or  $4 \cdot (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ , obtained with I from the reaction of cyclooctatetraene-iron tricarbonyl with the diphosphine, exhibits a single carbonyl stretching band at  $1887 \text{ cm}^{-1}$ , as is also shown by  $\text{trans-Fe}(\text{CO})_3(\text{P}(\text{C}_6\text{H}_5)_3)_2$ .<sup>2,3</sup> Hence we suggest its formulation as II.



Group VI carbonyls<sup>19, 20</sup> have been treated with the diphosphine, which was observed to function as a bridging ligand between two metal carbonyl moieties in compounds of the type  $(\text{diphosphine})_3\text{M}_2(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}$ ).<sup>20</sup> Similarly, we find that the ligand forms a bridged complex  $[\text{Fe}(\text{CO})_4]_2(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$  when heated with excess iron pentacarbonyl. The infrared spectrum of the carbonyl stretching region of

(17) After this paper had been submitted for publication, we became aware of an independent synthesis of this compound and certain related ones. (F. Zingales and F. Canziani, *Chem. Ind. (Milan)*, **44**, 1394 (1962).

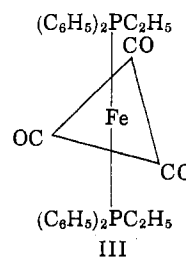
(18) A structure based on a rectangular pyramid is also possible for this compound. We depict I in analogy to the structure of  $\text{Fe}(\text{CO})_5$  itself.

(19) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

(20) F. Zingales and F. Canziani, *Gazz. chim. ital.*, **92**, 343 (1962).

this compound is identical with that of  $\text{Fe}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ .

In view of the difficulty in formation of tricarbonyl-*cis*-bis-(tertiary phosphine)-iron(0) complexes, it may be instructive to compare tricarbonyl-*trans*-bis-(ethyl-diphenylphosphine)-iron(0),  $\text{Fe}(\text{CO})_3((\text{C}_6\text{H}_5)_2\text{PC}_2\text{H}_5)_2$  (III), with its closest *cis* analog, tricarbonyl-(diphosphine)-iron(0) (I).



The phosphorus atoms in these two complexes should be quite similar in their electronic nature and ability to donate and accept electrons. We feel that differences in the behavior of the phosphine ligands or the complexes may fairly be ascribed to steric effects.

Qualitatively compound I is much more air-sensitive and more subject to decomposition on storage than the *trans* analog. Compound I begins to decompose at  $135^\circ$  in air and at  $200^\circ$  under nitrogen in thermogravimetric analysis, whereas compound III decomposes under the corresponding conditions at  $151$  and  $245^\circ$ , respectively. The reaction with an excess of heptafluoroiodopropane was rapid and complete in the case of the diphosphine complex, but the *trans* complex, even under more drastic conditions, was not appreciably attacked. The latter may be better shielded from attacking reagents than the *cis*-chelated compound. It is also possible that some strain imposed on the

chelate ring in the pentacoördinate structure is relieved by expansion to octahedral coördination.

Despite these evidences of reactivity, no additional carbonyl groups of the tricarbonyl-(diphosphine)-iron(0) could be replaced by cycloöctatetraene, triphenylphosphine,  $\alpha, \alpha'$ -dipyridyl, or excess of the diphosphine. The analogous *o*-phenylenebis-(dimethylarsine) compound, tricarbonyl-(diarsine)-iron(0), reacted with excess diarsine to yield monocarbonylbis-(diarsine)-iron(0),<sup>21</sup> whereas under similar conditions no formation of monocarbonylbis-(diphosphine)-iron(0) was observed by us. Such a difference in behavior might be due to dissimilar structures of the ligands or the complexes. The carbonyl stretching band pattern of tricarbonyl-(diarsine)-iron(0) (2009 (vs), 1916 (vs), 1880 (sh)  $\text{cm.}^{-1}$ )<sup>21</sup> differs from that of tricarbonyl-(diphosphine)-iron(0) (1992 (vs), 1923 (sh), 1901 (vs)  $\text{cm.}^{-1}$ ) in the relative positions of the shoulder and the main low frequency band.

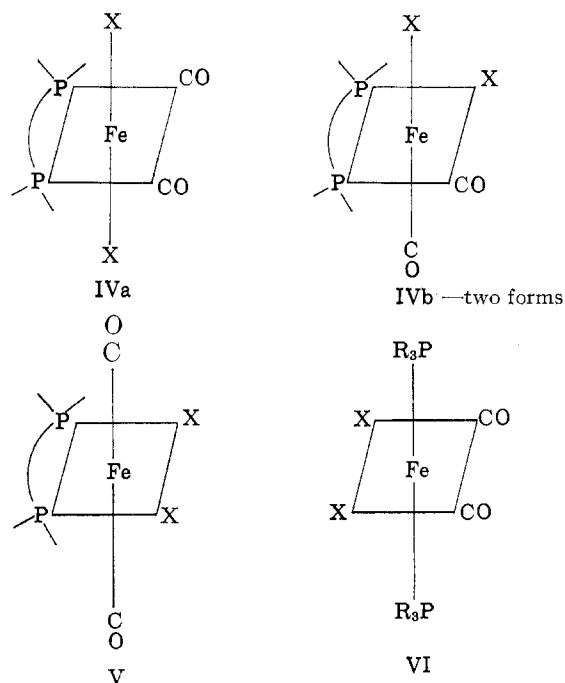
Recently Plowman and Stone found that it was possible to replace one and only one carbonyl group of heptafluoropropylidotetracarbonyliron(II),  $\text{FeC}_3\text{F}_7\text{I}(\text{CO})_4$ , with triphenylphosphine, giving a compound  $\text{FeC}_3\text{F}_7\text{I}(\text{CO})_3 \cdot \text{P}(\text{C}_6\text{H}_5)_3$ . They also found that no carbonyl groups of bis-(heptafluoropropyl)-tetracarbonyliron(II),  $\text{Fe}(\text{C}_3\text{F}_7)_2(\text{CO})_4$ , could be replaced by triphenylphosphine to give a stable compound.<sup>9</sup>

In this Laboratory stirring of  $\text{Fe}(\text{CO})_5 \cdot (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$  with heptafluoroiodopropane in ether gave  $\text{FeC}_3\text{F}_7\text{I}(\text{CO})_2 \cdot (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ , which also was obtained from the diphosphine and  $\text{FeC}_3\text{F}_7\text{I}(\text{CO})_4$ . As well, treatment of (octafluoro-tetramethylene)-tetracarbonyliron(II),  $\text{Fe}(\text{CF}_2)_4(\text{CO})_4$ , with the diphosphine yielded  $\text{Fe}(\text{CF}_2)_4(\text{CO})_2 \cdot (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ . Plowman and Stone suggest that "the carbon-iron  $\sigma$ -bond decreases in stability when carbonyl groups are replaced by ligands which  $\pi$ -bond with iron less effectively."<sup>9</sup> In view of the apparently high stability of  $\text{Fe}(\text{CF}_2)_4(\text{CO})_2 \cdot (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ , we believe steric factors more important than electronic ones in these cases.

In preparing  $\text{FeCl}_2(\text{CO})_2 \cdot (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$  we noticed a very enhanced absorption of carbon monoxide compared to that in the preparation of  $\text{FeCl}_2(\text{CO})_2((\text{C}_6\text{H}_5)_2\text{PC}_2\text{H}_5)_2$ ,<sup>4</sup> as well as a striking solvent effect. In benzene one obtains mainly IV, having two

carbonyl stretching bands, indicative of *cis*-carbonyl groups. In THF the same process yields the isomer V, having a single carbonyl band indicative of *trans*-carbonyl groups. Some of both isomers is formed in any case, with little predominance of one or the other if the diphosphine-ferrous chloride complex is prepared in benzene and carbonylated in THF. In refluxing acetone the *cis*-isomer is converted to its *trans* counterpart.

However, carbon monoxide treatment of  $\text{FeCl}_2((\text{C}_6\text{H}_5)_2\text{PC}_2\text{H}_5)_2$  in THF yields, as in benzene, only *cis*- $\text{FeCl}_2(\text{CO})_2((\text{C}_6\text{H}_5)_2\text{PC}_2\text{H}_5)_2$  (VI).<sup>4</sup> This compound is not converted into its *trans* (carbonyl) isomer in



refluxing acetone. Why isomerization should occur with *cis*-chelating phosphine ligands (IV) and not with *trans* ones (VI) is not clear. Geometrical isomerization of the diphosphine-substituted group VI carbonyls was observed,<sup>19</sup> and isomerization of substituted manganese carbonyls  $\text{Mn}(\text{CO})_3\text{L}_2\text{X}$  ( $\text{L} = \text{R}_3\text{P}$ ) recently was reported.<sup>22</sup>

Because of recently expressed interest in this area,<sup>23</sup> representative spectra of several types of phosphine-substituted iron carbonyls are shown in Fig. 1.

(21) H. Nigam, R. S. Nyholm, and D. V. Ramana Rao, *J. Chem. Soc.*, 1397 (1959).

(22) R. J. Angelici, F. Basolo, and A. J. Poë, *Nature*, **195**, 993 (1962).

(23) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).