TABLE IV

CALCULATED SPIN DENSITIES[a]

Position	LVMO HMO	LVMO MHMO	HFMO HMO	HFMO MHMO
		Benzaldimine[b]		
1	0.257	0.291	0.264	0.378
2	0.219	0.207	0.027	−0.070
3	0.106	0.097	0.221	0.267
4	0.111	0.133	0.084	0.066
5	0.015	−0.041	0.045	0.001
6	0.166	0.221	0.229	0.291
		Phenylisonitrile[c]		
1	0.485	0.718	0.238	0.312
2	0.164	0.013	0.128	0.075
3	0.067	0.068	0.164	0.179
4	0.077	0.067	0.107	0.115
5	0.009	−0.029	0.027	−0.028
6	0.112	0.125	0.201	0.261

[a] Spin densities were calculated with a Hückel molecular orbital calculation (HMO) and then spin correlation (MHMO) was introduced through polarizability according to McLachlan ($\lambda = 1.2$): A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960). [b] See structure **7**. [c] See structure **4**.

compared to the salicylaldimine complexes **6**. Nevertheless, an application of MHMO theory requires β-spin delocalization *via* an indirect mechanism in the former and α-spin delocalization for the latter class of compounds. It is clear from the above discussion that it is possible to obtain agreement between theory and experiment for almost any observed shift pattern. The conclusion must be that at present such agreement must be taken *cum grano salis*.

Effect of Coordination Number.—A comparison of the isotropic shift patterns for the four- and five-coordinate complexes containing benzaldimine groups shows a similarity between the two systems with the former exhibiting the larger downfield shifts. The alternation expected for π-spin delocalization is more evident in the five-coordinate complexes, *viz.*, the upfield shift of the 3-H resonance. Table V shows a comparison of the isotropic shifts (normalized to the 4-CH_3) for the present four- and five-coordinate complexes as well as six-coordinate complexes obtained as adducts of benzaldimine with nickel acetylacetonate.[19] A minor effect on the isotropic shift patterns of changes in coordination number is evident, as was found for salicylaldimine systems.[15,16] This minor effect may be indicative of the stereochemistry of the complexes.

TABLE V

ISOTROPIC SHIFT PATTERNS OF BENZALDIMINE PROTONS IN FOUR-, FIVE-, AND SIX-COORDINATE COMPLEXES[a]

Position	Isotropic shifts Four	Isotropic shifts Five	Isotropic shifts Six
2	−4.6	−5.0	−7.7
3	−0.5	+0.2	+2.2
4	−1.8	−1.1	−0.6
4-CH_3	+1.0	+1.0	+1.0

[a] The isotropic shifts are normalized to 4-CH_3 isotropic shifts.

Acknowledgment.—We wish to thank Peter Kollman for assistance with computer calculations.

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(19) R. W. Kluiber and W. DeW. Horrocks, Jr., *Inorg. Chim. Acta*, in press.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, BRITISH COLUMBIA, CANADA

Novel Polynuclear Iron Carbonyl Complexes Containing Phosphorus and Arsenic

BY W. R. CULLEN, D. A. HARBOURNE, B. V. LIENGME, AND J. R. SAMS

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Novel polynuclear iron carbonyl complexes have been isolated from the reactions between the iron carbonyls and the ligands $\mathrm{D}\overline{\mathrm{C{=}CD(CF_2)_nCF_2}}$ ($D = As(CH_3)_2$, $n = 1$, ffars; $D = (C_6H_5)_2P$, $n = 2$, f$_6$fos). The complexes have been found to possess the stoichiometry ffars$Fe_3(CO)_{10}$, ffars$Fe_3(CO)_9$, $As_2(CH_3)_2CH_2Fe_3(CO)_9$, and f$_6fosFe_2(CO)_7$ and their structures have been investigated using various spectroscopic techniques. Some attempt has been made to assign lines in the complicated Mössbauer spectra of ffars$Fe_3(CO)_9$ and $As_2(CH_3)_2CH_2Fe_3(CO)_9$.

Introduction

There has been, in recent times, considerable interest in the polynuclear metal carbonyl species from the point of view of structure, stability of metal–metal bonds, and carbonyl displacement.[1] In most cases replacement of carbonyls has led to a degradation of the metal atom arrangement although some ligands have been able to replace carbonyl groups and leave the rest of the molecule intact. The examination of the features and stabilities of these complexes so formed is not only of intrinsic interest but can be valuable in obtaining information about the parent compound.

In the case of the group VIII carbonyls of iron, ruthenium, and osmium the iron–iron bond is weak[2] and at the time this work started only one derivative of

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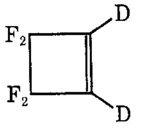
(1) F. Calderazzo, R. Ercoli, and G. Natta in "Organic Syntheses *Via* Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Interscience Publishers, New York, N. Y., 1968, pp 1–272.

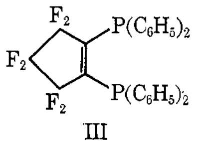
(2) M. I. Bruce and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, **7**, 427 (1968).

$Fe_3(CO)_{12}$ involving a ligand containing a group V donor atom was known. This is the compound $(C_6H_5)_3PFe_3(CO)_{11}$.[3] The X-ray-determined[4] structure of the compound showed it to have two different molecules in the unit cell. In one case the triphenylphosphine had replaced a terminal carbonyl group from the unique iron atom A of $Fe_3(CO)_{12}$ (I) (Figure 1)[5] and in the other a terminal carbonyl group from one of the two equivalent iron atoms B had been replaced.

In the course of a systematic study of the reactions of the versatile fluorocarbon-bridged ligands ffars (IIa), ffos (IIb), and $f_6$fos (III)[6-8] with the iron carbonyls we



IIa, D = $As(CH_3)_2$
IIb, D = $P(C_6H_5)_2$

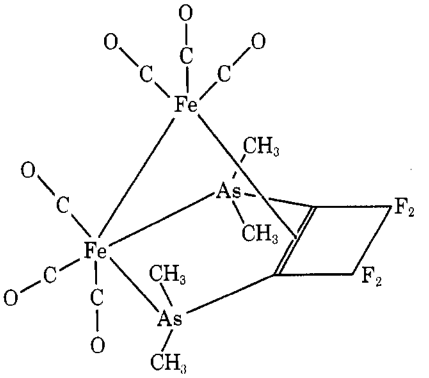


III

have been able to isolate several interesting substituted polynuclear iron carbonyl complexes. A preliminary report of the first of these, ffars$Fe_3(CO)_{10}$, one of the compounds to be discussed in this present paper, has been made.[9]

The fluorocarbon-bridged ligands also give a number of simple five-coordinate derivatives[7] and compounds such as ffars$Fe_2(CO)_6$[6] which has the structure IV,[10] where the ligand acts as a tridentate group. However the diiron fragment in IV lacks the bridging carbonyl groups of $Fe_2(CO)_9$.

In the case of the carbonyl-bridged dimer $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ substitution of one carbonyl group by a monodentate ligand and two carbonyl groups, one from each iron, by a di(tertiary phosphine) seems to occur with preservation of the bridged-carbonyl structure.[11,12]



IV

The present paper also describes two further complexes which may be obtained by allowing ffars to react with $Fe_3(CO)_{12}$ or merely by refluxing a solution of ffars$Fe_3(CO)_{10}$ in cyclohexane. These complexes are both triiron derivatives although neither has the $Fe_3(CO)_{12}$ skeleton and one no longer has the cyclobutene ring present. Complexes analogous to the three triiron derivatives mentioned above have not been obtained from the related phosphorus ligands ffos and $f_6$fos. However, $f_6$fos forms a unique complex which has the formula $f_6$fos$Fe_2(CO)_7$ and may be a precursor to $f_6$fos$Fe_2(CO)_6$.[6]

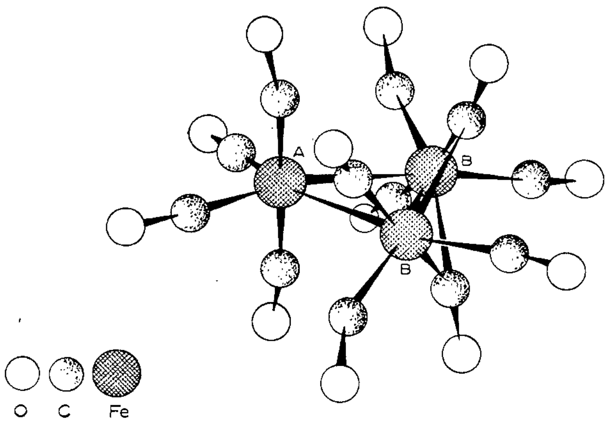


Figure 1.—Structure of $Fe_3(CO)_{12}$.

Recently Pollick and Wojcicki[13] have prepared the compounds $Fe_3(CO)_{11}P(OCH_3)_3$, $Fe_3(CO)_{10}[P(OCH_3)_3]_2$, and $Fe_3(CO)_9[P(OCH_3)_3]_3$ which appear to retain the iron triangle and bridging carbonyl groups of $Fe_3(CO)_{12}$.

Experimental Section

The experimental details given here have been selected from a number of related experiments and describe the conditions that have been found to result in the highest yields of the desired compounds. All chromatography was carried out under a nitrogen atmosphere using nitrogen-saturated solvents. The petroleum ether mentioned below is the 30–60° fraction. Melting points were determined in evacuated capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 457 instrument, mass spectra on an AEI MS-9 spectrometer, and nmr spectra on Varian A-60 and HA-100 spectrometers. Chemical shifts are given in ppm upfield from internal CCl_3F (^{19}F spectra) and downfield from internal TMS (^1H spectra). The Mössbauer spectrometer and attendant experimental details have been described previously.[6]

(1) **Preparation of ffars$Fe_3(CO)_{10}$.**—Triiron dodecacarbonyl (1.9 g, 3.8 mmol) and ffars (1.0 g, 3.0 mmol) were sealed under vacuum with acetone (20 ml) in a thick-walled Pyrex tube. The tube was irradiated with ultraviolet light for 110 hr. The tube was opened and the solution was filtered and evaporated to dryness. The residue was extracted with petroleum ether (to remove ffars$Fe(CO)_4$ and ffars$Fe_2(CO)_8$[7,8]) and then with acetone (*ca.* 10 ml). Some ffars$Fe_2(CO)_6$ may remain in the residue. The acetone solution was reduced in volume and chromatographed on Florisil. Petroleum ether elutes $Fe_3(CO)_{12}$, and diethyl ether–petroleum ether mixtures up to 50% diethyl ether elute ffars$Fe_3(CO)_{10}$ as a gray-green band (ffars$Fe_2(CO)_6$ may contaminate the tail of this band). The compound was recrystallized from diethyl ether–petroleum ether (0.16 g, 7%); mp ~160° dec.

(2) **Preparation of ffars$Fe_3(CO)_9$.**—Triiron dodecacarbonyl (3.5 g, 7.0 mmol) and ffars (1.3 g, 3.9 mmol) were refluxed together in cyclohexane (50 ml) for 5.5 hr. The cyclohexane was removed. The residue was taken up in a small volume of ben-

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[4] D. H. Dahm and R. A. Jacobson, *J. Amer. Chem. Soc.*, **90**, 5106 (1968).

[5] C. H. Wei and L. F. Dahl, *ibid.*, **91**, 1351 (1969).

[6] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **8**, 95 (1969).

[7] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *ibid.*, **8**, 1464 (1969).

[8] W. R. Cullen and D. A. Harbourne, unpublished results.

[9] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *J. Amer. Chem. Soc.*, **90**, 3293 (1968).

[10] F. W. B. Einstein and J. Trotter, *J. Chem. Soc., A*, 824 (1967).

[11] R. J. Haines and A. L. du Preez, *Chem. Commun.*, 1513 (1968).

[12] R. J. Haines, A. L. du Preez, and J. T. W. Wittman, *ibid.*, 611 (1968).

[13] P. J. Pollick and A. Wojcicki, *J. Organometal. Chem.*, **14**, 469 (1968).

TABLE I

ANALYTICAL DATA FOR NEW COMPLEXES

Complex	Element	Analytical figures, %	
		Calcd	Found
ffarsFe$_3$(CO)$_{10}$	C	27.62	27.85
	H	1.54	1.85
	F	9.73	9.62
ffarsFe$_3$(CO)$_9$	C	27.06	27.25
	H	1.58	1.76
	F	10.09	10.18
	As	19.88	19.89
	Fe	22.24	22.15
As$_2$(CH$_3$)$_2$CH$_2$Fe$_3$(CO)$_9$	C	23.47	23.63
	H	1.30	1.58
	F	0.00	0.00
		(mol wt 613.6644)	(mol wt 613.6581[b])
f$_6$fosFe$_2$(CO)$_7$	C	50.75	50.77
	H	2.35	2.36
	F	13.38	13.89
	P	7.28	7.40
	Fe	13.14	13.05
	O	13.15	13.46[a]
		(mol wt 852)	(mol wt 825[c])

[a] Average value. [b] Mass spectrometric determination. [c] Osmometric determination in acetone.

TABLE II

NMR DATA

Complex	^{1}H	^{19}F
ffarsFe$_3$(CO)$_{10}$ (acetone-d_6 soln)	Singlet 1.97, from 20 to −30°	Singlet, 108.8
ffarsFe$_3$(CO)$_9$ (chloroform soln)	4 singlets, 1.05, 1.56 1.70, 2.15 (areas 1:1:1:1)	8 poorly resolved resonances each showing four lines 93.6, 95.7, 99.1, 101.2, 101.8, 104.0, 105.2, 107.6
As$_2$(CH$_3$)$_2$CH$_2$Fe$_3$(CO)$_9$ (acetone-d_6 soln)	2 singlets, 3.26 (area 3), 2.34 (area 3), and an AB quartet with doublets (J = 2.1 Hz) centered at 1.76 (area 1) and 2.42 (area 1)	
f$_6$fosFe$_2$(CO)$_7$ (acetone soln)		12 poorly resolved resonances seen as 3 AB quartets: (a) 2 doublets (J = 264 Hz) centered at 99.4 (area 1) and 110.9 (area 1); (b) 2 doublets (J = 272 Hz) centered at 106.8 (area 1) and 111.4 (area 1); (c) 2 doublets (J = 238 Hz) centered at 124.4 (area 1) and 128.6 (area 1)

TABLE III

INFRARED CARBONYL BANDS OF NEW COMPLEXES[a]

ffarsFe$_3$(CO)$_{10}$	ffarsFe$_3$(CO)$_9$	As$_2$(CH$_3$)$_2$-CH$_2$Fe$_3$(CO)$_9$	f$_6$fosFe$_2$(CO)$_7$
2071 s	2074 s	2066 w	2050 s
2003 vs	2042 vs	2039 vs	1998 vs
1973 vw, br, sh	2021 vs	2014 vs	1984 m
	2008 m	2000 s	1977 s
~1803 vw, br[b]	1999 s	1992 s	1946 m
~1743 vw, br[b]	1988 s	1982 m	
	1980 m	1968 w	
	1963 w	1957 w	

[a] Cyclohexane solution, ±~3 cm^{-1}. [b] Bridging carbonyl bands at 1801 and 1753 cm^{-1} from KBr disk.

TABLE IV

INFRARED SPECTRA OF NEW COMPLEXES

ffarsFe$_3$(CO)$_{10}$		ffarsFe$_3$-(CO)$_9$[b]	As$_2$(CH$_3$)$_2$CH$_2$-Fe$_3$(CO)$_9$[a]	f$_6$fosFe$_2$-(CO)$_7$[b]
a	b			
				1480 w
		1416 w		1452 s
1413 w		1340 w		1434 m
1328 w, sh		1318 m		1326 m
1308 s	1309 m	1266 w	1251 vw	1270 m, sh
1275 w		1212 m	977 vw	1250 m, br
1263 w		1118 w, sh	948 vw	1200 m, sh
1225 m	1218 s	1106 m	840 vw, sh	1195 m
1136 s		1093 m	825 vw	1172 m
1116 s	1122 m	898 w	606 m	1152 s
910 m	910 w	857 w	585 m	1102 m
882 m	880 w	669 w	565 m	1024 w
806 m		603 m	512 w	1000 m
800 w, sh		587 m	487 vw	925 w
694 w			475 vw, sh	893 m
598 s			450 vw	841 w
512 s			400 vw	690 m
317 w				652 m
				615 m
				595 m
				580 m

[a] KBr disk, ±5 cm^{-1}. [b] CCl$_4$ solution, ±5 cm^{-1}.

zene and chromatographed on Florisil. After eluting the initial bands (other complexes[6-8]) with 2% diethyl ether–98% petroleum ether, a deep red-purple band of the compound was eluted with 2–5% diethyl ether–98–95% petroleum ether. This was rechromatographed and/or recrystallized from petroleum ether–diethyl ether to give pure ffarsFe$_3$(CO)$_9$ (2.65 g, 90%); mp ~150° dec.

(3) **Preparation of As$_2$(CH$_3$)$_2$CH$_2$Fe$_3$(CO)$_9$.**—ffarsFe$_3$(CO)$_9$ (expt 2) (2.5 g, 3.3 mmol) was refluxed in cyclohexane (100 ml) for 6 hr. The solution was reduced to small volume and chromatographed on Florisil. Elution with petroleum ether afforded (after elution of other trace products) a red-brown band of the compound. The product was recrystallized from cold petroleum ether under nitrogen (1.1 g, 54%); mp ~199° dec. Some unchanged ffarsFe$_3$(CO)$_9$ may be recovered from the column.

(4) **Preparation of f$_6$fosFe$_2$(CO)$_7$.**—Triiron dodecacarbonyl (6.0 g, 12.0 mmol) and f$_6$fos (1.6 g, 2.9 mmol) were refluxed in cyclohexane (50 ml) for 5 hr. The solution was reduced to small volume and chromatographed on Florisil. Elution with 98% petroleum ether–2% diethyl ether yielded a red-orange band of the complex followed by further bands. The product was recrystallized from diethyl ether–petroleum ether (0.9 g, 36%); mp 168–169°.

Results and Discussion

Analytical and spectroscopic data for the new complexes are given in Tables I–VII and in Figures 3–5.

The structure of ffarsFe$_3$(CO)$_{10}$ (V), which is prepared by an ultraviolet light induced reaction between ffars (IIa) and Fe$_3$(CO)$_{12}$ (I), was deduced from analytical, mass spectral, infrared, nmr, and Mössbauer data. The mass spectrum of V can be interpreted in terms of a stepwise loss of ten carbonyl groups. The infrared spectrum in the carbonyl region is very close to that reported for (C$_6$H$_5$)$_3$PFe$_3$(CO)$_{11}$.[3] The presence of only three bands at 2071 (s), 2003 (vs), and 1973 cm^{-1} (vw, br, sh) (C$_6$H$_{12}$ solution) indicates a symmetrical structure. Weak bridging carbonyl bands are present at 1803 and 1743 cm^{-1}. Their intensity is greater in a KBr disk. Both the ^{1}H and ^{19}F nmr spectra show only one absorption; thus the ligand is bonded symmetrically to the rest of the molecule and is either planar or is flexing rapidly about the As···As axis. The ^{1}H nmr peak broadens only slightly on cooling the sample (−30°); hence the ligand is probably planar.

All these data are consistent with structure V, but the most convincing evidence comes from a comparison of

TABLE V
MASS SPECTRAL DATA[a]

m/e	Ion
	$ffarsFe_3(CO)_{10}$
782	$(ffarsFe_3(CO)_{10})^+ \equiv P^+$
754	$(P - CO)^+$
726	$(P - 2CO)^+$
707	$(P - 2CO - F)^+$
698	$(P - 3CO)^+$
688	$(P - 2CO - 2F)^+$
679	$(P - 3CO - F)^+$
670	$(P - 4CO)^+$
660	$(P - 3CO - 2F)^+$
651	$(P - 4CO - F)^+$, $(P - FeF - 2CO)^+$
642	$(P - 5CO)^+$
632	$(P - 4CO - 2F)^+$, $(P - FeF_2 - 2CO)^+$
623	$(P - 5CO - F)^+$, $(P - FeF - 3CO)^+$
614	$(P - 6CO)^+$, $(LFe_2(CO)_6)^+$
604	$(P - 5CO - 2F)^+$, $(P - FeF_2 - 3CO)^+$
595	$(P - 6CO - F)^+$, $(P - FeF - 4CO)^+$
586	$(P - 7CO)^+$, $(LFe_2(CO)_5)^+$
576	$(P - 6CO - F_2)^+$, $(P - FeF_2 - 4CO)^+$
567	$(P - 7CO - F)^+$, $(P - FeF - 5CO)^+$
558	$(P - 8CO)^+$, $(LFe_2(CO)_4)^+$
548	$(P - 7CO - F_2)^+$, $(P - FeF_2 - 5CO)^+$
539	$(P - 8CO - F)^+$, $(P - FeF - 6CO)^+$
530	$(P - 9CO)^+$, $(LFe_2(CO)_3)^+$
520	$(P - 8CO - 2F)^+$, $(P - FeF_2 - 6CO)^+$
511	$(P - 9CO - F)^+$, $(P - FeF - 7CO)^+$
502	$(P - 10CO)^+ \equiv (LFe_3)^+$, $(LFe_2(CO)_2)^+$
492	$(P - 9CO - 2F)^+$, $(P - FeF_2 - 7CO)^+$
474	$(LFeCO)^+$
464	$(P - 10CO - 2F)^+$, $(P - FeF_2 - 8CO)^+$
446	$(LFe_2)^+$
436	$(P - FeF_2 - 9CO)^+$, $(P - FeF_2 - Fe - 7CO)^+$
418	$(LFeCO)^+$
408	$(P - FeF_2 - 10CO)^+$, $(P - FeF_2 - Fe - 8CO)^+$
352	$(LFe - F_2)^+$
334	$(L)^+ \equiv (ffars)^+$
319	$(L - CH_3)^+$
195	$(L - As(CH_3)_3F)^+$
105	$(As(CH_3)_2)^+$
	$ffarsFe_3(CO)_9$
$\sim782^b$	$(LFe_3(CO)_{10})^+$?
$\sim654^b$	$(ffarsFe_3(CO)_9{}^+ \equiv P^+$
726	$(P - CO)^+$
698	$(P - 2CO)^+$
670	$(P - 3CO)^+$
642	$(P - 4CO)^+$
614	$(P - 5CO)^+$, $(P - Fe - 3CO)^+$
595	$(P - 5CO - F)^+$, $(P - FeF - 3CO)^+$
585	$(P - 6CO)^+$, $(P - Fe - 4CO)^+$
576	$(P - 5CO - 2F)^+$, $(P - FeF_2 - 3CO)^+$
558	$(P - 7CO)^+$, $(P - Fe - 5CO)^+$
548	$(P - 6CO - 2F)^+$, $(P - FeF_2 - 4CO)^+$
530	$(P - 8CO)^+$, $(P - Fe - 6CO)^+$
520	$(P - 7CO - 2F)^+$, $(P - FeF_2 - 5CO)^+$
502	$(P - 9CO)^+$ $(LFe_3)^+$
492	$(P - 8CO - 2F)^+$, $(P - FeF_2 - 6CO)^+$
490	$(P - 8CO - 2HF)^+$, $(P - Fe - 6CO - 2HF)^+$
486	$(LFe_3 - CH_4)^+$, $(LFe_2(CO)_2 - CH_4)^+$
482	
474	$(P - Fe - 8CO)^+$, $(P - 2Fe - 6CO)^+$
464	$(P - 9CO - 2F)^+$, $(P - FeF_2 - 7CO)^+$
446	$(LFe_2)^+$, $(P - 2Fe - 7CO)^+$
	$ffarsFe_3(CO_9)$ (*Continued*)
436	$(P - FeF_2 - 8CO)^+$, $(P - FeF_2 - Fe - 6CO)^+$
432	
430	$(LFe_2 - CH_4)^+$, $(LFe(CO)_2 - CH_4)^+$
418	$(LFeCO)^+$
408	$(LFe_2 - F_2)^+$, $(LFe_3 - FeF_2)^+$
~390	$(LFe)^+$
~379	$(LFeCO - 2F)^+$? $(Fe_3As_2(CH_3)_4)^+$?
~362	$(Fe_3As_2(CH_3)_3)^+$?
~353	$(LFe - 2F)^+$?
332	$(Fe_3As_2CH_3)^+$?
317	$(LFe - 3F - 3H_4)^+$ or equivalent, $(Fe_3As_2)^+$?
262	$(Fe_2As_2)^+$, $(Fe(CO)_2As_2)^+$
258	
243	$(Fe_3As)^+$, $(Fe_2(CO)_2(As)^+$
219	
205	
195	
153	
149	
125	
123	
113	
112	
111	
109	
105	$(As(CH_3)_2)^+$
	$As_2(CH_3)_2CH_2Fe_3(CO)_9$
614	$(As_2(CH_3)_2CH_2Fe_3(CO)_9)^+ \equiv P^+$
600	$(P - CH_2)^+$
586	$(P - CO)^+$
572	$(P - CO - CH_2)^+$
558	$(P - 2CO)^+$
544	$(P - 2CO - CH_2)^+$
530	$(P - 3CO)^+$
516	$(P - 3CO - CH_2)^+$
502	$P - 4CO$
486	$(P - 4CO - CH_4)^+$
474	$(P - 5CO)^+$, $(P - Fe - 3CO)^+$
458	$(P - 5CO - CH_4)^+$, $(P - Fe - 3CO - CH_4)^+$
446	$(P - 6CO)^+$, $(P - Fe - 4CO)^+$
430	$(P - 6CO - CH_4)^+$, $(P - Fe - 4CO - CH_4)^+$
418	$(P - 7CO)^+$, $(P - Fe - 5CO)^+$
402	$(P - 7CO - CH_4)^+$, $(P - Fe - 5CO - CH_4)^+$
390	$(P - 8CO)^+$, $(P - Fe - 6CO)^+$
362	$(P - 9CO)^+$, $(P - Fe - 7CO)^+$
~333	$(Fe_3As_2(CH_3)^+$, $(Fe_3As_2CH_2)^+$?
~329	
~317	$(Fe_3As_2)^+$?
~315	$(P - 8CO - As)^+$, $(P - Fe - 6CO - As)^+$
287	$(P - 9CO - As)^+$, $(P - Fe - 7CO - As)$
274	
263	$(FeCOAs_2CH_3CH_2)^+$
262	$(Fe_2As_2)^+$, $(Fe(CO)_2As_2)^+$
243	$(Fe_3As)^+$, $(Fe_2(CO)_2As)^+$
201	
200	
189	
188	$(FeCOAsCH_3CH_2)^+$?
120	
105	$(As(CH_3)_2)^+$

[a] Major or assignable peaks above m/e 150. [b] Very weak peaks.

its ^{57}Fe Mössbauer spectrum with that of $Fe_3(CO)_{12}$, which has been reported[6,14,15] to consist of three lines of nearly equal intensity. We have now resolved the quadrupole splitting of the central line in the spectrum

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(15) N. E. Erickson and A. W. Fairhall, *ibid.*, **4**, 1320 (1965).

TABLE VI

ISOMER SHIFTS δ, QUADRUPOLE SPLITTINGS Δ, AND LINE WIDTHS Γ(FWHM), FOR IRON CARBONYL COMPLEXES

Compound	Temp, °K	$\delta^{a,b}$	Δ^a	Γ^a	Iron atom[c]
$Fe_3(CO)_{12}$	80	0.29	0.12	0.29	A
		0.37	1.13	0.27	B
	295	0.24	0.20	0.29	A
		0.29	0.97	0.28	B
ffars$Fe_3(CO)_{10}$	80	0.27	0.14	0.23	A
		0.42	1.52	0.24	B
	295	0.22	*d*	0.36	A
		0.34	1.42	0.21	B
$f_6$fos$Fe_2(CO)_7$	80	0.20	0.17	0.25	A
		0.32	1.55	0.23	B
	295	0.13	*d*	0.36	A
		0.25	1.53	0.23	B
$f_6$fos$Fe_2(CO)_6$[e]	80	0.22	0.65	0.23	A
		0.32	1.19	0.23	B
	295	0.16	0.65	0.23	A
		0.26	1.18	0.23	B

[a] In mm sec^{-1}, ±0.01 mm sec^{-1}. [b] Relative to sodium nitroprusside. [c] See appropriate diagram. [d] Splitting not resolved. [e] Reference 6.

TABLE VII

MÖSSBAUER DATA[a] FOR ffars$Fe_3(CO)_9$ AT 80°K

	1	2	3	4	5
1	−0.28	0.33	0.45	0.68	**1.00**
2	−0.11	0.05	0.12	0.34	**0.67**
3	−0.05	0.11	0.17	**0.23**	0.55
4	0.06	0.23	**0.29**	0.40	0.33
5	**0.22**	**0.39**	0.45	0.56	0.72
Γ^b	0.27	0.28	0.23	0.21	0.29
AF[c]	0.186	0.192	0.137	0.135	0.350

[a] In mm sec^{-1}, ±0.01 mm sec^{-1}; relative to sodium nitroprusside. [b] Full width at half-maximum. [c] Area fraction contained in each line.

of $Fe_3(CO)_{12}$, which is shown in Figure 3a and b by computer-fitting to Lorentzian line shapes. This very small splitting, which is near the limit of resolution, arises from the single octahedrally coordinated iron atom in I (Fe^A), and the outer lines constitute a quadrupole doublet arising from the two equivalent iron atoms (Fe^B) connected by bridging carbonyl groups in the triangular structure. The exact magnitudes of the quadrupole splittings for the inner doublet are very sensitive to such effects as instrumental broadening and are therefore subject to a larger error than the other values reported here.[16] For a Δ value of 0.20 mm sec^{-1} or less, the experimental uncertainty is about ±0.04 mm sec^{-1}. The uncertainty was determined by adding to the calibration errors the uncertainty in reproducibility.

Replacement of two carbonyl groups by the ffars ligand leaves the central doublet virtually unaltered both in splitting and in position, but markedly increases the splitting of the outer lines and shifts their center of gravity to higher velocity (Figure 3 and Table VI). It is thus clear that the ligand is attached symmetrically to the two equivalent iron atoms (so that they remain equivalent) rather than bonded to the third, nonequivalent iron atom. This structure has now been confirmed in the solid state.[17]

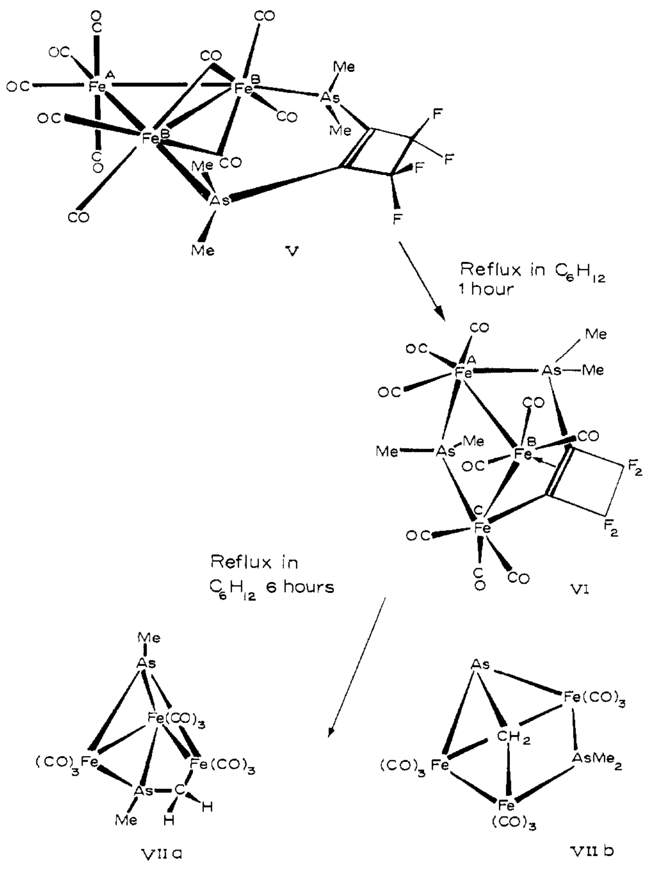

Figure 2.—Degradative scheme for ffars$Fe_3(CO)_{10}$.

The increase in isomer shift for the outer lines indicates a lower total s-electron density at these iron nuclei in the ffars compound. This could be caused by a decrease in 4s population or by an increase in 3d density which would shield the nucleus from the 4s electrons. The former would imply that a CO group is a slightly more efficient σ donor than the $As(CH_3)_2$ group. The alternative explanation, an augmented 3d-electron density, could arise from three possible effects: (1) an increase in σ donation of $As(CH_3)_2$ relative to CO which could then increase the 3d character, (2) an increase in ligand-to-metal π donation, and (3) a decrease in metal-to-ligand back-π-donation. It seems likely that the direct 4s term is greater than the direct 3d term, in which case an increase in σ donation would cause a negative rather than positive change in the isomer shift. Both the other possible explanations would yield positive shifts.

The larger electric field gradient at the equivalent iron nuclei (Fe^B) in the ffars compound may arise both from π delocalization in the cyclobutene ring and from the fact that the ligand lies in the plane of the iron atoms. The splittings for Fe^B in $Fe_3(CO)_{12}$ and ffars$Fe_3(CO)_{10}$ show a stronger temperature dependence than most d^{10} iron complexes. This may be due to the bridging carbonyls and merits further study as it implies

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(16) The splitting of the central line has also been observed by N. N. Greenwood, personal communication.

(17) P. J. Roberts, B. R. Penfold, and J. Trotter, in preparation.

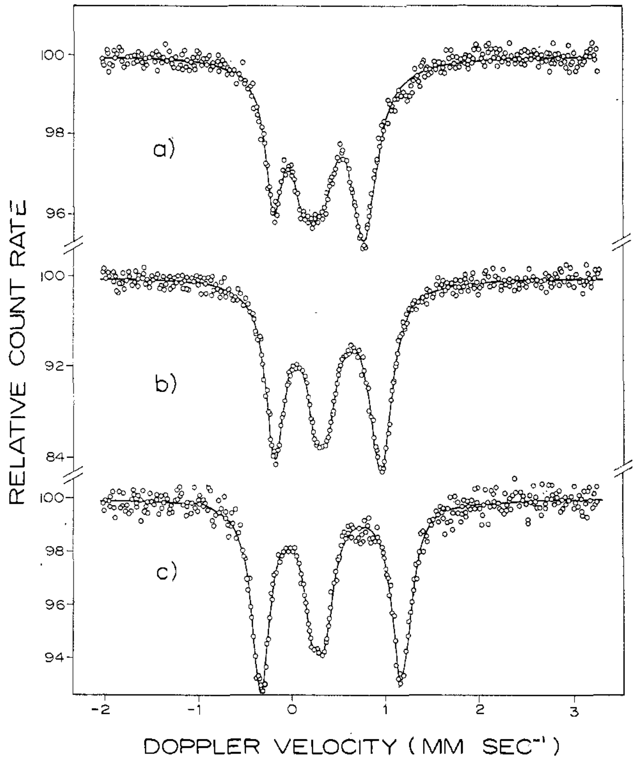

Figure 3.—Mössbauer spectra of (a) $Fe_3(CO)_{12}$ at 295°K, (b) $Fe_3(CO)_{12}$ at 80°K, and (c) ffars$Fe_3(CO)_{10}$ at 80°K.

the existence of a fairly low-lying electronic excited state in these compounds.

Although the solid structure of $Fe_3(CO)_{12}$ is now known,[5] its structure and those of derivatives in solution have been the subject of some discussion with respect to the lability of the bridging carbonyl groups.[5,18] However Pollick and Wojcicki[13] found no evidence for migration, the ^1H nmr spectrum of $(CH_3O)_3PFe_3(CO)_{11}$ remaining a singlet at temperatures down to $-100°$. Our complex, ffars$Fe_3(CO)_{10}$, should perhaps be more sensitive to these effects since bridging carbonyl migration would destroy the symmetry of the molecule. The sharp singlet ^1H resonance obtained for this complex at temperatures between 20 and $-30°$ indicates that migration is unlikely.

Although ffars$Fe_3(CO)_{10}$ is reasonably air stable at room temperature, even in solution, a short period at elevated temperatures (*e.g.*, 1 hr in refluxing cyclohexane) causes it to be completely converted into a mixture of other compounds in which a complex of empirical formula ffars$Fe_3(CO)_9$ is the major component. This result explains the almost complete absence (<1% yield) of the $Fe_3(CO)_{10}$ complex from the products of the reaction between ffars and $Fe_3(CO)_{12}$ in refluxing cyclohexane (expt 2) which gives a 90% yield of ffars$Fe_3(CO)_9$. It is possible that ffars$Fe_3(CO)_{10}$ is the precursor to the $Fe_3(CO)_9$ complex. It would also seem that under conditions enabling ffars$Fe_3(CO)_{10}$ to be formed without decomposition, but in low yield (expt 1), other processes yielding ffars$Fe(CO)_4$, ffars$Fe_2(CO)_8$ (both previously[9] believed to be $Fe(CO)_3$ complexes), and ffars$Fe_2(CO)_6$ are obviously preferred.

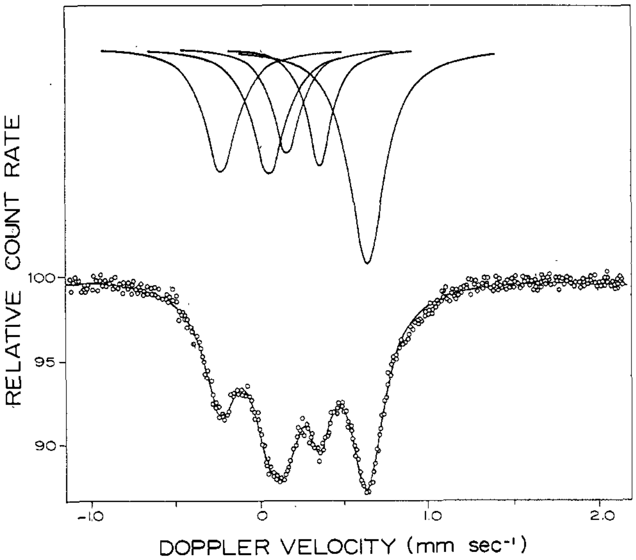

Figure 4.—Mössbauer spectrum of ffars$Fe_3(CO)_9$ at 80°K showing resolution into five independent lines.

Analytical data for this new complex give the empirical formula ffars$Fe_3(CO)_9$; thus the ligand was expected to be intact. However the large number of carbonyl infrared stretching bands, the ^1H nmr spectrum of four singlets, and the extremely complex ^{19}F nmr spectrum indicated that the symmetry of ffars$Fe_3(CO)_{10}$ had been largely destroyed. The Mössbauer spectrum indicated the presence of three dissimilar iron atoms. In addition, the mass spectrum, even though it confirmed the empirical formula and the presence of nine carbonyl groups, did not appear to show a peak assignable to ffars$^+$ (m/e 334), although it was possible that a peak estimated at m/e 332 was within counting error. Final details of the structure were elucidated by an X-ray crystallographic study,[19] and the result is shown in Figure 2 (VI). This structure which would have the observed spectroscopic properties is related to that of ffars$Fe_2(CO)_6$ (IV) by the insertion of an $Fe(CO)_3$ group into one of the arsenic–carbon bonds.

The Mössbauer spectrum of the complex can be resolved into five independent Lorentzian lines, as shown in Figure 4. Data for this spectrum, calculated from the results of a least-squares fit, are given in matrix form in Table VII. Let us designate the matrix elements as $E_{i,j}$, where i gives the row and j the column in which the element appears. The diagonal elements ($i = j$) give the positions (in mm sec^{-1}, relative to sodium nitroprusside) of each line. The off-diagonal elements having $i > j$ are the isomer shifts of all possible pairs of lines, and those elements with $i < j$ are the corresponding quadrupole splittings. Thus, $E_{5,2} = 0.39$ is the isomer shift for lines 2 and 5 taken as a pair, and $E_{2,5} = 0.67$ is the quadrupole splitting of this pair. Also included in Table VII are the line widths Γ (full width at half-maximum) and fractions of the total area contained in each resonance line.

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[18] D. F. Keeley and R. E. Johnson, *J. Inorg. Nucl. Chem.*, **11**, 33 (1959).

[19] F. W. B. Einstein and A. M. Svensson, *J. Amer. Chem. Soc.*, **91**, 3663 (1969).

The highest velocity line ($E_{5,5}$) must be either a single absorption or a sum of two almost exactly superimposed Lorentzians, since its width is only slightly greater than those of the other lines. We can rule out the former possibility for two reasons. First, the X-ray structure shows all three iron atoms have distorted octahedral symmetry, and even if one atom gave rise to an unsplit line, we would expect a width at least as great as the absorption envelope for the octahedral iron atom, Fe^A in V. Second, the isomer shift for this line is much greater than is reasonable for a low-spin iron complex. We can therefore safely assume that $E_{5,5}$ is a sum of the high-velocity components of two quadrupole doublets.

This simplifies the situation somewhat, but there still remain six combinations of pairs of lines, with 3! permutations of the iron atoms for each combination, making a total of 36 ways of assigning the lines. None of the quadrupole splittings is unreasonable for distorted octahedral symmetry, so narrowing the number of possible assignments must be done on the basis of isomer shift, line width, and intensity data.

Consider first the isomer shifts, which it will be seen allow us to rule out most of the remaining assignments. In the related complexes ffars$Fe(CO)_4$ and ffars$Fe_2(CO)_8$ each iron atom receives 10 electrons to obtain the krypton configuration, and the isomer shifts at 80°K for both compounds are 0.21 mm sec^{-1}.[7] In IV, where there are only 18 electrons donated to the two iron atoms, the shifts at 80°K and 0.28 and 0.32 mm sec^{-1} or an average of 0.30 mm sec^{-1} (Table VI). Finally the isomer shifts for V at this temperature are 0.27, 0.42, and 0.42 mm sec^{-1}, for an average of 0.37 mm sec^{-1} (Table VI). In the last case a total of 24 electrons are donated to the three iron atoms. Two important points are evident from these results. First, as the number of electrons donated per iron atom decreases, there is a regular increase in the average isomer shift. Since δ is inversely proportional to the s-electron density at the iron nucleus, this trend is to be expected. In complex VI, the iron atoms receive a total of 26 electrons, and we would expect an average δ value of 0.30–0.32 mm sec^{-1}. Second, and more importantly, none of the three isomer shifts for this complex should be less than 0.21 mm sec^{-1}.

It turns out that the average isomer shift is no help in assigning the lines, since all possible assignments (even those considering $E_{5,5}$ as a singlet) lead to an average δ of 0.30 mm sec^{-1}. However, if we impose the restriction $\delta \geq 0.21$ mm sec^{-1}, only five pairs of lines remain as possibilities ($E_{5,1}$, $E_{5,2}$, $E_{5,3}$, $E_{4,2}$, $E_{4,3}$). Since line 5 must be paired with two and only two other lines while lines 1–4 can be used only once, there are then only two possible combinations of pairs: (1) $E_{5,1}$, $E_{5,2}$, $E_{4,3}$; (2) $E_{5,1}$, $E_{5,3}$, $E_{4,2}$.

Neither of these combinations can be ruled out with certainty, although we favor (1) for the following reasons. (i) Combination (2) requires two iron atoms to have small and virtually identical isomer shifts while the third iron atom has a much larger shift. However, from the structure of VI we would expect Fe^A to show a significantly smaller shift than either Fe^B or Fe^C. (ii) In all the iron carbonyl complexes of ffars, ffos, f$_6$fos, diphos, and diars [diphos = 1,2-bis(diphenylphosphino)ethane and diars = 1,2-bis(dimethylarsino)benzene] which we have studied thus far, we have observed no appreciable asymmetry in either line width or absorption area for the two lines of any quadrupole doublet, although inequivalent iron atoms in such compounds as IV and V can show somewhat different recoilless fractions. Note that combination (2) demands substantial asymmetry in both line width and area fraction, while (1) does not.

Taking (1) as the preferred combination, there are then only six ways of assigning the three pairs of lines to the three iron atoms. We mentioned above that we expect Fe^A to show the smallest isomer shift. The reason for this is that Fe^A receives the largest number of electrons from donor atoms (excluding Fe–Fe bonds). Our experience with the $Fe_2(CO)_6$ complexes of ffars, ffos, and f$_6$fos is that redistribution of electron density along Fe–Fe bonds such as that between Fe^A and Fe^B in VI leads to a final situation in which the Fe atom at the "acceptor end" of the bond remains electron deficient compared with the Fe atom at the "donor end," so that the latter shows a greater s-electron density and smaller isomer shift (see below also). Let use therefore tentatively assign lines (1,5) to Fe^A, leaving us with but two choices for the remaining lines. It seems likely that the electron-withdrawing tendency of the fluorine atoms will decrease the donation from the cyclobutene ring to Fe^B, and we feel it reasonable to assign the largest isomer shift to this iron atom. Thus, we suggest the following line assignments for the three iron atoms of structure VI: lines (1,5) to Fe^A; lines (2,5) to Fe^B; lines (3,4) to Fe^C. The Mössbauer isomer shifts and quadrupole splittings obtained for this assignment are printed in boldface in Table VII. We must emphasize that this assignment is by no means definitive but merely what we consider to be a "best guess" on the basis of available evidence.

The formation of ffars$Fe_3(CO)_9$ (VI) is interesting in that it involves the breaking of a normally reasonably strong As–C bond under mild conditions and results in the formation of Fe–C and Fe–As σ bonds. ffars-$Fe_3(CO)_{10}$ is sensitive to heat presumably because of strained ring systems. Relief of ring strain by rearrangement probably allows the double bond to approach one of the iron atoms and replace a carbonyl group. Such rearrangement and fragmentation of ligands during reaction may well be more common than is currently thought. The compound originally reported to be $[(diars)_3Ni][ClO_4]_2$ is in fact $[(diars)(triars)Ni][ClO_4]_2$[20] where rearrangement of the diars has occurred. diars also apparently rearranges (with loss of CH_4) when it reacts with iron carbonyls.[21]

Further change occurs on refluxing the complex VI in cyclohexane for 6 hr which results in good conversion

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[20] B. Bosnich, R. S. Nyholm, P. J. Pauling, and M. L. Tobe, *J. Amer. Chem. Soc.*, **90**, 4741 (1968).

[21] W. R. Cullen and D. A. Harbourne, *Can. J. Chem.*, **47**, 3371 (1969).

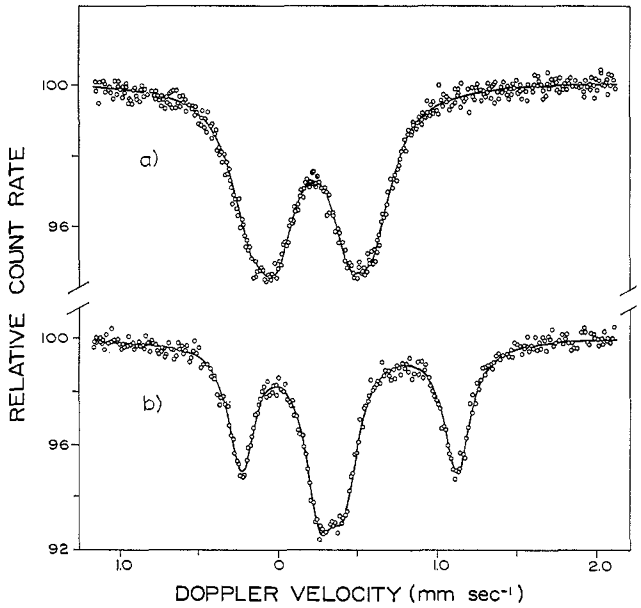

Figure 5.—Mössbauer spectra at 80°K of (a) $As_2(CH_3)_2CH_2Fe_3(CO)_9$ and (b) $f_6fosFe_2(CO)_7$.

to a new fluorine-free complex. This new complex is somewhat less stable than those previously discussed and for this reason has not as yet been subjected to X-ray analysis. However it has been possible to propose a structure using information gained from the usual techniques. Analytical data show the absence of fluorine and a carbon and hydrogen content consistent with a formulation such as $As_2C_3H_{8-11}Fe_3(CO)_9$. The carbonyl infrared spectrum shows eight bands indicating, once more, low symmetry. The proton nmr spectrum shows two singlets, each of area 3 and an AB quartet of area 2 in the same general chemical shift region as the singlets. No resonances above TMS are observed. The mass spectrum shows a consecutive loss of nine carbonyl groups and a high-resolution molecular weight determination on the parent peak was found to be in reasonable agreement (Table I) with that required for $As_2C_3H_8Fe_3(CO)_9$. This combined with the nmr results leads us to postulate structures for this complex such as VIIa or, seemingly less likely, VIIb. The Mössbauer spectrum consists of two broad absorptions, as shown in Figure 5a. The appearance of the spectrum suggests that all three iron atoms have quite similar environments. We have been able to fit this spectrum either to two or to four independent Lorentzian lines. However, the computer cannot resolve six independent lines as required for three dissimilar iron atoms. This is presumably because the full half-maximum width of each resonance envelope ($\sim$0.45 mm sec^{-1}) is only 2.5 times the minimum observable line width. The solid line shown in Figure 5a is the sum of four Lorentzians.

The inability to obtain a six-line fit precludes the assignment of definite values for the Mössbauer parameters. However, the values obtained from the four-line fit should set fairly accurate extrema for the true parameters since the third pair of lines is probably intermediate (the fit to the outer shoulders is quite good). The minimum and maximum isomer shifts found are 0.17 and 0.35 mm sec^{-1}, with a mean value of 0.26 mm sec^{-1}, while the quadrupole splittings range from 0.52 to 0.88 mm sec^{-1} with a mean of 0.70 mm sec^{-1}.

Although these results are only tentative, two comments should be made. First, although the same numbers of electrons are donated to the three iron atoms in VI and in VII, the mean isomer shift is appreciably lower in the latter compound. This conceivably could be caused by the absence of the perfluorocyclobutene ring in VII. Second, it is difficult to reconcile the quadrupole splitting data with structure VIIa. On the basis of results for $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and ffars$Fe_3(CO)_{10}$, the heptacoordinate iron atom in VIIa should show a quadrupole splitting in the range 1.2–1.6 mm sec^{-1}, rather than the maximum value of 0.88 mm sec^{-1} found here. Even with a "true" six-line fit of the spectrum it is extremely unlikely that a splitting greater than 0.92 mm sec^{-1} could be obtained. Thus a structure containing three octahedral or near-octahedral iron atoms is required to fit the Mössbauer data more convincingly. However it does not appear possible to construct such a molecule of formula $As_2(CH_3)_2CH_2Fe_3(CO)_9$ utilizing two "normal" trivalent arsenic atoms as two-electron donors. However if we allow one four-electron donor arsenic atom we may postulate a somewhat unusual structure such as VIIb which satisfies all of the spectroscopic data. Some evidence for this type of structure may be found in that a peak occurring in the mass spectrum of the compound at *m/e* 105 would seem to indicate the ion $(As(CH)_3)_2^+$ possibly derived from VIIa but a more likely fragment of VIIb.

The conversion of ffars$Fe_3(CO)_{10}$ through $As(CH_3)_2Fe_3(CO)_9As(CH_3)_2C_4F_4$ to $As_2(CH_3)_2CH_2Fe_3(CO)_9$ is a very interesting one and presumably gives some clue to the way in which metal carbonyls degrade or isomerize organic molecules.

The complex $f_6fosFe_2(CO)_7$, produced from $f_6$fos and $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ in refluxing cyclohexane, has been formulated as such mainly because of analytical and spectroscopic data. The calculated analytical percentages of C, H, F, P, and Fe for the two possible formulations $f_6fosFe_2(CO)_7$ and $f_6fosFe_2(CO)_8$ are closely similar and with the percentages obtained experimentally for the complex it is difficult to decide between these two formulations. However on the basis of the oxygen analysis we prefer the heptacarbonyl formulation. Unfortunately the mass spectrum of the complex is of little help as the molecule appears to lose one carbonyl group very easily to give a peak of highest *m/e* equivalent to $f_6fosFe_2(CO)_6^+$,[6,22] even at low ionizing voltages. The ^{19}F nmr spectrum of $f_6fosFe_2(CO)_7$ shows a basic pattern of three AB quartets. This in itself is indicative of asymmetry both in the plane of the cyclopentene ring and in the plane of the perpendicular bisector of the ring. This information suggests VIII as a possible structure for the complex. The Mössbauer spectrum is in agreement with this structure. It is shown in

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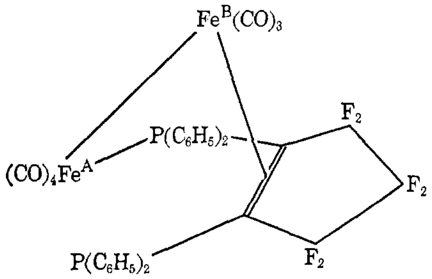
(22) As the mass spectra of $f_6fosFe_2(CO)_7$ and $f_6fosFe_2(CO)_6$ appear so similar, we have not included data on the former in Table V.



VIII

Figure 5b and consists of a four-line pattern, which like those of Figure 3 can be interpreted in terms of two quadrupole doublets, the inner pair showing a very small splitting. In this case, however, the total area of lines 1 and 4 is approximately equal to the total area of lines 2 and 3. There are thus two inequivalent iron atoms in the molecule. The Mössbauer parameters derived from the spectrum are given in Table VI, where Fe^A denotes the octahedrally coordinated iron atom which gives rise to the small splitting and Fe^B denotes the iron atom of lower symmetry.

It is instructive to compare the Mössbauer parameters for this compound with those for $f_6fosFe_2(CO)_6$,[6] which have been included in Table VI. In this latter compound Fe^A is bonded to three carbonyl groups, the two phosphorus atoms of the f_6fos ligand, and Fe^B. The second iron atom, in addition to the Fe–Fe bond, is coordinated to three carbonyl groups and to the cyclopentene ring (*cf.* IV). The first thing to note is that the isomer shifts for Fe^B in these two compounds are identical, which suggests they have similar bonding (the differences in quadrupole splittings have to do with structural differences and are discussed below). On the other hand, Fe^A shows a slightly lower shift in the $Fe_2(CO)_7$ complex and hence a higher s-electron density than does Fe^A in the $Fe_2(CO)_6$ compound. If Fe^A in the heptacarbonyl complex is coordinated to the remaining four carbonyl groups and to one phosphorus of the f_6fos ligand (as well as to Fe^B), this difference in δ could be explained in terms of the more efficient d–π acceptor properties of a carbonyl group as compared with a diphenylphosphino group.

In both $f_6fosFe_2(CO)_6$ and $f_6fosFe_2(CO)_7$, Fe^A shows a much smaller isomer shift than does Fe^B. Thus, although one might have been tempted to describe the Fe–Fe bonds in these complexes in terms of overlap of a d^2sp^3 orbital on Fe^A and a dsp^3 orbital on Fe^B, so that both iron atoms adopt the krypton configuration, these results show clearly that there remains a deficiency in s-electron density at the Fe^B nucleus. Moreover, the fact that Fe^A in the $Fe_2(CO)_7$ complex shows a smaller shift than Fe^A in the $Fe_2(CO)_6$ compound, whereas the shifts for Fe^B in the two complexes are identical, suggests that Fe^A tends to approach the inert-gas configuration independently of the s-electron density about Fe^B.

Turning now to the quadrupole splittings listed in Table VI, we see that in $f_6fosFe_2(CO)_7$, Fe^A shows a splitting of only 0.17 mm sec^{-1} at 80°K (the splitting could not be resolved at room temperature), whereas in $f_6fosFe_2(CO)_6$, Fe^A shows a splitting of 0.65 mm sec^{-1}. This difference is readily understood in terms of the steric requirements of the f_6fos ligand. When both phosphorus atoms are coordinated to Fe^A, the P–Fe^A–P angle is fixed and leads to appreciable distortion from octahedral symmetry. In the heptacarbonyl complex, on the other hand, there is more freedom of arrangement for the six bonds to Fe^A, and they clearly take up positions which tend to minimize the electric field gradient at the iron nucleus.

We have commented previously[6] on the rather unusual Δ values found for Fe^B in the $Fe_2(CO)_6$ complexes with ffars, ffos, and f_6fos, which are larger than values normally observed for distorted octahedral symmetry ($\lesssim 1.0$ mm sec^{-1}) but smaller than those found for trigonal-bipyramidal complexes[7] such as $LFe(CO)_3$, $LFe(CO)_4$, and $LFe_2(CO)_8$ ($\gtrsim 2.0$ mm sec^{-1}). We have suggested that in these complexes the Fe^B bonding orbitals adopt a quasioctahedral configuration, forming σ bonds to Fe^A, three carbonyl groups, and two carbon atoms of the cyclobutene (or cyclopentene) ring. Fe^B in $f_6fosFe_2(CO)_7$ gives a significantly greater quadrupole splitting than does Fe^B in $f_6fosFe_2(CO)_6$, but only slightly greater than the splitting shown by the corresponding iron atom in $ffarsFe_2(CO)_6$ (1.45 mm sec^{-1}). It therefore seems that in the heptacarbonyl complex as well, Fe^B is in a quasioctahedral environment. The most likely explanation for the differences in Fe^B quadrupole splittings among these compounds is differences in the distance from Fe^B to the ring systems, leading to marked changes in the C–Fe^B–C angle. Thus, the shorter the distance between Fe^B and the ring, the wider will be this angle and the lower will be the quadrupole splitting.

Acknowledgments.—We thank the National Research Council for generous financial support of this project and J. C. Scott for the use of his computer program.