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Coordination Complexes of Acetylenic Phosphines and Diphosphines. IV.^{1a} Characterization and Mössbauer Spectra of Derivatives of Cyclopentadienyliron Dicarbonyl Dimer and Cyclopentadienyliron Dicarbonyl Halides

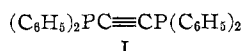
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$(C_5H_5)_2Fe_2(CO)_4$ reacts with $(C_6H_5)_2PC\equiv CP(C_6H_5)_2$ (DPPA) under ultraviolet irradiation to yield $[(C_5H_5)_2Fe_2(CO)_3]_2$ -DPPA, a novel, monosubstituted diphosphine-bridged substitution product. Chlorine, bromine, and iodine cleave $[(C_5H_5)_2Fe_2(CO)_3]_2$ DPPA unsymmetrically, affording ionic complexes of the type $\{[(C_5H_5)_2Fe_2(CO)_3]DPPA\}[X]_2$ ($X^- = FeCl_4^-, FeBr_4^-, I_3^-$). $(C_5H_5)Fe(CO)_2X$ ($X = Cl, Br, I$) give binuclear diphosphine-bridged complexes of the type $[(C_5H_5)Fe(CO)-X]_2$ DPPA with DPPA. Mössbauer studies failed to detect the two chemically nonequivalent iron atoms in the molecule $[(C_5H_5)_2Fe_2(CO)_3]_2$ DPPA. The implications of this result for the structural elucidation of organoiron compounds by Mössbauer spectroscopy are discussed. Infrared, nmr, and Mössbauer results are reported for other compounds prepared.

Introduction

The nonchelating ligand bis(diphenylphosphino)-acetylene (I, DPPA) stabilizes a variety of binuclear



and polymeric diphosphine-bridged halide complexes of the later transition elements.¹ Moreover reaction with nickel carbonyl yields remarkably air-stable compounds of the type $[Ni(CO)_x]_2(DPPA)_{4-x}$ ($x = 1, 2$).² The unique bridging properties of this ligand and an apparent π -acceptor ability comparable with phosphites^{2,3} suggested that reactions with other metal carbonyl derivatives might lead to a series of interesting new binuclear diphosphine-bridged substitution products. Apart from a recent paper by Basolo and coworkers⁴ on bridged complexes of 1,2-bis(diphenylphosphino)ethane, there have been no systematic attempts to synthesize and study such compounds although several groups have prepared diphosphine-bridged metal carbonyl substitution products in the course of related work.⁵

This paper describes the reaction of $[(C_5H_5)Fe(CO)_2]_2$ with I to give $[(C_5H_5)_2Fe_2(CO)_3]_2$ DPPA, a novel air-stable complex containing two monosubstituted $[(C_5H_5)Fe(CO)_2]_2$ units. Reaction of $[(C_5H_5)_2Fe_2(CO)_3]_2$ DPPA with chlorine, bromine, and iodine gives the unusual dication $[C_5H_5Fe(CO)_2]_2$ DPPA²⁺ stabilized by FeX_4^- ($X = Cl, Br$) and I_3^- . Substitution reactions of $(C_5H_5)Fe(CO)_2X$ ($X = Cl, Br, I$) with I are also reported. Mössbauer studies of all these products have been carried out. A preliminary report of part of this work has already appeared.⁶

Experimental Section

Microanalyses were performed by Chemalytics Inc., Tempe, Ariz., and Alfred Bernhardt, 5251 Elbach über Engelskirchen, West Germany. Infrared spectra were recorded on Beckman IR-9 (2500–650 cm^{-1}) and Beckman IR-12 (650–200 cm^{-1}) spectrometers. Proton magnetic resonance spectra were measured in chloroform-*d*, acetone-*d*₆, or benzene using Varian HA-100 and T-60 spectrometers. Melting points were taken in sealed capillaries and are uncorrected.

Apparatus described in an earlier publication was used for Mössbauer measurements.⁷

All preparations necessitated the use of nitrogen atmospheres and work-up of solutions was accomplished using conventional Schlenk-tube or drybox techniques. Ultraviolet irradiations were performed by a Rayonet Model RPR-208 photochemical reactor with a low-pressure mercury lamp of 3500-Å high intensity and an Engelhard-Hanovia water-cooled 450-W lamp.

The diphosphine I was prepared as previously described.⁸ Cyclopentadienyliron dicarbonyl halides were prepared by published procedures.⁹

Preparation of $[(C_5H_5)_2Fe_2(CO)_3]_2$ DPPA.—A mixture of $[(C_5H_5)Fe(CO)_2]_2$ (3.5 g) and I (1.9 g) in benzene (250 ml) was irradiated using the high-intensity 3500-Å mercury lamp for 12 hr at room temperature. The green solution was evaporated *in vacuo* to yield green crystals of the required product. The material was recrystallized from benzene-ethanol as blue-green prisms; mp 162–163°. (Using benzene alone, the product retained one molecule of solvent even after pumping *in vacuo*.) Uv irradiation in acetone gave the same compound. *Anal.* Calcd for $[(C_5H_5)_2Fe_2(CO)_3]_2$ DPPA: C, 59.80; H, 3.83; P, 5.70; Found: C, 60.00; H, 4.03; P, 5.90.

Reactions of $[(C_5H_5)_2Fe_2(CO)_3]_2$ DPPA with Chlorine, Bromine, and Iodine.—(a) Chlorine gas was slowly bubbled through a dichloromethane solution of $[(C_5H_5)_2Fe_2(CO)_3]_2$ DPPA until the color of the solution changed to pale yellow. Solvent was rapidly removed *in vacuo* and *n*-heptane was added to precipitate the product. Recrystallization from ethanol-acetone afforded yellow blocks of $\{[(C_5H_5)Fe(CO)_2]_2DPPA\}(FeCl_4)_2$; mp 189–192°. *Anal.* Calcd for $\{[(C_5H_5)Fe(CO)_2]_2DPPA\}(FeCl_4)_2$: C, 42.0; H, 2.8; Cl, 24.8. Found: C, 42.1; H, 2.6; Cl, 24.7.

(b) Bromine (0.64 g) in dichloromethane (20 ml) was slowly added to $[(C_5H_5)_2Fe_2(CO)_3]_2$ DPPA (2.0 g) in dichloromethane (200 ml) while stirring. The brown solution was then refluxed for 6 hr and the precipitated crude product was filtered off.

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TABLE I
 INFRARED AND NMR DATA FOR DERIVATIVES OF $(C_5H_5)_2Fe_2(CO)_4$

Compound	$\nu(CO),^a$ cm^{-1}	Far-infrared (400–200 cm^{-1})	Proton nmr spectra ^b	
			$\tau(C_5H_5)$	J_{P-H}, Hz
$[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$	Mull 1953 s, 1910 w, 1765 w, 1724 s C ₆ H ₆ soln 1960 m, br, 1780 m, 1732 vs		(B) 5.78 s, 5.61 d	1.8
$[(C_5H_5)_2Fe_2(CO)_4]_2DPPA(FeCl_4)_2$	Mull 2058 vs, 2018 vs, 1989 s	381 vs	Paramagnetic	
$[(C_5H_5)_2Fe_2(CO)_4]_2DPPA(FeBr_4)_2$	Mull 2053 vs, 2018 vs, 1980 s	288 vs	Paramagnetic	
$[(C_5H_5)_2Fe_2(CO)_4]_2DPPA(I_3)_2$	Mull 2059 vs, 2021 vs, 1990 m, 1985 m	...	(A) 4.21 d	1.9
$[(C_5H_5)_2Fe_2(CO)_4]_2DPPA(PF_6)_2$	Mull 2058 vs, 2018 vs, 1984 m	...	(A) 4.22 d	1.9
$[(C_5H_5)Fe(CO)Cl]_2DPPA$	Mull 1956 s, 1972 s CHCl ₃ soln 1973 s		(C) 5.47 d	1.9
$[(C_5H_5)Fe(CO)Br]_2DPPA$	Mull 1950 s, 1970 s CHCl ₃ soln 1970 vs		(C) 5.48 d	1.9
$[(C_5H_5)Fe(CO)I]_2DPPA$	Mull 1945 s, 1972 s CHCl ₃ soln 1970 s		(C) 5.48 d	1.9
$[(C_5H_5)Fe(CO)SnCl_3]_2DPPA$	Mull 1983 s		c	
$(C_5H_5)Fe(Br)[P(OCH_3)_3]_2$	(C) 5.68 s	

^a Abbreviations: s, strong; vs, very strong; m, medium; br, broad; w, weak. ^b Measured in benzene-*d*₆ (B), acetone-*d*₆ (A), or chloroform-*d*₁ (C). Abbreviations: s, singlet; d, doublet. ^c Insufficiently soluble.

Recrystallization from boiling acetone-ethanol gave red crystals of the product; mp 171–173°. The filtrate on evaporation and cautious treatment with *n*-heptane and ethanol gave a further yield of the same material. *Anal.* Calcd for $[(C_5H_5)Fe(CO)_2]_2DPPA(FeBr_4)_2$: C, 32.0; H, 2.0; Br, 42.7. Found: C, 32.4; H, 2.1; Br, 43.7.

(c) A reaction similar to that in (b) above using iodine in dichloromethane gave red-brown needles of $[(C_5H_5)Fe(CO)_2]_2DPPA(I_3)_2$; mp 167–169°. *Anal.* Calcd for $[(C_5H_5)Fe(CO)_2]_2DPPA(I_3)_2$: C, 31.8; H, 2.0; I, 50.4. Found: C, 32.2; H, 2.1; I, 49.8.

Reaction of $[(C_5H_5)Fe(CO)_2]_2DPPA(X)_2$ ($X^- = FeCl_4^-, FeBr_4^-, I_3^-$) with KPF_6 .—Acetone solutions of the products from the reactions of (a)–(c) above (0.25 g) were treated with a hot concentrated solution of potassium hexafluorophosphate in water. A brown gelatinous precipitate was formed which was quickly removed by filtration. Slow evaporation of acetone from the solutions using a rotary evaporator afforded bright yellow plates of the hexafluorophosphate salt $[(C_5H_5)Fe(CO)_2]_2DPPA(PF_6)_2$. This was recrystallized from acetone-benzene. The product retained acetone even on pumping *in vacuo* for several hours. A weak band due to $\nu(CO)$ of coordinated acetone appeared at 1810 cm^{-1} in the infrared spectrum of the purified material; mp 245–247°. *Anal.* Calcd for $[(C_5H_5)Fe(CO)_2]_2DPPA(PF_6)_2$: C, 46.3; H, 2.9. Found: C, 46.9; H, 3.2.

Reactions of $(C_5H_5)Fe(CO)_2X$ ($X = Cl, Br, I$) with I.—(a) $(C_5H_5)Fe(CO)_2Br$ (4.0 g) and I (3.5 g) were refluxed in benzene (75 ml) for 2.5 hr. The hot reaction mixture was filtered and the filtrate was taken to dryness. The green product was recrystallized from chloroform-ethanol as green plates; mp 173–174°. *Anal.* Calcd for $[(C_5H_5)Fe(CO)(Br)]_2DPPA$: C, 53.5; H, 3.5; Br, 18.8; mol wt, 851. Found: C, 53.4; H, 3.6; Br, 18.9; mol wt, 844 (osmometric in CH_2Cl_2).

(b) $(C_5H_5)Fe(CO)_2Cl$ and $(C_5H_5)Fe(CO)_2I$ reacted in an analogous manner with I. Great care was necessary in working up $[(C_5H_5)Fe(CO)(Cl)]_2DPPA$ since decomposition occurs even in thoroughly degassed chloroform. $[(C_5H_5)Fe(CO)(Cl)]_2DPPA$ formed as green crystals; mp 155–156°. *Anal.* Calcd for $[(C_5H_5)Fe(CO)(Cl)]_2DPPA$: C, 59.8; H, 3.9; Cl, 9.3. Found: C, 60.7; H, 4.1; Cl, 8.9. $[(C_5H_5)Fe(CO)(I)]_2DPPA$ formed as green plates; mp 163–164°. *Anal.* Calcd for $[(C_5H_5)Fe(CO)(I)]_2DPPA$: C, 48.2; H, 3.2; I, 26.9. Found: C, 47.95; H, 3.4; I, 27.0.

Reaction of $[(C_5H_5)Fe(CO)(Br)]_2DPPA$ with Trimethyl Phosphite.— $[(C_5H_5)Fe(CO)(Br)]_2DPPA$ (1.7 g) and trimethyl phosphite (0.5 g) in benzene (200 ml) were refluxed for 16 hr. The resulting red-brown solution was taken almost to dryness and chromatographed on Florisil. Elution with 2:1 benzene-pentane produced a red-brown band which gave red crystals on cooling. The product was recrystallized from benzene-pentane

and dried *in vacuo*; mp 95–97°. Absorptions due to $\nu(CO)$ and coordinated DPPA were completely absent from an infrared spectrum of this compound. *Anal.* Calcd for $(C_5H_5)Fe(Br)[P(OCH_3)_3]_2$: C, 29.4; H, 5.2. Found: C, 29.5; H, 5.2.

Reaction of $[(C_5H_5)Fe(CO)(Br)]_2DPPA$ with Stannous Chloride.—A methanolic solution of stannous chloride (1.0 g) was added to $[(C_5H_5)Fe(CO)(Br)]_2DPPA$ (1.7 g) in benzene (50 ml). After 6 hr at reflux temperature the solution had changed to a bright orange. Filtration and slow removal of solvent afforded orange needles of the product; mp 137–139° dec. *Anal.* Calcd for $[(C_5H_5)Fe(CO)SnCl_3]_2DPPA$: C, 39.9; H, 2.6. Found: C, 39.5; H, 2.9.

Results and Discussion

$[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$.—The reaction of $(C_5H_5)_2Fe_2(CO)_4$ with DPPA proceeds smoothly in benzene or acetone at room temperature under ultraviolet irradiation to give crystalline $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$. The complex is insoluble in ethanol but can be readily recrystallized from carefully degassed ethanol-benzene mixtures. In the solid state the compound is stable in air for several weeks but solutions in halogenated solvents decompose rapidly over a period of 30 min. The air stability of $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ contrasts sharply with the sensitivity of compounds of the type $(C_5H_5)_2Fe_2(CO)_3L$ ($L = PR_3, P(OR)_3$) recently prepared by Haines and Du Preez.¹⁰ Indeed, although π -cyclopentadienyliron dicarbonyl dimer has been known for many years the synthesis of monosubstituted derivatives of the type $(C_5H_5)_2Fe_2(CO)_3PR_3$ has been hindered by the extreme air sensitivity of these compounds.

The solid-state infrared spectra of $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ in the $\nu(CO)$ region (Table I) consists of two strong and two weak bands and suggests the presence of both terminal and bridging carbonyl groups. Comparison with the mull spectrum of $(C_5H_5)_2Fe_2(CO)_4$ ^{9a} shows that the strong terminal $\nu(CO)$ band of $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ is at a frequency similar to that of the doublet due to terminal C–O stretching in the parent compound. The strong bridging $\nu(CO)$ mode of the DPPA derivative is however at markedly lower frequency than in $(C_5H_5)_2Fe_2(CO)_4$. These results suggest a structure in which one terminal carbonyl

TABLE II
 MÖSSBAUER DATA FOR DERIVATIVES OF $(C_5H_5)_2Fe_2(CO)_4$

Compound	Temp, °K	^{57}Fe spectra, ^a mm/sec		^{119}Sn spectra, ^b mm/sec	
		Isomer shift	Quadrupole splitting	Isomer shift	Quadrupole splitting
$[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$	77	0.53	1.94		
	295	0.45	1.95		
$[(C_5H_5)Fe(CO)Cl]_2DPPA$	77	0.57	1.91		
	295	0.51	1.87		
$[(C_5H_5)Fe(CO)Br]_2DPPA$	77	0.58	1.96		
	295	0.50	1.91		
$[(C_5H_5)Fe(CO)I]_2DPPA$	77	0.56	1.88		
	295	0.49	1.87		
$(C_5H_5)Fe(CO)_2Cl^c$	78	0.47	1.87		
$(C_5H_5)Fe(CO)_2Br^c$	78	0.48	1.87		
$(C_5H_5)Fe(CO)_2I^c$	78	0.46	1.83		
$(C_5H_5)Fe(CO)_2SnCl_3^d$	78	0.48	1.94	1.74	1.77
$[(C_5H_5)Fe(CO)SnCl_3]_2DPPA$	77	0.48	1.79	2.05	1.99
	295	0.40	1.77		
$(C_5H_5)Fe(Br)[P(OCH_3)_3]_2$	77	0.63	1.96		
	295	0.55	1.95		
$\{[(C_5H_5)_2Fe_2(CO)_4]DPPA\}(FeCl_4)_2$	77	0.50 0.35	1.80		
	295	0.28	1.74		
$\{[(C_5H_5)_2Fe_2(CO)_4]DPPA\}(FeBr_4)_2$	77	0.62 0.36	1.79		
	295		
$\{[(C_5H_5)_2Fe_2(CO)_4]DPPA\}(I_3)_2$	77	... 0.36	1.80		
	295	... 0.31	1.79		
$\{[(C_5H_5)_2Fe_2(CO)_4]DPPA\}(PF_6)_2$	77	... 0.35	1.82		
	295	0.28	1.80		
$[(C_5H_5)Fe(CO)_3]PF_6$	77	0.31	1.88		
$[(C_5H_5)Fe(CO)_2]_2SnCl_2^d$	77	...		1.95	2.38

^a Relative to sodium nitroprusside. ^b Relative to barium stannate. ^c Reference 21a. ^d Reference 21b.

group of $(C_5H_5)_2Fe_2(CO)_4$ has been replaced by a phosphorus atom of the diphosphine. This would be expected to have little effect on the remaining terminal carbonyl groups attached to the unsubstituted iron atom but might affect the bridging carbonyls by virtue of increasing the dative π bonding ($Fe(d\pi) \rightarrow C(p\pi^*)$) from the substituted iron atom to the bridging CO groups as a result of replacement of a CO group by a poorer π acceptor. Solution infrared studies were hindered by the insolubility of $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ in hydrocarbon solvents and decomposition in halogenated solvents. Data for benzene solutions (Table I) confirm that a carbonyl-bridged isomer is also present in solution. It should be noted that two bridging $\nu(CO)$ modes are expected for a C_s carbonyl-bridged substitution product of the type $(C_5H_5)_2Fe_2(CO)_3L$. However, for the analogous compounds $(C_5H_5)_2Fe_2(CO)_3L$ ($L = PR_3, P(OR)_3$) Haines and Du Preez found only one bridging $\nu(CO)$ frequency in solutions in cyclohexane with a closely spaced doublet appearing in solid-state spectra. They attributed the latter behavior to different molecular sites in the solids. No resolution of the strong bridging $\nu(CO)$ band of $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ was observed in the solid state. Moreover the structure determination (see later) shows no evidence of different molecular sites. This lends some support to the tentative conclusions of Haines and Du Preez for the solid-state structures of $(C_5H_5)_2Fe_2(CO)_3L$.

The nmr spectrum of $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ in benzene exhibits two π -cyclopentadienyl resonances (Table I)—a singlet (τ 5.78) and a doublet (τ 5.61,

$J_{P-H} = 1.8$ Hz—consistent with the presence of two different iron atoms one of which is coordinated by a phosphorus atom of DPPA. Interestingly the π -cyclopentadienyl resonance to low field is associated with the substituted iron atom. This is an unexpected result since π -cyclopentadienyl resonance chemical shifts usually increase on substitution of carbon monoxide groups by tertiary phosphines.^{6b}

The microanalyses and infrared and nmr spectra are all consistent with a structure in which the diphosphine symmetrically bridges two $(C_5H_5)_2Fe_2(CO)_3$ units. Furthermore the well-established ligand geometry¹¹ and nonchelating properties⁸ of the ligand favor this structure. The absence of any absorption at 2100 cm^{-1} also argues against a monodentate DPPA.^{5,8} Mössbauer spectra of $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ did not however give the expected two quadrupole split resonances for a structure with nonequivalent iron atoms. The data (Table II) show only two lines with quadrupole splittings of 1.95 and 1.94 mm/sec at 295 and 77°K and isomer shifts of 0.45 and 0.53 mm/sec. Moreover the line widths for the two lines are 0.28 and 0.31 mm/sec, at 77°K compared with a line width of 0.26 mm/sec for sodium nitroprusside at 295°K. Thus the appearance of only one quadrupole-split line does not seem to be due to a lack of resolution. Isomer shifts and quadrupole coupling constants are comparable with related parameters for other iron carbonyl complexes.¹² To justify our structural assignment based on infrared and nmr

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(12) (a) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **8**, 95 (1969); (b) R. H. Herber, *Progr. Inorg. Chem.*, **8**, 1 (1967).

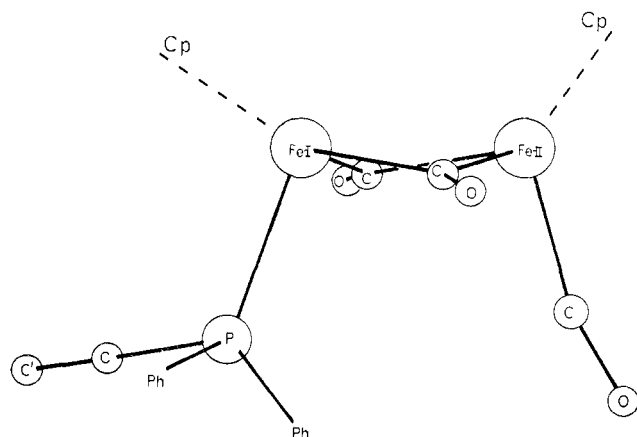


Figure 1.—Idealized structure of half of the $[(\pi\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3]_2\text{-}(\text{C}_6\text{H}_5)_2\text{P}\equiv\text{CP}(\text{C}_6\text{H}_5)_2$ molecule. $\pi\text{-C}_5\text{H}_5$ is represented by Cp.

data and also to shed further light on the anomalous Mössbauer result, an X-ray structural study of $[(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3]_2\text{DPPA}$ was carried out.¹³ The structure of the complex is shown diagrammatically in Figure 1. The molecule consists of two $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3$ units linked by a DPPA molecule situated at a center of symmetry. The $\pi\text{-C}_5\text{H}_5$ groups of each $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3$ system are *cis* to one another with the overall symmetry being C_i . Repulsion between the phenyl rings of DPPA and the adjacent π -cyclopentadienyl groups results in a lengthening of the average Fe-C ($\pi\text{-C}_5\text{H}_5$) distance when compared to other π -cyclopentadienyliron derivatives.¹⁴ This may explain the apparently anomalous π -cyclopentadienyl chemical shifts in the complex.

Apart from splitting of the two strongest bands, the Nujol spectrum of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OC}_6\text{H}_5)_3]$ ¹⁰ closely resembles that of $[(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3]_2\text{DPPA}$. Although Haines and Du Preez¹⁰ could not distinguish between *cis* and *trans* isomers, it now appears, in view of the above structural data, that the triphenyl phosphite complex is also a *cis* isomer in the solid state.

We are now faced with the problem of explaining the nonappearance of two distinct Mössbauer resonances for the nonequivalent iron atoms I and II (Figure 1). Using the concept of partial isomer shifts developed earlier by Herber,^{12b} we have attempted to evaluate the isomer shift for each of the iron atoms I and II. Values of ξ_i the partial shift for a given ligand were taken from the literature while a value of 0.055 mm/sec was estimated as the contribution for DPPA by comparing isomer shifts for known iron carbonyl derivatives with shifts for the DPPA complexes described herein. Calculated parameters for Fe-I and Fe-II are shown in Table III. It is clear that the difference in isomer shift between Fe-I and Fe-II (0.017 mm/sec) is beyond resolution. Furthermore the data illustrate that changes associated with replacement of a CO group by a phosphine are swamped by the large contribution from a $\pi\text{-C}_5\text{H}_5$ group. It should be pointed out that two different resonances would still be observable for Fe-I

(13) Preliminary data have already been published.⁹ Full X-ray results will be reported elsewhere.

(14) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 716 (1969).

TABLE III
CALCULATED MÖSSBAUER PARAMETERS FOR
 $[(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3]_2\text{DPPA}$

Ligand	Iron atom	ξ_i , ^a mm/sec
$\text{CO}_{\text{terminal}}$	II	0.034
$\text{CO}_{\text{bridge}}$	II	0.084
Fe-Fe bond	II	0.008
$\pi\text{-C}_5\text{H}_5$	II	$0.223(5.78 - 4.23) = 0.346^b$
		$\Sigma\xi_i = 0.556$
$\text{CO}_{\text{bridge}}$	I	0.084
Fe-Fe bond	I	0.008
$\pi\text{-C}_5\text{H}_5$	I	$0.223(5.61 - 4.23) = 0.308^b$
DPPA	I	0.055
		$\Sigma\xi_i = 0.539$

^a Partial isomer shift. ^b Calculated from empirical relationship: $\xi_i = 0.223(\tau - 4.23)$.

and Fe-II if there were different electric field gradients at the two sites. Clearly this is not the case and substitution of a terminal CO group by DPPA appears to have little effect on the electronic environment of the metal. It is of interest to note that Cotton and co-workers¹⁵ have also recently pointed out the inadequacies of Mössbauer spectroscopy for molecular structure determination of organoiron compounds containing large π -bonded organic moieties.

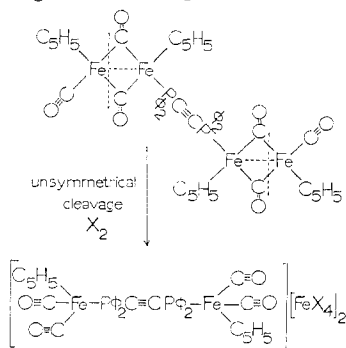
$\{[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2\text{DPPA}\}^{2+}, (\text{X}^-)_2$ ($\text{X}^- = \text{FeCl}_4^-, \text{FeBr}_4^-, \text{I}_3^-, \text{PF}_6^-$).—Recent work¹⁶ has shown that halogenation of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ can proceed *via* symmetric and asymmetric cleavage to give covalent $(\text{C}_5\text{H}_5)\text{-Fe}(\text{CO})_2\text{X}$ and ionic $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_3]\text{X}$. In a similar manner monosubstituted complexes of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ react with iodine to give three products: covalent $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$, covalent $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})\text{I}(\text{L})$, and ionic $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{L}]\text{I}$.¹⁰ Chlorination and bromination of $[(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3]_2\text{DPPA}$ proceed smoothly yielding yellow or red complexes of formula $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4\text{X}_8\text{-}(\text{DPPA})$ ($\text{X} = \text{Cl}, \text{Br}$). The infrared spectra of these complexes are virtually identical in the $\nu(\text{CO})$ region with three bands appearing above 1980 cm^{-1} . Both complexes are extremely paramagnetic and no nmr spectra could be obtained under any conditions. Although the ligand DPPA absorbs only weakly in the far-infrared region,⁸ the chloride complex has a strong symmetrical absorption at 381 cm^{-1} . This strong absorption is characteristic of ν_3 of the tetrahedral ion FeCl_4^- .¹⁷ In the corresponding bromide complex, this band is absent, but the ν_8 mode of FeBr_4^- occurs as a strong band at 288 cm^{-1} . Reactions of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4\text{X}_8(\text{DPPA})$ ($\text{X} = \text{Cl}, \text{Br}$) with sodium hexafluorophosphate afford golden yellow crystals of $\{[(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4]\text{DPPA}\}(\text{PF}_6)_2$. The PF_6^- derivative has an infrared spectrum virtually identical with those of the chloride and bromide complexes in the $\nu(\text{CO})$ region. In the far-infrared spectrum however the bands due to ν_3 of FeCl_4^- and FeBr_4^- are missing. The PF_6^- compound is diamagnetic giving a proton nmr spectrum in acetone-*d*₆ consisting of a complex phenyl proton reso-

(15) F. A. Cotton and W. T. Edwards, *J. Am. Chem. Soc.*, **90**, 5412 (1968), and references therein.

(16) A. J. Carty and A. Efraty, *Can. J. Chem.*, **47**, 2573 (1969).

(17) D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

nance due to DPPA and a doublet π -cyclopentadienyl resonance at low field (τ 4.22 $J_{P-H} = 1.9$ Hz). These results prove conclusively that the chloride and bromide complexes can be formulated as the ionic salts $\{[(C_5H_5)Fe(CO)_2]_2DPPA\}^{2+}$, $(FeX_4^-)_2$ ($X = Cl, Br$) containing a dication. The reaction with iodine proceeded in similar fashion. However the dication in this case was isolated as the diamagnetic I_3^- salt. A trace of the covalent compound $(C_5H_5)Fe(CO)_2I$ was also identified from this reaction by infrared spectroscopy. All four derivatives clearly contain the same dication $\{[(C_5H_5)Fe(CO)_2]_2DPPA\}^{2+}$ and are hence produced by asymmetric cleavage of the parent complex. Several



other features of these compounds are worth noting. The π -cyclopentadienyl resonance chemical shifts are among the lowest recorded for π -cyclopentadienyliron compounds, owing to the presence of a dipositive charge on the cation. The remarkable stability of the $C\equiv C$ bond of the ligand $(C_5H_5)_2PC\equiv CP(C_5H_5)_2$ under conditions which would normally facilitate rapid halogenation of an acetylenic triple bond is also noteworthy. This lends some support to the hypothesis^{8,11} of $Cp(\pi)-Pd(\pi)$ interaction in the ligand although steric factors may also be responsible in part for the low reactivity of the $C\equiv C$ bond. The stability of the system $(C_5H_5)Fe(CO)_2L^+$ to further attack by halogen under vigorous conditions suggests that the as yet unknown cobalt(III) species $(C_5H_5)Co(CO)_2L^{2+}$ and $(C_5H_5)Co(CO)_2L^{2+}$ might well be preparable.

$[(C_5H_5)Fe(CO)X]_2DPPA$ ($X = Cl, Br, I$).—Reactions of $(C_5H_5)Fe(CO)_2X$ ($X = Cl, Br, I$) with DPPA in refluxing benzene under nitrogen yielded the dark green crystalline complexes $[(C_5H_5)Fe(CO)X]_2DPPA$. The complexes are analogous to the products obtained from monodentate tertiary phosphines¹⁸ although molecular weight measurements established the binuclear nature of the products. King¹⁹ has recently obtained a similar binuclear diphosphine complex of $C_5H_5Fe(CO)_2I$ with $(CH_3)_2PCH_2CH_2P(CH_3)_2$. No further replacement of carbonyl groups could be affected by further reaction with DPPA. This contrasts with the behavior of $(C_5H_5)Fe(CO)_2X$ ($X = Cl, Br$) with other chelating diphosphines where both carbonyl groups can be replaced.¹⁹ The results illustrate once again the importance of ligand geometry in dictating the nature of the eventual product.

Interestingly the complexes $[(C_5H_5)Fe(CO)X]_2DPPA$ exhibit almost identical nmr and infrared spectra but have two $\nu(CO)$ bands in the solid-state infrared spectra and only one $\nu(CO)$ band in solution. This suggests nonequivalence of the two CO environments in the lattice. The effect is not however sufficiently marked to affect the Mössbauer spectra of these complexes.

Trimethyl phosphite reacts under reflux with the compound $[(C_5H_5)Fe(CO)Br]_2DPPA$ to replace both carbonyl groups and DPPA yielding red crystals of the nonionic carbonyl-free complex $(C_5H_5)FeBr[P(OCH)_3]_2$ and free DPPA. This compound, which is formally analogous to $(C_5H_5)Fe(CO)_2Br$, is of interest for Mössbauer spectroscopy in view of the similarity of phosphite ligands and carbon monoxide in stabilizing low-valent metal complexes.

Excess $SnCl_2$ reacts with $[(C_5H_5)Fe(CO)Br]_2DPPA$ in the expected manner to afford orange $[(C_5H_5)Fe(CO)SnCl_3]_2DPPA$. In contrast to the derivatives $[(C_5H_5)Fe(CO)X]_2DPPA$ this compound showed only one C—O stretching mode in the infrared spectrum of a Nujol mull. The reaction is thus entirely analogous to the reactions of other cyclopentadienyl metal halides and complexes with $SnCl_2$ in methanol.²⁰

Mössbauer Spectra.—Mössbauer parameters for the compounds examined are given in Table II, together with some data for related compounds.²¹ Compounds of the type $[(C_5H_5)Fe(CO)X]_2DPPA$ ($X = Cl, Br, I$) are analogous to the series $(C_5H_5)Fe(CO)_2X$ except that the DPPA ligand has replaced a carbonyl group. It is of interest therefore to compare their parameters. For the DPPA complexes an increase in both isomer shift and quadrupole splitting is observed compared to the corresponding dicarbonyl halide. This indicates a reduced s-electron density at the iron nucleus and a somewhat greater asymmetry. Although the data for $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ suggest that DPPA has much the same effect as a terminal CO group (see earlier), the data for $[(C_5H_5)Fe(CO)X]_2DPPA$ and $(C_5H_5)_2Fe(CO)_2X$ indicate that CO is a better π acceptor than DPPA. An equimolar mixture of $[(C_5H_5)Fe(CO)X]_2DPPA$ and $(C_5H_5)Fe(CO)_2X$ would be expected to give a spectrum showing two quadrupole split resonances. Closer examination of the data in Table II reveals however that these two resonances would overlap considerably, being separated by less than half of a natural line width, and would almost certainly be irresolvable. The spectrum observed for $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ is thus very reasonable in this light.

Variation in parameters are small for the $[(C_5H_5)Fe(CO)X]_2DPPA$ complexes and are of the same order of magnitude as the error (*i.e.*, ± 0.01 mm/sec). However it is worth noting that the order of increasing "s" electron density ($I > Cl > Br$) is the same as that observed for the $(C_5H_5)Fe(CO)_2X$ series.²¹

Substitution of $SnCl_3^-$ for the bromide in $[(C_5H_5)Fe(CO)Br]_2DPPA$ results in a significant decrease in both Mössbauer parameters whereas $(C_5H_5)Fe(CO)_2SnCl_3$

(18) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).

(19) R. B. King, L. W. Houk, and K. H. Pannell, *ibid.*, **8**, 1042 (1969).

(20) M. J. Mays and S. M. Pearson, *J. Chem. Soc., A*, 136 (1969).

(21) (a) R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, **3**, 101 (1964); (b) R. H. Herber and Y. Gosciny, *ibid.*, **7**, 1293 (1968).

shows a slight increase compared to $(C_5H_5)Fe(CO)_2Br$. By analogy with the series $[(C_5H_5)Fe(CO)X]_2DPPA$ and $(C_5H_5)Fe(CO)_2X$ we would have expected $[(C_5H_5)Fe(CO)SnCl_3]_2DPPA$ to have a higher isomer shift than the corresponding compound $(C_5H_5)Fe(CO)_2SnCl_3$. In these complexes, however, isomer shifts and quadrupole coupling constants will be dependent on the detailed stereochemistry at both tin and phosphorus atoms. Thus interaction of $SnCl_3^-$ and $(C_6H_5)_2P$ might be expected to decrease the Cl-Sn-Cl and C-P-C angles resulting in increased "s" contributions to the Sn-Fe and P-Fe bonds and a consequent smaller isomer shift. Since the X-ray study⁶ of $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ shows considerable steric interaction between the π - C_5H_5 and $(C_6H_5)_2P$ groups, a similar distortion is likely in the tin compound. Moreover the molecular structure of $[(C_5H_5)Fe(CO)_2]_2SnCl_2$ indicates a marked deviation from tetrahedral geometry at the tin atom with a Cl-Sn-Cl angle of $94^\circ 10'$.²² This distortion at the tin atom is reflected in the large quadrupole splitting in the ^{119}Sn Mössbauer spectrum (Table II). Although a direct comparison of parameters for $[(C_5H_5)Fe(CO)_2]_2SnCl_2$ and $[(C_5H_5)Fe(CO)SnCl_3]_2DPPA$ is inadvisable in view of the different symmetry at the tin atom in each case, the data in Table II clearly suggest a larger distortion at the tin atom in $[(C_5H_5)Fe(CO)SnCl_3]_2DPPA$ than in $(C_5H_5)Fe(CO)_2SnCl_3$. Complete X-ray data for this series would be interesting.

Mössbauer parameters for $(C_5H_5)FeBr[P(OCH_3)_3]_2$ illustrate the effect of replacing the two carbonyl groups

(22) J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, **6**, 968 (1967).

of $(C_5H_5)Fe(CO)_2Br$ with $P(OCH_3)_3$. The increase in isomer shift reflects the lower π -bonding ability of the $P(OCH_3)_3$ group compared to CO. A more distorted iron environment and higher quadrupole splitting are also noticeable for the phosphite complex.

The Mössbauer spectrum of $[\{(C_5H_5)Fe(CO)_2\}_2DPPA](FeBr_4)_2$ gives excellent confirmation of the ionic formulation. The spectrum reveals two kinds of iron atom, one with a lower isomer shift and highly distorted environment, the other with a higher shift and symmetric environment. The more symmetric iron atom has the same isomer shift as $FeBr_4^-$.²³ Replacement of $FeBr_4^-$ by $FeCl_4^-$ gave a further single resonance, isomer shift 0.50 mm/sec characteristic of the $FeCl_4^-$ ion (lit.²⁴ value 0.55 mm/sec). Replacement of the anions in $[\{(C_5H_5)Fe(CO)_2\}_2DPPA](FeX_4)_2$ by PF_6^- removed the single unsplit resonances from the spectra. For the iodide $[\{(C_5H_5)Fe(CO)_2\}_2(DPPA)](I_3)_2$ no absorption due to tetrahedral iron(III) was observed. It can be seen that the asymmetric iron site in the $FeCl_4^-$, $FeBr_4^-$, I_3^- , and PF_6^- derivatives remains unaffected by anion changes and the parameters for the cation $[(C_5H_5)Fe(CO)_2]_2DPPA^{2+}$ are very similar to those of the analogous unsubstituted carbonyl derivative $(C_5H_5)Fe(CO)_3^+$.

Acknowledgment.—We acknowledge the support of the National Research Council of Canada.

(23) C. A. Clausen, III, and M. L. Good, "Mössbauer Effect Methodology," Vol. 4, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1968, p 197.

(24) G. M. Bancroft, A. G. Maddock, W. K. Ong, and R. H. Prince, *J. Chem. Soc., A*, 723 (1966).

Notes

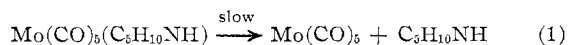
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MCGILL UNIVERSITY, MONTREAL, QUEBEC, CANADA

Kinetics and Mechanism of the Thermal Decomposition Reactions of the *trans*-Bis(triphenylphosphine)manganese Tricarbonyl Halides¹

BY H. K. SPENDJIAN² AND I. S. BUTLER

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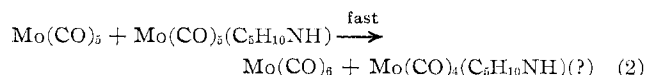
Recently, Darensbourg and Brown reported³ kinetic data for the thermal decomposition of $Mo(CO)_5(C_5H_{10}NH)$ to form $Mo(CO)_6$ and proposed that the decomposition proceeded by the two-step mechanism shown in the equations



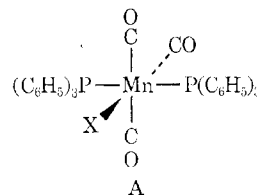
(1) This research was supported by a grant from the National Research Council of Canada.

(2) Holder of a National Research Council of Canada postgraduate scholarship, 1967–present.

(3) D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 1679 (1968).



The net result of the decomposition was the replacement of piperidine by CO. We have been investigating the thermal decomposition reactions of some other metal carbonyl complexes in which a coordinated ligand is substituted by CO. In this note, we present kinetic data for the thermal decomposition reactions of the *trans*- $Mn(CO)_3[P(C_6H_5)_3]_2X$ ($X = Cl, Br, I$) derivatives (A) in *s*-tetrachloroethane at 40.0–



60.0° to give *cis*- $Mn(CO)_4[P(C_6H_5)_3]_2X$ and suggest a possible mechanism for the reactions.

Experimental Section

The *trans*- $Mn(CO)_3[P(C_6H_5)_3]_2X$ complexes were prepared by maintaining a chloroform solution of the appropriate Mn-