

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA**Iron Carbonyl Complexes of Triphenylphosphine,
Triphenylarsine, and Triphenylstibine**

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The preparation in solution at atmospheric pressure of the compounds $(C_6H_5)_3MFe(CO)_4$ and $((C_6H_5)_3M)_2Fe(CO)_3$, where $M = P, As, Sb$, has been accomplished. The arsenic and antimony compounds have not been reported previously. The corresponding compounds where $M = N, Bi$ could not be isolated.

Iron carbonyl phosphines were first mentioned by Reppe and Schweckendiek¹ as products of direct reaction between triphenylphosphine and iron pentacarbonyl. However, no details were given.

Later, Hallam and Pauson² prepared $((C_6H_5)_3P)_2Fe(CO)_3$ by heating triphenylphosphine in an autoclave with an equimolecular amount of $(C_5H_5Fe(CO)_2)_2$ or $C_5H_5Fe(CO)_2Cl$ or by treating $((C_6H_5)_3P)Fe(CO)_3I_2$ with sodium cyclopentadienide in tetrahydrofuran. Recently, Cotton and Parish³ obtained the phosphine derivatives by heating $(C_6H_5)_3P$ and $Fe(CO)_5$ in a Carius tube in the absence of solvent. It has been found possible to prepare both mono- and diphosphine derivatives as well as the corresponding arsines and stibines much more simply, however, by reaction in an appropriate solvent.

The reaction of $(Fe(CO)_4)_3$ with triphenylphosphine, -arsine, or -stibine proceeded readily in refluxing tetrahydrofuran or dioxane, the principal product depending on the proportions of the reactants. During the reaction evolution of carbon monoxide occurred and the green color of the carbonyl was discharged. The products were obtained by evaporating most of the solvent *in vacuo* and precipitating with methanol or ethanol. Separation of the mono and bis derivatives then was accomplished, in the case of the phosphine and arsine derivatives, by sublimation, as described for the phosphine derivatives by Cotton and Parish,³ or by fractional crystallization from benzene and methanol in the case of the stibine derivatives, the bis derivative being the less soluble. The lower stability of the monostibine derivative obviated the use of the sublimation technique. The compounds isolated in this work are listed in Table I.

All the compounds are insoluble in water but soluble in most organic solvents. All of them are very stable to air and light, although on long exposure to daylight bis-(triphenylphosphine)-tricarbonyliron was observed to darken. It is interesting to note that though the corresponding di-(tertiaryarsine)-(α -phenylenebisdimethylarsine) substitution compounds⁴ of $Fe(CO)_5$ are more stable to light than $Fe(CO)_5$, yet both $Fe(CO)_3$ -diarsine and $Fe(CO)(diarsine)_2$ gradually darken on standing. As compared with the considerable stability of both $(C_6H_5)_3SbFe(CO)_4$ and $((C_6H_5)_3Sb)_2Fe(CO)_3$, the $SbCl_3$ substitution compound $Fe(CO)_3(SbCl_3)_2$ is reported⁵ to be unstable and photosensitive. A series of substitution products of dicarbonylnitrosyliron⁶ with triarylphosphites, phosphines, arsines, and stibines has been prepared; all these are oxidized spontaneously in air when not perfectly dry and stored at low temperatures, whereas the compounds listed in Table I all are stable to air, light, and water. $((C_6H_5)_3P)_2Fe(CO)_3$ is not attacked by hot alcoholic alkali, sodium in liquid ammonia, or cold concentrated acids, and remains unchanged even when heated at 110° for 24 hr. Even potassium in refluxing dioxane attacks it only slowly, but with rupture of the molecule, one of the products being $(C_6H_5)_2PK$. The bis derivatives are uniformly more stable than the corresponding mono ones, and in either type the stability decreases from phosphine to arsine to stibine compounds. Thus both the monophosphine and monoarsine compounds can be sublimed under vacuum but the monostibine compound decomposes under these conditions. Another notable feature of the complexes is the stability of the carbon monoxide-metal bond. The direct replacement of carbon monoxide by pyridine in these complexes did not appear possible. However, the reaction of iodine with bis-(triphenylphosphine)-tricarbonyliron in anhydrous ether gave $((C_6H_5)_3P)_2Fe(CO)_2I_2$. This chocolate-brown compound was soluble in ethanol and nitrobenzene but insoluble in benzene, carbon tetrachloride, and ether. A suspension of the compound in water gave a precipitate of silver iodide with silver nitrate solution. The infrared spectrum of this compound in Nujol showed two bands in the carbonyl re-

TABLE I

Compound	Color	M.p., °C. (with dec.)
$(C_6H_5)_3PFe(CO)_4$	Pale yellow	201-203
$((C_6H_5)_3P)_2Fe(CO)_3$	Yellow	272
$(C_6H_5)_3AsFe(CO)_4$	Yellow	178
$((C_6H_5)_3As)_2Fe(CO)_3$	Yellow	193-195
$((C_6H_5)_3Sb)Fe(CO)_4$	Yellowish brown	136 ^a
$((C_6H_5)_3Sb)_2Fe(CO)_3$	Yellowish brown	196

^a Sharp, no decomposition.(1) W. Reppe and W. J. Schweckendiek, *Ann.*, **560**, 104 (1948).(2) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).(3) F. A. Cotton and R. V. Parish, *ibid.*, 1440 (1960).(4) H. Nigam, R. S. Nyholm, and D. V. Ramana Rao, *ibid.*, 1397 (1959).(5) G. Wilkinson, *J. Am. Chem. Soc.*, **73**, 5502 (1951).(6) L. Malatesta and A. Araneo, *J. Chem. Soc.*, 3803 (1957).

gion, one weak at 2100 cm^{-1} and the other strong at 2046 cm^{-1} . The infrared spectra in the CO stretching region of the other complexes are presented in Table II. The data of Cotton and Parish also are included for convenient comparison.

No reaction was found to occur when iron pentacarbonyl was mixed with triphenylphosphine in boiling tetrahydrofuran, dioxane, xylene, methanol, or ethanol. On the other hand, in cyclohexanol iron pentacarbonyl reacted readily with triphenylphosphine at the reflux temperature, forming a mixture of mono- and bisphosphine derivatives. The arsine and stibine derivatives could not be prepared by this method because of their decomposition at the reflux temperature of cyclohexanol.

TABLE II

Compound	Medium ^a	CO-stretching frequency ^b		
		(cm. ⁻¹)		
$(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})_4$	Nujol	2050	1970	1930
	CCl_4	2055.0	1978.0	1943.0
	CCl_4^b	2059	1984	1946
	CHCl_3^b	2059	1978	1938
	CS_2^b	2063	1982	1943
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{Fe}(\text{CO})_3$	Nujol		1890	
	CS_2		1884.8	
	CS_2^b		1886	
	CHCl_3^b		1887	
$(\text{C}_6\text{H}_5)_3\text{AsFe}(\text{CO})_4$	Nujol	2063	1985	1946
	CCl_4	2053.7	1977.1	1945.3
$((\text{C}_6\text{H}_5)_3\text{As})_2\text{Fe}(\text{CO})_3$	Nujol		1894	
	CS_2		1884.3	
$(\text{C}_6\text{H}_5)_3\text{SbFe}(\text{CO})_4$	Nujol	2058	1985	1946
	CCl_4	2048.0	1975.3	1942.3
$((\text{C}_6\text{H}_5)_3\text{Sb})_2\text{Fe}(\text{CO})_3$	Nujol		1873	
	CS_2		1882.0	

^a The spectra in Nujol were obtained with an Infracord with NaCl optics. The spectra in CCl_4 and CS_2 were obtained with a Perkin-Elmer Model 421 grating instrument. ^b Cotton and Parish, ref. 3.

Attempts to prepare the corresponding amine and bismuthine complexes by these methods were unsuccessful. Triphenylamine does not replace carbon monoxide in iron carbonyl, probably because of steric effects due to the small size of nitrogen as well as non-availability of vacant orbitals on nitrogen which are necessary for the formation of π -bonds with iron, which operate to stabilize metal complexes of this type. The non-activity of triphenylbismuthine may be due to the increasing inertness of the electron pair in bismuthine as compared with phosphine, arsine, and stibine. Presumably there is also a lowered tendency to form π -bonds.

Experimental

Mono-(triphenylphosphine)-tetracarbonyliron and Bis-(triphenylphosphine)-tricarboyliron.—Two g. of $(\text{C}_6\text{H}_5)_3\text{P}$ (0.0071 mole) was dissolved in 100 ml. of dioxane or tetrahydrofuran (THF) and 1 g. of $(\text{Fe}(\text{CO})_5)_2$ (0.0020 mole) was added to it. The mixture then was stirred in an atmosphere of nitrogen at a temperature of about 70° for 45 min. or until the green color of the solution completely disappeared. The mixture then was cooled to room temperature, filtered, and the brown residue

washed with dioxane or THF. Most of the solvent from the filtrate and washings was taken off *in vacuo* and the residue treated with 50 ml. of methanol or ethanol and cooled. A yellow crystalline product was obtained. The crystals were filtered, washed with two 10-ml. portions of petroleum ether, and then sublimed *in vacuo* at 180°. The sublimate consisted of $(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})_4$, m.p. 201–203° dec. The residue from the sublimation was dissolved in a minimum amount of benzene, filtered, and the filtrate diluted with about 4–6 times its own volume of petroleum ether and cooled to give yellow crystals of $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Fe}(\text{CO})_3$, m.p. 272° dec. Another fraction of the products could be isolated from the brown residue by extracting with benzene and filtering. Benzene was taken off from the yellow filtrate *in vacuo* and the products were separated and isolated from the residue by vacuum sublimation as mentioned before. The final yield was 0.88 g. of $(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})_4$ and 1.1 g. of $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Fe}(\text{CO})_3$.

If, however, excess $(\text{C}_6\text{H}_5)_3\text{P}$ was used, then only the bis compound $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Fe}(\text{CO})_3$ was obtained.

The compounds also could be prepared using $\text{Fe}(\text{CO})_5$ as the starting material. Thus 2 ml. of $\text{Fe}(\text{CO})_5$ (0.015 mole) and 5 g. of $(\text{C}_6\text{H}_5)_3\text{P}$ (0.018 mole) were added to about 100 ml. of pure distilled cyclohexanol (b.p. 161.0°) and the mixture was refluxed for about 1 hr. in an atmosphere of nitrogen, diluted with an equal volume of petroleum ether, and cooled. The resulting yellow precipitate, consisting of a mixture of $(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})_4$ and $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Fe}(\text{CO})_3$, then was filtered, washed with petroleum ether, and dried and the two compounds then were separated from each other by vacuum sublimation; yield, 0.98 g. of $(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})_4$ and 1.2 g. of $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Fe}(\text{CO})_3$.

The identity of these compounds was assumed from the similarity of their spectra, color, and melting points with previously published data.

Mono-(triphenylarsine)-tetracarbonyliron and Bis-(triphenylarsine)-tricarboyliron.—A mixture of 6 g. of $(\text{C}_6\text{H}_5)_3\text{As}$ (0.016 mole) and 2 g. of $(\text{Fe}(\text{CO})_5)_2$ (0.0040 mole) was either refluxed in 150 ml. of THF or heated at 80–90° in dioxane in an atmosphere of nitrogen for 45 min. This then was cooled and filtered. The residue was rejected because it contained very little product due to the greater solubility of the arsine complexes in dioxane or THF than of the phosphine derivatives. The residue from the filtrate was vacuum sublimed at 100° to remove unreacted triphenylarsine, then at 160° to obtain yellow monoclinic crystals of $(\text{C}_6\text{H}_5)_3\text{AsFe}(\text{CO})_4$. $(\text{C}_6\text{H}_5)_3\text{AsFe}(\text{CO})_4$: m.p. 178° dec.; yield, 0.402 g. *Anal.* Calcd. for $\text{C}_{22}\text{H}_{15}\text{O}_4\text{AsFe}$: C, 55.71; H, 3.19; Fe, 11.77; mol. wt., 474. Found: C, 55.56; H, 3.29; Fe, 11.26; mol. wt., 466, determined cryoscopically in benzene. $((\text{C}_6\text{H}_5)_3\text{As})_2\text{Fe}(\text{CO})_3$: yield, 0.575 g. *Anal.* Calcd. for $\text{C}_{30}\text{H}_{20}\text{O}_3\text{As}_2\text{Fe}$: C, 62.26; H, 4.02; Fe, 7.42; mol. wt., 725. Found: C, 62.55; H, 4.02; Fe, 7.16; mol. wt., 767.

Mono-(triphenylstibine)-tetracarbonyliron and Bis-(triphenylstibine)-tricarboyliron.—A mixture of $(\text{C}_6\text{H}_5)_3\text{Sb}$ (6 g., 0.017 mole) and $(\text{Fe}(\text{CO})_5)_2$ (2 g., 0.0040 mole) was refluxed in THF or heated in dioxane at 90–95° in an atmosphere of nitrogen for 1 hr. and filtered. The mixed products then were isolated from the filtrate by removing the solvent *in vacuo* and treating the residue with alcohol. The compounds then were separated from each other by fractional crystallization from benzene and methanol. The less soluble fraction gave $((\text{C}_6\text{H}_5)_3\text{Sb})_2\text{Fe}(\text{CO})_3$, m.p. 196–198° dec.; yield, 1.3 g. *Anal.* Calcd. for $\text{C}_{30}\text{H}_{20}\text{O}_3\text{Sb}_2\text{Fe}$: C, 55.37; H, 3.57; Fe, 6.60; mol. wt., 846. Found: C, 55.00; H, 3.93; Fe, 6.41; mol. wt., 838. From the more soluble fraction the pure monoderivative was obtained, $(\text{C}_6\text{H}_5)_3\text{SbFe}(\text{CO})_4$, m.p. 135°; yield, 1.2 g. *Anal.* Calcd. for $\text{C}_{22}\text{H}_{15}\text{O}_4\text{SbFe}$: C, 50.61; H, 2.90; Fe, 10.72; mol. wt., 521. Found: C, 50.66; H, 2.60; Fe, 10.49; mol. wt., 523.

Triphenylbismuthine and Triphenylamine Derivatives.—Similar treatment of iron tetracarbonyl solutions with triphenylbismuthine or triphenylamine gave no isolable products. In the former case the original green color of the solution was discharged in about 2 hr. and an unidentifiable amorphous, brown, uncrystallizable solid precipitated. In the latter case a brown solid

also was obtained which, however, contained no nitrogen, and the triphenylamine was recovered unchanged.

Bis-(triphenylphosphine)-dicarbonyliron(III) pentaiodide.—A solution of iodine (2 g.) in anhydrous ether (100 ml.) was added drop by drop with stirring to a suspension of $((C_6H_5)_3P)_2Fe(CO)_2$ (1 g.) in 75 ml. of ether over a period of 30 min. The mixture then was stirred for 15 min. more. The chocolate-brown precipitate then was filtered, washed thoroughly with ether until the washings were colorless, and then vacuum-dried; yield, 1.85 g.; m.p. 121–122° dec. *Anal.* Calcd. for $((C_6H_5)_3P)_2Fe(CO)_2I_5$:

$(CO)_2I_5$: Fe, 4.39; I, 49.93; mol. wt., 1271. Found: Fe, 4.33; I, 50.2; mol. wt., 1248 ± 1.5 (determined cryoscopically in nitrobenzene). The stoichiometry and slightly low molecular weight (indicating some ion-pair dissociation) suggest that the compound may be $((C_6H_5)_3P)_2Fe(CO)_2I_5$.

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Mössbauer Effect in Iron Pentacarbonyl and Related Carbonyls

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Four related iron carbonyls, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $Fe(CO)_4I_2$, have been used as stationary absorbers in a Mössbauer experiment in which Co^{57} diffused into metallic chromium was employed as a source. All four absorbers show significant resonance absorption of the 14.4-keV γ -ray of Fe^{57} at 78°K. The observed isomer shifts are interpreted in terms of the chemical bonding in transition metal-carbonyl compounds. The two major Mössbauer parameters (isomer shift and quadrupole splitting) in the case of $Fe(CO)_5$ and $Fe_2(CO)_9$ are in agreement with a trigonal bipyramid structure and a (3,3,3) structure, respectively. The data for $Fe_3(CO)_{12}$ strongly suggest the linear (3,3,3,3) structure and cannot be accounted for by the trigonal arrangement of the three iron atoms which has been proposed on the basis of X-ray data. The quadrupole splitting for $Fe(CO)_4I_2$ is essentially independent of temperature in the range 78 to 298°K., in contrast to the large temperature dependences which have been observed for some related Fe(II) compounds. The isomer shift is consistent with an assignment of +2 for the oxidation state of iron in this compound.

Introduction

As part of a continuing investigation^{1–4} of the resonant absorption of γ -radiation in solids (Mössbauer effect), a number of iron carbonyl compounds have been studied as stationary absorbers at various temperatures.

The choice of iron carbonyl compounds as absorbers was prompted by the fact that a portion of the $Fe(CO)_n$ framework of these molecules survives in a number of the reactions which iron carbonyl compounds undergo, especially with olefinic hydrocarbons. Consequently, the eventual interpretation of the resonance spectra of these adducts, such as the $C_8H_8Fe(CO)_3$ and $C_8H_8[Fe(CO)_3]_2$ molecules reported earlier,³ requires detailed knowledge regarding the contributions of the carbonyl groups to the characteristic parameters which can be extracted from the resonance data. In terms of molecular structure, the two parameters of major interest are the isomer shift, i.s., and the quadrupole splitting, ΔE .^{5–7}

The isomer shift arises from differences in the inter-

action of the isomeric and ground states of the iron atom with the electronic charge densities at the nuclei in the source and in the absorber. The values of this parameter which have been observed for the four accessible oxidation states of the iron atom (metallic, +2, +3, and +6) not only permit the use of the isomer shift as a diagnostic measure of the oxidation state, but—for a given oxidation state—can be related⁷ (at least qualitatively) to the effective contribution of bonding orbitals to the charge density at the nucleus. The quadrupole splitting of the resonance peak arises from the interaction between the nuclear quadrupole moment, Q , of the 3/2-excited state, and the electric field gradient tensor, q , due to inhomogeneities in the electrostatic field at the iron nucleus. When the iron atom is in a cubic environment (e.g., tetrahedral or octahedral), the e.f.g. tensor vanishes and the upper nuclear state in the 14.4-keV transition is fourfold degenerate. Under these conditions, no quadrupole splitting will be observed.

In the present study, both the isomer shift and the quadrupole splitting have been determined for four related iron carbonyls.

Experimental

The experimental techniques related to Mössbauer effect studies have been described in detail in previous communications.³ All measurements were made with respect to a room tem-

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