

$P(OC_6H_5)_3$] with iodine in dichloromethane was shown by infrared spectroscopy to afford a third product in addition to $\pi-C_5H_5Fe(CO)_2I$ and $\pi-C_5H_5Fe(CO)LI$; these three compounds were formed in approximately equal amounts. When this iodination was performed in benzene, however, the unknown product separated out while trace quantities of $\pi-C_5H_5Fe(CO)_2I$ and $\pi-C_5H_5Fe(CO)LI$ remained in the benzene solution. The precipitate was shown to be ionic and characterization of the tetraphenylborate derivative showed it to be $[\pi-C_5H_5Fe(CO)_2L]B(C_6H_5)_4$. The neutral compounds $\pi-C_5H_5Fe(CO)LI$ were identified by comparing their infrared spectra with the spectra of authentic samples previously synthesized from $\pi-C_5H_5Fe(CO)_2I$.²⁸

The physical and spectroscopic data for the ionic complexes are given in the tables. Conductivity data and spectroscopic evidence show, respectively, these derivatives to be 1:1 electrolytes in acetone and diamagnetic. The infrared spectra of these compounds in solution contain two peaks corresponding to C–O stretching modes; the frequencies decrease with the increase of the over-all (σ – π) donor ability of the phos-

phorus donor ligand as expected. The single cyclopentadienyl proton resonance in the nmr spectra of these ionic compounds is split into a doublet due to phosphorus–hydrogen coupling. The coupling constant could only be measured for the compounds containing the ligands $P(C_2H_5)_3$ and $P(O-i-C_3H_7)_3$.

The formation of both ionic and neutral compounds in the iodination of the monosubstituted derivatives demonstrates that this reaction occurs by at least two mechanistic pathways, one involving a symmetric cleavage and the other an asymmetric cleavage of the dinuclear parent. A similar scheme has been proposed for the halogenation of $[\pi-C_5H_5Fe(CO)_2]_2$ on the basis of the isolation of $[\pi-C_5H_5Fe(CO)_2]X$ and $\pi-C_5H_5Fe(CO)_2X$ (X = halogen) from the reaction mixture.²⁹

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(28) A. L. du Preez, M.S. Thesis, University of Pretoria.

(29) R. J. Haines and A. L. du Preez, *J. Am. Chem. Soc.*, **91**, 769 (1969).

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Five-Coordinate Iron Carbonyl Complexes with Fluorocarbon-Bridged Ligands

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The fluorocarbon-bridged di(tertiary phosphines) f_{fos} and f_6fos react with iron pentacarbonyl to yield the compounds $f_{fos}Fe(CO)_8$, $f_{fos}Fe(CO)_4$, and $f_6fosFe(CO)_3$. A related di(tertiary arsine) gives $f_{fars}Fe(CO)_4$ and $f_{fars}Fe_2(CO)_8$. The $Fe(CO)_8$ compounds have C_{2v} symmetry and the structures are probably based on a distorted trigonal bipyramid with equatorial–equatorial substitution. The ligands act, respectively, as monodentate and bridging groups in the $Fe(CO)_4$ and $Fe_2(CO)_8$ compounds. The Mössbauer spectra of these and related compounds show little variation in isomer shift. However it seems that the Mössbauer quadrupole splittings can be used to distinguish between *cis*- and *trans*-disubstituted derivatives of a trigonal-bipyramidal iron(0) complex. Other spectroscopic data for these compounds are given. In particular the carbonyl infrared spectra show some interesting features.

Tertiary phosphine and arsine derivatives of iron pentacarbonyl of the sorts $R_3EFe(CO)_4$ and $(R_3E)_2Fe(CO)_3$ are well known and have been obtained by a variety of methods.¹ It has been shown^{1c} that the triphenylphosphine derivatives have the trigonal-bipyramidal structure of the parent carbonyl with monosubstitution occurring in an apical position (C_{3v} symmetry with three CO stretching bands) and disubstitution in both apical positions (D_{3h} symmetry with one CO stretching band). Chelating di(tertiary phosphines and arsines) also react with iron carbonyl compounds to yield complexes such as $diarsFe(CO)_3$,

$diphosFe(CO)_3$, and $diphosFe_2(CO)_8$ ^{1d,1e,2} ($diphos$ = 1,2-bis(diphenylphosphino)ethane and $diars$ = 1,2-bis(dimethylarsino)benzene). The $Fe_2(CO)_8$ derivative is a bridged compound. Nothing appears to have been written about the structures of the chelate complexes, although if a trigonal-bipyramidal structure is assumed, it is apparent that the ligand could be coordinated in either an equatorial–equatorial or apical–equatorial manner (Figure 1).

The present paper describes the preparation and possible structures of some new five-coordinate iron carbonyl complexes of the novel fluorocarbon-bridged

ligands $DC=CD(CF_2)_nCF_2$: f_{fos} , $n = 1$, $D = (C_6H_5)_2P$; f_6fos , $n = 2$, $D = (C_6H_5)_2P$; f_{fars} , $n = 1$,

(1) (a) W. Reppe and W. J. Schueckendick, *Ann.*, **560**, 104 (1948); (b) A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.*, **2**, 151 (1963); (c) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960); (d) T. A. Manuel, *Inorg. Chem.*, **2**, 854 (1963); (e) J. Lewis, R. S. Nyholm, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 2825 (1964).

(2) H. Nigam, R. S. Nyholm, and D. V. Ramana Rao, *ibid.*, 1397 (1959).

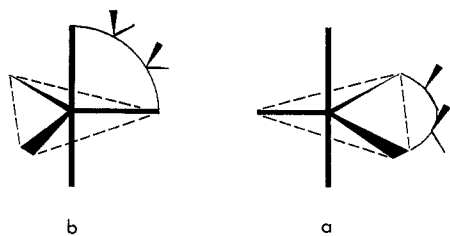


Figure 1.—Possible structures for (chelate)Fe(CO)₅ complexes based on a trigonal bipyramid.

D = (CH₃)₂As. Other complexes of these ligands have been recently reported.³⁻⁵

Experimental Section

The techniques used in this investigation were the same as previously described.³ Melting points are uncorrected and determined on samples sealed in evacuated capillaries. Preparations of the ligands ffos, f₆fos, and ffars have been previously reported.³⁻⁷ The known complexes diphosFe(CO)₃, diphosFe₂(CO)₈, and diarsFe(CO)₃ were prepared by methods similar to those previously described.^{3d,10,8} The preparations of the fluorocarbon complexes described below are selected from a number of related experiments⁸ and give the optimum conditions so far found for obtaining the particular compound. Spectroscopic data for the complexes are listed in Tables I-VI.

(a) **ffosFe(CO)₃**.—Iron pentacarbonyl (4.4 g, 22.4 mmol), ffos (0.4 g, 0.81 mmol), and acetone (10 ml) were sealed under vacuum in a thick-walled Pyrex tube. The tube was irradiated for 112 hr with ultraviolet light (100-W lamp at 20 cm) while shaking. The tube was opened and the volatile contents removed. The remaining solid was recrystallized from ether-petroleum ether (bp 30–60°) to give brown crystals of ffosFe(CO)₃, mp 177–180° (330 mg, 64%). *Anal.* Calcd for C₃₁H₂₀F₄FeO₃P₂: C, 58.8; H, 3.20; F, 12.0; MW, 634. Found: C, 58.8; H, 3.4; F, 12.3; MW, 603 (chloroform⁹). The mother liquors yielded small amounts of a yellow gum, which was identified by its infrared spectrum as ffosFe(CO)₄ (experiment b).

(b) **ffosFe(CO)₄**.—Iron pentacarbonyl (5.8 g, 29.6 mmol) and ffos (1.5 g, 3.04 mmol) were refluxed in benzene (50 ml) under nitrogen for 2 days. The solution was evaporated to yield a sticky oil. This was extracted with petroleum ether; the resulting solution was filtered and concentrated to yield pale yellow crystals of impure ffos (contaminated with ffosFe₂(CO)₈).³ The total amount of slightly impure ffos recovered by this procedure was 0.9 g. The remaining solution was evaporated to yield a yellow-brown oily sample of ffosFe(CO)₄ (550 mg, 72% based on ffos consumed). The infrared spectrum of this sample showed that a very small amount of the previously mentioned ffosFe(CO)₃ was present. Attempted purification by column chromatography on Florisil under nitrogen and eluting with 0–5% benzene-petroleum ether mixtures did not give a clear separation. However, by collecting the latter half of the chromatographic band separately and recrystallizing from cold pentane, bright yellow flakes of ffosFe(CO)₄ could be obtained, mp 129–131°. *Anal.* Calcd for C₃₂H₂₀F₄FeO₄P₂: C, 58.0; H, 3.0; F, 11.5; P, 9.4; MW, 662. Found: C, 57.9; H, 3.2; F, 12.2; P, 10.0; MW, 676 (acetone⁹).

(c) **ffarsFe(CO)₄** and **ffarsFe₂(CO)₈**.—Iron pentacarbonyl (7.25 g, 37.0 mmol), ffars (1.15 g, 3.45 mmol), and petroleum

ether (9 ml) were sealed under vacuum in a thick-walled Pyrex tube. The tube was irradiated for 90 hr with ultraviolet light (100-W lamp at 20 cm) while shaking. The tube was opened and the volatile contents were removed. The residue was dissolved in a small amount of petroleum ether and chromatographed on Florisil. Elution with petroleum ether gave a trace of a yellow band followed by a pale yellow band which on removal of solvent gave a yellow oily sample of ffarsFe(CO)₄ which slowly crystallized, mp 35–36° (990 mg, 57%). *Anal.* Calcd for C₁₂H₁₂F₄As₂FeO₄: C, 28.7; H, 2.4; F, 15.1; O, 12.7; MW, 502. Found: C, 28.6; H, 2.3; F, 15.6; O, 13.0; MW, 490 (acetone⁹).

Elution with 2% diethyl ether–98% petroleum ether gave a deep golden yellow oily sample of ffarsFe₂(CO)₈ which could be crystallized from cold hexane as yellow needles, mp 68–70° (860 mg, 37%). *Anal.* Calcd for C₁₆H₁₂F₄As₂Fe₂O₈: C, 28.7; H, 1.8; F, 11.3; MW, 670. Found: C, 28.8; H, 1.7; F, 11.6; MW, 677 (acetone⁹).

(d) **f₆fosFe(CO)₃**.—Iron pentacarbonyl (1.5 g, 7.6 mmol) and f₆fos (0.15 g, 0.28 mmol) were refluxed in benzene (50 ml) under nitrogen for 26 hr. The solution was evaporated to dryness and the residue was recrystallized from benzene–heptane to give brown crystals¹⁰ of f₆fosFe(CO)₃, mp 211–212° (170 mg, 90%). *Anal.* Calcd for C₃₂H₂₀F₆FeO₃P₂: C, 56.1; H, 2.9; F, 16.7; MW, 684. Found: C, 56.2; H, 2.9; F, 16.4; MW, 657 (chloroform⁹).

Discussion

The complexes described in this paper may be classified into two groups as regards substitution of iron pentacarbonyl (1) LFe(CO)₃ (L = ffos, f₆fos, diphos, diars), and (2) LFe(CO)₄ (L = ffos, ffars) and LFe₂(CO)₈ (L = diars, diphos, ffars).

The infrared spectra of the LFe(CO)₃ complexes are tabulated in Tables I and II. They show three strong

TABLE I
INFRARED BANDS OF NEW COMPLEXES^a

ffarsFe(CO) ₄	ffarsFe ₂ (CO) ₈	ffosFe(CO) ₃	ffosFe(CO) ₄	f ₆ fosFe(CO) ₃
1416 m	1418 m	1480 w	1480 w	1480 w
1332 w, sh		1435 m	1440 m	1475 w, sh
1311 s	1317 s	1367 s	1320 s	1441 m
1277 w	1280 w	1231 m	1225 m	1437 m
1267 m	1267 w	1152 m, sh	1136 m, sh	1331 m
1252 w, sh	1255 w, sh	1135 s	1129 s	1280 m
1225 s	1220 s	1095 m, sh	1095 w	1253 m
		1087 m		1195 m
1145 s	1138 s	1067 w		1158 s
1117 s	1126 s	1025 w		1099 s
914 m	914 m	995 w		1008 m
900 w		850 w		694 s
882 m	879 s	713 w		624 s
861 w	862 w	705 w		593 s
		690 m	694 m	
			679 m	
		630 m	625 s	
621 s	619 s			

^a In cm⁻¹ below 1850 (±3 cm⁻¹). Carbon tetrachloride solution.

CO stretching frequencies (Table II) with a characteristic pattern. The fluorocarbon bridged di(tertiary phosphine) complexes have bands at higher energies than the hydrocarbon compounds perhaps indicating that they are better π acceptors.⁴ It is difficult to

(10) Samples recrystallized from acetone yield green crystals which become brown on prolonged exposure to vacuum or recrystallization from benzene–heptane.

(3) W. R. Cullen, D. A. Harbourn, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **8**, 95 (1969).

(4) W. R. Cullen, C. J. Stewart, and P. S. Dhaliwal, *ibid.*, **6**, 2256 (1967).

(5) W. R. Cullen, D. A. Harbourn, B. V. Liengme, and J. R. Sams, *J. Am. Chem. Soc.*, **90**, 3293 (1968).

(6) W. R. Cullen, P. S. Dhaliwal, and G. E. Styan, *J. Organometal. Chem. (Amsterdam)*, **6**, 633 (1966).

(7) W. R. Cullen, D. S. Dawson, and P. S. Dhaliwal, *Can. J. Chem.*, **45**, 683 (1967).

(8) W. R. Cullen and D. A. Harbourn, submitted for publication.

(9) Osmometric measurement in the solvent indicated.

TABLE II
CARBONYL INFRARED ABSORPTION BANDS^a

$\text{ffosFe}(\text{CO})_3$	$\text{f}_6\text{fosFe}(\text{CO})_3$	$\text{diphosFe}(\text{CO})_3^b$	$\text{diarsFe}(\text{CO})_3^b$	$\text{ffarsFe}(\text{CO})_4$	$\text{ffarsFe}_2(\text{CO})_8$	$\text{ffosFe}(\text{CO})_4$	$\text{Fe}_2(\text{CO})_8\text{diphos}^b$	$\text{Fe}_2(\text{CO})_8\text{diars}$
2008 vs	2007 vs			2058 s	2059 s	2060 s	2058 s	2053 s
		1997 vs	1991 vs		1991 s			
				1987 s		1989 s	1984 s	1981 s
	1950 s			1951 vs, br	1958 vs	1959 vs		
1947 vs	1946 s				1948 vs, sh	1949 vs	1948 vs	1944 vs
		1933 s					1941 vs, sh	
1927 vs	1928 vs		1923 s					
		1913 vs	1909 vs					

^a Cyclohexane solution ($\pm \sim 2 \text{ cm}^{-1}$). ^b Spectra have been reported for these compounds.^{1d,1e,11} For comparison purposes they were rerun on the PE 457 used in this investigation.

TABLE III
NUCLEAR MAGNETIC RESONANCE DATA^a

Complex	Nucleus	Spectrum, ppm	Conditions
$\text{ffarsFe}(\text{CO})_4$	^1H	S, 1.44 (area 1); S, 1.90 (area 1) ^{b,d}	CS_2 soln; ext TMS ref
	^{19}F	Symmetric complex multiplet centered ^e at 106.65	CCl_3F as solvent and reference
$\text{ffarsFe}_2(\text{CO})_8$	^1H	S, 2.00 ^d	As for $\text{ffarsFe}(\text{CO})_4$
	^{19}F	S, 106.75 ^e	As for $\text{ffarsFe}(\text{CO})_4$
$\text{ffosFe}(\text{CO})_3$	^{19}F	S, 109.15	$(\text{CH}_3)_2\text{CO}$ soln; int CCl_3F ref
$\text{ffosFe}(\text{CO})_4$	^1H	Unresolved complex multiplet with two strong peaks, 7.39 and 7.47	$(\text{CH}_3)_2\text{CO}$ soln; int TMS ref
	^{19}F	Complex multiplet centered at 107.8	CHCl_3 soln; int CCl_3F ref
$\text{f}_6\text{fosFe}(\text{CO})_3$	^{19}F	Poorly resolved T, 108.52 ($J \simeq 6$ cps); Poorly resolved QN, 129.22 ($J \simeq 6$ cps)	CHCl_3 soln; int CCl_3F ref
$\text{diphosFe}(\text{CO})_3$	^1H	D, ^f 2.49 ($J \simeq 18$ cps) (area 1); multi- plet, $\simeq 7.5$ (area 4.8)	CS_2 soln; ext TMS ref
$\text{diphosFe}_2(\text{CO})_8$	^1H	D, 2.68 ($J \simeq 2.2$ cps) (area 1); multi- plet with two strong peaks, 7.44 and 7.50 (area 5)	CS_2 solution; int TMS ref
diphos	^1H	T, 2.05 ($J \simeq 4.5$ cps) (area 1); S, 7.28 (area 5.2)	CS_2 soln; ext TMS ref
$\text{diarsFe}(\text{CO})_3$	^1H	S, 1.78 ^e (area 3.1); complex multiplet, 7.77 ^e (area 1)	CS_2 soln; ext TMS ref
$\text{diarsFe}_2(\text{CO})_8$	^1H	S, 1.79 (area 3.2); complex multiplet, 7.75 (area 1)	CS_2 soln; ext TMS ref

^a Key: S, singlet; D, doublet; T, triplet; QN, quintuplet. ^b Relative positions dependent upon solvent. ^c No change 20 to 70°. ^d No change 20 to -60°. ^e No change 20 to -80°. ^f Possibly part of an unresolved multiplet.

account for the slight doublet structure of the 1950- cm^{-1} band of $\text{f}_6\text{fosFe}(\text{CO})_3$. This splitting is absent when the spectrum is run in carbon tetrachloride or carbon disulfide.

The nmr spectra of the $\text{LFe}(\text{CO})_3$ complexes (Table III) indicate that the $\text{Fe}(\text{CO})_3$ moiety is attached to the ligand in such a way as to preserve the original symmetry of the ligand. Thus the ^{19}F spectrum of $\text{ffosFe}(\text{CO})_3$ shows only a single peak with approximately the same chemical shift as that of the uncomplexed ligand.⁷ Similarly the ^{19}F spectrum of $\text{f}_6\text{fosFe}(\text{CO})_3$ shows two regions of absorption (relative area 2:1) as does f_6fos itself.⁸ $\text{diarsFe}(\text{CO})_3$ shows only a singlet in the As-CH_3 region which is unaffected by cooling the sample to -80° . Possible stereochemical arrangements for the molecules are depicted in Figures 1 and 2, where the substituents shown on the chelating group may be regarded as either fluorine atoms or methyl groups.

In view of the nmr results structures 1b, 2a, and 2b must be rejected. Only 1a and 2c are possible.¹¹

According to Reckziegel and Bigorgne,¹² the infrared carbonyl band intensities of compounds of the sort $(\text{chelate})\text{Fe}(\text{CO})_3$ and $\text{D}_2\text{Fe}(\text{CO})_3$ (including the first *cis*-disubstituted derivatives), where D is a monodentate ligand, indicate that considerable distortion of the trigonal-bipyramidal structure must take place. On this basis the structures of the $\text{LFe}(\text{CO})_3$ compounds prepared in this investigation are somewhere in between the extremes of 1a and 2c. [The bite of the ligand would not be large enough to allow 2c as such.]

It is worth noting that during the present investiga-

(11) A referee has pointed out that rapid exchange of apical and equatorial positions could occur in the $\text{LFe}(\text{CO})_3$ complexes. This would not allow us to discard structures 1b, 2a, and 2b. However, since the nmr spectrum of $\text{diarsFe}(\text{CO})_3$ is unaltered on cooling to -80° , exchange seems unlikely.

(12) A. Reckziegel and M. Bigorgne, *Compt. Rend.*, **258**, 4065 (1964).

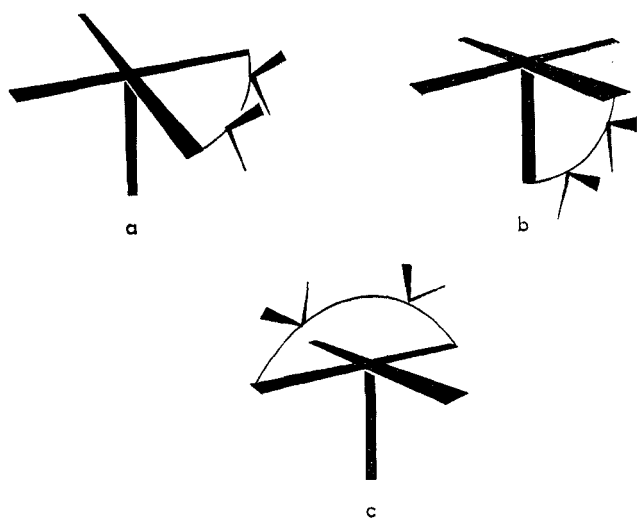
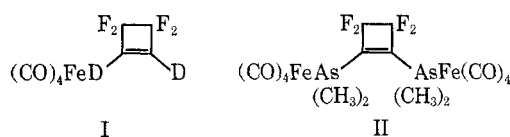


Figure 2.—Possible structures for (chelate) $\text{Fe}(\text{CO})_3$ complexes based on a square pyramid.

tion no evidence for an apical-equatorial substituted derivative, 1b, was found.

A structure similar to that found for butadieneiron tricarbonyl is favored by Bigorgne¹² for diphos $\text{Fe}(\text{CO})_3$. This has C_{3v} local symmetry for the $\text{Fe}(\text{CO})_3$ fragment. However, the band positions reported for the butadiene complex are at much higher wave numbers than those given for diphos $\text{Fe}(\text{CO})_3$.¹² Assuming that the structure of diphos $\text{Fe}(\text{CO})_3$ is no different from that of the other $\text{LFe}(\text{CO})_3$ complexes (*cf.* infrared spectra, Table II), then ligand symmetry in these butadieneiron tricarbonyl type structures could only be preserved by rotation of the ligand as a whole about the C_3 axis. The low-temperature nmr study on diars $\text{Fe}(\text{CO})_3$ indicates that this is unlikely.

The cyclobutenyl $\text{Fe}(\text{CO})_4$ and $\text{Fe}_2(\text{CO})_8$ compounds presumably have the structures indicated in I and II



($\text{D} = (\text{CH}_3)_2\text{As}$ or $(\text{C}_6\text{H}_5)_2\text{P}$) with the $\text{Fe}_2(\text{CO})_8$ derivatives of diars and diphos being similar to II. Numerous examples are known where a di(tertiary arsine or phosphine) has been postulated to bridge two metal carbonyl moieties as in II.^{1d,1e,12,13} Such a structure has been confirmed in the case of diars $[\pi\text{-CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_2]_2$.¹⁴ The ^1H nmr spectrum of $\text{ffarsFe}(\text{CO})_4$ (Table III) shows the expected two singlets due to the inequivalent dimethylarsino groups. The methyl groups are equivalent in $\text{ffarsFe}_2(\text{CO})_8$ and in $\text{diarsFe}_2(\text{CO})_8$ so only a singlet results. The ^{19}F nmr spectrum of $\text{ffarsFe}_2(\text{CO})_8$ consists of only one peak as does that of the uncomplexed ligand. The ^{19}F nmr spectra of $\text{ffosFe}(\text{CO})_4$ and $\text{ffarsFe}(\text{CO})_4$ are as expected, compli-

cated. It is worth noting that in both $\text{ffosFe}(\text{CO})_4$ and $\text{ffarsFe}(\text{CO})_4$ the pattern is in halves, with one half the mirror image of the other. In the case of $\text{ffosFe}(\text{CO})_4$ half of the pattern is such that each line is further split into a doublet. This is presumably a P-F coupling effect.

From the point of view of symmetry about iron the $\text{LFe}(\text{CO})_4$ and $\text{LFe}_2(\text{CO})_8$ complexes may be considered together. The infrared carbonyl spectra of the ffars complexes (Table II) are interesting as the $\text{Fe}(\text{CO})_4$ complex shows a three-band spectrum while the $\text{Fe}_2(\text{CO})_8$ complexes show a four-band spectrum although, as seen in Figure 3, the difference apparently arises

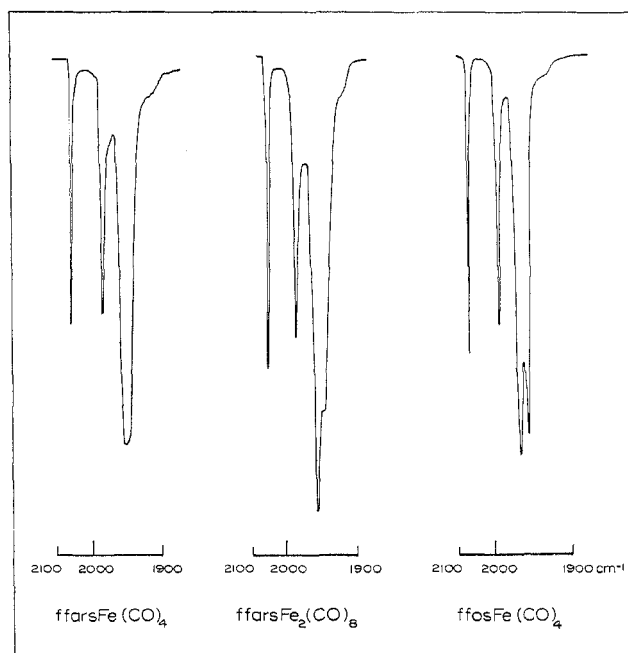


Figure 3.—CO stretching band patterns of $\text{Fe}(\text{CO})_4$ derivatives (cyclohexane solution).

through splitting of a single band. The bands have energies very similar to those reported for $(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})_4$ (2059, 1978, 1938 cm^{-1}).^{1c} The three-band spectrum of the $\text{Fe}(\text{CO})_4$ derivative may be indicative of apical substitution in a trigonal bipyramid^{1c} if we assume all bands present are being resolved. The four-band spectrum of the $\text{Fe}_2(\text{CO})_8$ derivative may suggest equatorial substitution in a trigonal-bipyramidal structure or a basal substitution in a square-pyramidal structure.^{1c} However it is also possible that a four-band spectrum could arise from a structure with an asymmetric substituent. In this case the molecule would have over-all C_s symmetry and the extra band could be regarded as arising from a splitting of the E mode in a C_{3v} spectrum.¹⁵ In view of the similarity of the spectra of $\text{ffarsFe}(\text{CO})_4$ and $\text{ffarsFe}_2(\text{CO})_8$ this latter explanation seems attractive. We believe also that the stereochemistry about the iron atom in both complexes is similar as the Mössbauer spectra (*qv*) of the complexes are essentially the same although whether

(13) E.g., R. J. Mawby, D. Morris, E. M. Thorsteinson, and F. Basolo, *Inorg. Chem.*, **5**, 27 (1966); R. S. Nyholm, S. S. Sandu, and M. H. B. Stiddard, *J. Chem. Soc.*, 5916 (1963); F. Zingales, E. Canziani, and R. Ugo, *Gazz. Chim. Ital.*, **92**, 434, 761 (1962).

(14) M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 395 (1964).

(15) For a description of the analogous C_{4v} case see J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

this is a valid criterion is uncertain. Four-band carbonyl spectra are also noted for $\text{ffarsFe}(\text{CO})_4$ (ffos is a bulkier ligand than ffars) and for $\text{diphosFe}_2(\text{CO})_8$, but $\text{diarsFe}_2(\text{CO})_8$ exhibits a three-band spectrum. It should be borne in mind however that in the $\text{Fe}_2(\text{CO})_8$ derivatives coupling between the $\text{Fe}(\text{CO})_4$ units may well occur. From consideration of band intensities it has been concluded that $\text{DFe}(\text{CO})_4$ derivatives are much distorted from the ideal apically substituted trigonal-bipyramidal structure, with the incoming ligand repelling the three equatorial carbonyl groups below the iron atom.¹² Recently Schumann and Stelzer¹⁶ have reported derivatives of the type $\text{DFe}(\text{CO})_4$ with a four-band carbonyl spectrum. These are claimed to have an equatorially substituted trigonal-bipyramidal structure. It is interesting to note that the pattern of the carbonyl bands is somewhat different from those of the $\text{Fe}(\text{CO})_4$ complexes of ffars and ffos [e.g., $\text{D} = \text{P}(\text{Si}(\text{CH}_3)_3)_3$: 2020, 1946, 1908, 1873 cm^{-1}].

The infrared spectra of all of the complexes (Table I) are similar to those of the appropriate uncomplexed ligand and there is not much change in going from the $\text{Fe}(\text{CO})_4$ to the $\text{Fe}_2(\text{CO})_8$ compound. It is worth noting the absence of any $\text{C}=\text{C}$ stretching bands, a feature which is also lacking in the spectra of the uncomplexed ligands.

The mass spectra of the new compounds are listed in Tables IV and V. Both $\text{ffarsFe}(\text{CO})_4$ and $\text{ffosFe}(\text{CO})_4$ do not show a parent ion, the highest peak corresponding to $\text{LFe}(\text{CO})_3$. This is presumably due to the rapid transition, in the spectrometer, from mono- to bidentate with the loss of one carbonyl group. In some spectra of pure $\text{ffarsFe}(\text{CO})_4$ extremely weak peaks at mass intervals of 28 may be seen up to $\text{ffarsFe}_2(\text{CO})_8$. This is not surprising as pyrolysis of $\text{ffarsFe}(\text{CO})_4$ at 160° for 9 hr produces a good yield of $\text{ffarsFe}_2(\text{CO})_8$. The mass spectrum of $\text{ffarsFe}_2(\text{CO})_8$ also shows $\text{LFe}(\text{CO})_3$ as a very strong peak, the other peaks at 28 mass unit intervals up to $\text{LFe}_2(\text{CO})_7$ being of low intensity. Otherwise the spectra show the features of successive loss of carbonyl groups, loss of fluorine, hydrogen fluoride, and FeF_2 already observed for this type of complex.³

Mössbauer Spectra

The Mössbauer spectra of all of these compounds consist of rather widely split quadrupole doublets. Isomer shifts δ , quadrupole splittings Δ , and line widths Γ (full width at half-maximum of the resonance line), obtained from least-squares fitting of the spectra to Lorentzian line shapes, are given in Table VI. None of the spectra showed any significant asymmetry in either width or intensity of the lines.

At 80°K the isomer shifts span only the relatively narrow range of values $0.20 \pm 0.04 \text{ mm sec}^{-1}$, indicating that in simple pentacoordinate compounds of this type where Fe has essentially the krypton configuration, δ is fairly insensitive to the nature of the ligand which donates electrons. It is interesting to note that the

TABLE IV
MASS SPECTRAL DATA FOR ffars COMPLEXES^b

m/e		Ion
$\text{ffarsFe}(\text{CO})_4$	$\text{ffarsFe}_2(\text{CO})_8$	
(~614) ^a	(~642) ^a	$\text{LFe}_2(\text{CO})_7^+$
(~586) ^a	(~614) ^a	$\text{LFe}_2(\text{CO})_6^+$
(~558) ^a	(~586) ^a	$\text{LFe}_2(\text{CO})_5^+$
(~530) ^a	(~558) ^a	$\text{LFe}_2(\text{CO})_4^+$
(~502) ^a	(~530) ^a	$\text{LFe}_2(\text{CO})_3^+$
(~490) ^a	(~502) ^a	$\text{LFe}_2(\text{CO})_2^+$, $\text{LFe}(\text{CO})_4^+$
474	(~490) ^a	
~461	474	$\text{LFe}(\text{CO})_3^+ \equiv \text{P}^+$
~458	~461	
~454	~458	$(\text{P} - \text{CH}_3)^+$, $(\text{P} - \text{CH}_4)^+$
446	~454	$(\text{P} - \text{F})^+$, $(\text{P} - \text{HF})^+$
	446	$(\text{P} - \text{CO})^+$
	~436	
~434	~434	
~431	~431	$(\text{P} - \text{CO} - \text{CH}_3)^+$
427		$(\text{P} - \text{CO} - \text{F})^+$
418	418	$(\text{P} - 2\text{CO})^+$
	~407	
~403	~402	
399	~399	$(\text{P} - 2\text{CO} - \text{F})^+$
398	~398	$(\text{P} - 2\text{CO} - \text{HF})^+$
390	390	$(\text{P} - 3\text{CO})^+$
	379	
~371	~370	$(\text{P} - 3\text{CO} - \text{F})^+$
	352	
350	350	
	347	
334	334	$(\text{P} - \text{Fe} - 3\text{CO})^+ \equiv \text{L}^+$
~318	~318	$(\text{L} - \text{CH}_3)^+$, $(\text{L} - \text{CH}_4)^+$
	304	
~295	~296	
	281	
	230	
	215	
	210	
	199	$(\text{L} - \text{As}(\text{CH}_3)_3 - \text{CH}_3)^+$
	195	$(\text{L} - \text{As}(\text{CH}_3)_3 - \text{F})^+$
	191	$(\text{L} - \text{As}(\text{CH}_3)_2\text{F} - \text{F})^+$
	180	
	165	
	151	
	113	
	109	
	105	$(\text{As}(\text{CH}_3)_2)^+$
	103	

^a Weak peaks increasing in intensity with temperature of the mass spectral source. ^b Major or assignable peaks (above m/e 150).

isomer shift for stainless steel (relative to sodium nitroprusside) is $0.175 \text{ mm sec}^{-1}$. Here the iron atom presumably has a $(3d^7 4s^1)$ electron configuration, as compared with the dsp^3 -bonded iron configuration $(3d^{10} 4s^2 4p^6)$ in the present compounds. There is thus an increase in both 3d and 4s occupancy. While the increase in 4s density might be expected to decrease δ , this is clearly offset by the increased 3d electron density which shields the nucleus from the 4s electrons, causing the 4s wave function to expand.

Despite these similarities, certain trends are apparent in the isomer shift data. First, the compounds containing the $(\text{CH}_3)_2\text{As}$ group show greater shifts than those containing $(\text{C}_6\text{H}_5)_2\text{P}$, indicating a lower s-electron density at the iron nucleus in the former. Similar

(16) H. Schumann and O. Stelzer, *J. Organometal. Chem.* (Amsterdam), **13**, 25 (1968).

TABLE V
 MASS SPECTRAL DATA FOR f₅os AND f₆os COMPLEXES^a

m/e			Ion
f ₅ os- Fe(CO) ₃	f ₅ os- Fe(CO) ₄	f ₆ os- Fe(CO) ₃	
634	634	684	LFe(CO) ₃ ⁺ ≡ P ⁺
636	606	656	(P - CO) ⁺
		637	(P - CO - F) ⁺
578	578	628	(P - 2CO) ⁺
559	559	609	(P - 2CO - F) ⁺
550	550	600	(P - 3CO) ⁺
531	531	581	(P - 3CO - F) ⁺
	509		
494	494	544	L ⁺ = (P - 3CO - Fe) ⁺
475	475		(L - F) ⁺
456	456	506	(L - 2F) ⁺ ≡ (P - 3CO - FeF ₂) ⁺
	455		(L - F - HF) ⁺
		487	(L - 3F) ⁺
436			(L - 2F - HF) ⁺
		468	(L - 4F) ⁺
417	417		(L - C ₆ H ₅) ⁺ , (L - 3F - HF) ⁺
398	398		(L - C ₆ H ₅ - F) ⁺
	394		
		435	
379	379	429	(L - C ₆ H ₅ - 2F) ⁺
	367		
	336		
	310	360	
	272		(P - 3CO - C ₄ F ₄ - 2C ₆ H ₅) ⁺
251	251	251	
220	220		
219	219		
202	202		
		232	
		231	
185	185		(P(C ₆ H ₅) ₂) ⁺
183	183	183	(P(C ₆ H ₅) ₂ - 2H) ⁺
		153	
152	152		
151	151	151	

^a Major or assignable peaks (above m/e 150).
 TABLE VI
 MÖSSBAUER SPECTRAL PARAMETERS

Compound	Temp, °K	mm sec^{-1}		
		δ^a	Δ	Γ^b
f ₅ osFe(CO) ₃	80	0.200	2.336	0.25
	295	0.132	2.314	0.21
f ₆ osFe(CO) ₃	80	0.197	2.342	0.25
	295	0.130	2.315	0.23
diphosFe(CO) ₃	80	0.185	2.124	0.25
	295	0.118	2.089	0.20
diarsFe(CO) ₃	80	0.227	2.267	0.23
f ₅ osFe(CO) ₄	80	0.188	2.607	0.29
f ₆ osFe(CO) ₄	80	0.207	2.791	0.23
diphosFe ₂ (CO) ₃	80	0.161	2.463	0.28
	295	0.102	2.431	0.27
diarsFe ₂ (CO) ₃	80	0.188	2.681	0.25
f ₆ osFe ₂ (CO) ₃	80	0.207	2.820	0.24

^a Relative to sodium nitroprusside. ^b Full width at half-maximum; average of the two resonance lines.

behavior has been observed¹⁷ for *cis*- and *trans*-[π -C₅H₅(CO)Fe]₂[As(CH₃)₂]₂ and their (C₆H₅)₂P analogs. Greenwood and coworkers¹⁸ have also found that [(C₆H₅)₂P]₂Fe₂(CO)₃ exhibits a larger shift than

[(CH₃)₂P]₂Fe₂(CO)₃ and have suggested that the additional electron-withdrawing power of the phenyl groups reduces the phosphorus-to-metal donation. It therefore seems reasonable to conclude that phosphorus is an appreciably better π acceptor than arsenic and that the principal cause of the differences observed in the δ values between phosphorus- and arsenic-containing compounds is an increase in metal-to-ligand back- π -donation in the former cases.

It can also be seen from Table VI by comparing f₅osFe(CO)₃ with f₅osFe(CO)₄ and LFe(CO)₃ with LFe₂(CO)₃ (L = diphos and diars) that the Fe(CO)₃ complexes have the larger isomer shift, although it is not readily apparent why this should be so.

It is worth noting that the isomer shifts for the Fe(CO)₄ and Fe₂(CO)₃ complexes of f₅ars are identical. One might have anticipated somewhat different donor properties for the ligand depending upon whether or not it is acting as a bridging group. It appears that such is not the case. As mentioned above, the quadrupole splittings for these two compounds are also essentially the same, and it seems likely that the iron atoms have the same stereochemistry in both complexes. On the other hand it is doubtful that the Mössbauer parameters would allow one to distinguish between apical and equatorial substitution in a trigonal-bipyramidal structure (*vide infra*).

Note that each of the LFe₂(CO)₃ complexes shows but a single doublet with no appreciable line broadening, confirming that the two iron atoms are equivalent. This is in contrast with the situation in LFe₂(CO)₆ compounds (L = f₅os, f₆os, f₅ars), where four-line Mössbauer spectra are observed.³

The quadrupole splittings for the Fe(CO)₃ complexes are all smaller than those for the Fe(CO)₄ and Fe₂(CO)₃ complexes, the differences amounting to 10–15%. These results should be contrasted with those of Collins and Pettit¹⁹ for (C₆H₅)₃PFe(CO)₄ and [(C₆H₅)₃P]₂Fe(CO)₃, and the results of Herber, *et al.*,²⁰ for [(CH₃)₂N]₃PFe(CO)₄ and {[(CH₃)₂N]₃P}₂Fe(CO)₃, where in both cases the Fe(CO)₃ compounds show the larger splittings. With these monodentate ligands, the disubstituted derivatives have local D_{3h} symmetry about the iron atom,^{1c} whereas the symmetry for the LFe(CO)₃ complexes reported here can be no higher than C_{2v} (*vide supra*). It is interesting that in the (C₆H₅)₃P and [(CH₃)₂N]₃P derivatives the change from C_{3v} to D_{3h} symmetry increases the quadrupole splitting, while in the f₅os, diphos, and diars complexes the change in symmetry is probably from C_{3v} to C_{2v} with a concomitant decrease in splitting. (We are speaking here only of the local symmetry about the iron atom and not of the overall symmetry of the molecule, since the quadrupole splitting is insensitive to longer range effects.) The fact that an increase in the formal point group symmetry about iron increases rather than decreases the quadrupole splitting warrants some discussion.

(19) R. L. Collins and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2332 (1963); *J. Chem. Phys.*, **39**, 3433 (1963).

(17) R. H. Herber and R. G. Hayter, *J. Am. Chem. Soc.*, **86**, 301 (1964).
 (18) T. C. Gibb, R. Gratrix, N. N. Greenwood, and D. T. Thompson, *J. Chem. Soc., A*, 1663 (1937).

(20) R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, **3**, 101 (1964).

The electric field gradient (*efg*) can be completely specified in terms of $V_{zz} \equiv \partial^2 V / \partial z^2$, the z component of the *efg* tensor, and the asymmetry parameter η , defined by $\eta = (V_{xx} - V_{yy}) / V_{zz}$. For ^{57}Fe , the nuclear spin of the first excited state is $I = 3/2$, and the Hamiltonian for the interaction between the nuclear electric quadrupole moment Q and the *efg* has eigenvalues

$$E_Q = \pm \frac{1}{4} eQ V_{zz} (1 + \eta^2/3)^{1/2}$$

Let us consider first a molecule with either D_{3h} or C_{3v} symmetry and choose the threefold axis as the z direction of the *efg* tensor. Then η vanishes identically and the field gradient is axially symmetric. In this case the splitting of the $I = 3/2$ state is simply $\Delta = 1/2 eQ V_{zz}$, and the magnitude of Δ depends entirely upon V_{zz} . For the triphenylphosphine derivatives studied by Collins and Pettit,¹⁹ $[(C_6H_5)_3P]_2Fe(CO)_3$ with D_{3h} symmetry has $\Delta = 2.76 \text{ mm sec}^{-1}$, while $(C_6H_5)_3PFe(CO)_4$ with C_{3v} symmetry has $\Delta = 2.54 \text{ mm sec}^{-1}$. Thus, substitution at both apical positions *increases* V_{zz} rather than leading to a partial cancellation of effects. It is to be expected, of course, that the actual magnitude of this increase will depend upon the nature of the substituents.

Turning now to the complexes reported here, we can assume for the purpose of the present discussion that to first approximation the local symmetry about Fe in the $LF_2Fe(CO)_4$ and $LF_2Fe(CO)_8$ complexes is again C_{3v} . Note that the *efg* will depend principally on the atoms bonded directly to Fe and that, even if the ligand repels the equatorial carbonyl groups below the iron atom, this will not destroy the threefold axis. Thus, the quadrupole splitting will again be a function of only V_{zz} . If we now

consider forming an $LF_2Fe(CO)_3$ complex, we must have either C_{2v} or C_s symmetry, as shown in Figures 1 and 2. In either case there will be a nonvanishing asymmetry parameter, which removes the axial symmetry, and the quadrupole splitting must be greater than for the C_{3v} case *unless* there is a decrease in V_{zz} . In view of the results for $farsFe(CO)_4$ and $farsFe_2(CO)_8$, which suggest that the splitting is essentially the same for apical substitution whether the ligand acts as a monodentate or bidentate group, we would anticipate that apical-equatorial substitution in the $LF_2Fe(CO)_3$ compounds (structures 1b and 2b) would not decrease V_{zz} by any appreciable extent. Such structures would therefore be expected to show an increase in splitting over that observed for the $LF_2Fe(CO)_4$ or $LF_2Fe_2(CO)_8$ complexes. Since both of the structures which are possible on the basis of the nmr measurements involve only equatorial substitution, we must conclude that this leads to a substantial reduction in V_{zz} as compared with the C_{3v} case.

These considerations suggest that in trigonal-bipyramidal complexes of the type $D_2Fe(CO)_5$ the Mössbauer quadrupole splittings can be used to distinguish between *cis*- and *trans*-disubstituted derivatives, since the latter appear to have significantly larger Δ values. On the other hand the quadrupole splitting is not likely to be sensitive to a change of structure such as between 1a and 2c. It is also doubtful that with $D_2Fe(CO)_4$ complexes one could distinguish between C_{3v} and C_{2v} symmetry on the basis of the Mössbauer spectrum, since both V_{zz} and η will have different values for the two symmetry types.

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The Kinetics of Monomer-Dimer Interconversion of Iron(III)-Ethylenediaminetetraacetate and Related Chelates

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The kinetics of formation and decomposition of the Fe(III) dimers of EDTA, HEDTA, and CyDTA have been determined in aqueous solution by temperature-jump and stopped-flow methods. For the formation of the dimer, designated Fe_2L_2O , from the monomeric species, in labile equilibrium $FeL(OH)$ and $FeL(H_2O)$, $d[Fe_2L_2O]/dt = k_{12}[FeL(OH)]^2 + k_{12}'[FeL(H_2O)][FeL(OH)] - k_{21}[Fe_2L_2O] - k_{21}'[Fe_2L_2O][H^+]$. For the three systems the values of the rate constants at 25° and $I = 1.0 \text{ M}$ with $NaNO_3$ are, respectively: $k_{12} = 6.0 \times 10^2$, 9.0×10^2 , and $90 \text{ M}^{-1} \text{ sec}^{-1}$; $k_{12}' = 2.0 \times 10^4$, 6.0×10^4 , and $\sim 10^2 \text{ M}^{-1} \text{ sec}^{-1}$; $k_{21} = 1.2$, 4.0 , and 9.0 sec^{-1} ; $k_{21}' = 5.0 \times 10^8$, 3.0×10^6 , and $\sim 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. The values are discussed.

There have been a large number of studies of the thermodynamics of polynuclear complex formation in aqueous solution, particularly by Sillén and his school.¹ The investigation of the kinetics of the formation and breakdown of these $-O-$ and $-OH-$ bridged complexes

had lagged behind, mainly because of their rapidity and complexity. This situation however is beginning to change and the kinetics of reactions of bridged hydroxy or oxy species of iron(III),² uranium(VI) and vanadium-

(1) L. G. Sillén, *Quart. Rev. (London)*, **13**, 146 (1959).

(2) H. Wendt, *Z. Elektrochem.*, **66**, 235 (1962); T. J. Conocchioli, R. J. Hamilton, Jr., and N. Sutin, *J. Am. Chem. Soc.*, **87**, 926 (1965).