tra for $(DTO)M(CO)_4$ complexes all show singlet absorptions due to *t*-butyl protons and another singlet which may be ascribed to the ethylene protons; these occur in the expected 4.5:1 intensity ratios and are shifted somewhat downfield with respect to the absorptions for the free ligand. Deshielding of the protons is to be expected upon coordination of sulfur.

The solubility of $(DTO)Cr(CO)_4$ was sufficient to permit an infrared spectrum to be taken in cyclohexane. The spectrum was run on a sample the purity of which was verified by chemical analysis; it was also observed that no decomposition occurred over the time required to scan the carbonyl stretching region several times. Six bands in the carbonyl stretching region, suggesting the presence of more than one species, are observed (see Experimental Section). Rough estimates of the relative sizes of k_1 and k_2 for $(DTO)Cr(CO)_4$ do not rule out the possibility that the second species is $(DTO)Cr(CO)_4$ in which one end of the DTO molecule is dissociated. Unfortunately, it was not possible to obtain a proton nmr spectrum in a deuterated hydrocarbon solvent, and thus the origin of the two additional carbonyl stretching bands cannot be assigned with confidence.

Reactions of $(DTO)W(CO)_4$.—The inertness of $W(CO)_6$ toward carbonyl replacement has prevented the direct preparation of some organometallic complexes of tungsten. An indirect route to the preparation of such compounds, *e.g.*, $(diolefin)W(CO)_4$, through use of $(CH_3CN)_3W(CO)_3$ has been reported.[4] The potential usefulness of $(DTO)W(CO)_4$ as such an intermediate has been briefly investigated; details are given in the Experimental Section. Reaction of $(DTO)W(CO)_4$ with norbornadiene in refluxing *n*-hexane gives a 23% yield of $(C_7H_8)W(CO)_4$ as shown by the infrared spectrum and melting point of the product. Although the yield of $(C_7H_8)W(CO)_4$ was lower than those reported by Fronzaglia and King,[4] who obtained a 56% yield based on moles of $(CH_3CN)_3W(CO)_3$ used, the ease of preparation and air stability of $(DTO)W(CO)_4$ would appear to offer advantages for the indirect synthesis of organometallic complexes of tungsten, particularly so for cases in which the use of large excesses of the substituent ligand is economically feasible.

Acknowledgments.—We wish to thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research under Grant 2613-A3. We also thank Mr. Gary C. Faber for his help and interest, Dr. R. C. Taylor for the infrared spectrum of $(DTO)Cr(CO)_4$ in cyclohexane, Dr. Joel Padmore for the proton nmr spectra, and Mr. Earl P. Ross for kinetic measurements of the reaction of $(DTO)Mo(CO)_4$ with phosphites.

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The Characterization of $(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2C}F_2Fe_2(CO)_6$ and Related Complexes

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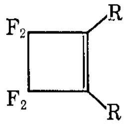
The complexes $R\overline{C{=}CR(CF_2)_nCF_2}Fe_2(CO)_6$ [R = $(CH_3)_2As$ or $(C_6H_5)_2P$, n = 1; R = $(C_6H_5)_2P$, n = 2] have been isolated and evidence is presented that the phosphorus compounds have structures analogous to that of the known arsenic derivative (Figure 1). In particular, information about their structure and bonding has been obtained from their Mössbauer spectra.



Ia, R = $(CH_3)_2As$
Ib, R = $(C_6H_5)_2P$

The novel cyclobutene derivatives Ia, ffars, and Ib, ffos, have recently been found to form chelate complexes when treated with derivatives of the heavier transition metals and with certain metal carbonyls.[1] It has also been reported[2] that ffars forms a complex $(ffars)Fe_2(CO)_6$ whose structure is indicated in Figure 1. Here the ligand is not only acting as a chelating group to one iron atom in the usual way[3] but is also using the double bond of the cyclobutene bridging group to coordinate to the second iron atom. Olefins,[4] including perfluorocycloalkenes,[5] are known to react with iron carbonyls to give derivatives of the type $(olefin)Fe(CO)_4$. Furthermore, iron pentacarbonyl and its derivatives, like some other metal car-

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(1) W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *Inorg. Chem.*, **6**, 2256 (1967).

(2) (a) F. W. B. Einstein and J. Trotter, *J. Chem. Soc., A*, 824 (1967); (b) F. W. B. Einstein, W. R. Cullen, and J. Trotter, *J. Am. Chem. Soc.*, **88**, 5670 (1966).

(3) T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1965).

(4) *E.g.*, P. Corradini, C. Pedone, and A. Sirigu, *Chem. Commun.*, 341 (1966); A. R. Luxmore and M. R. Truter, *Acta Cryst.*, **15**, 1117 (1962); E. K. Gustorf, M. C. Henry, and C. D. Pietro, *Z. Naturforsch.*, **19b**, 284 (1964).

(5) R. Fields, M. M. Germain, R. N. Haszeldine, and P. W. Wiggans, *Chem. Commun.*, 243 (1967).

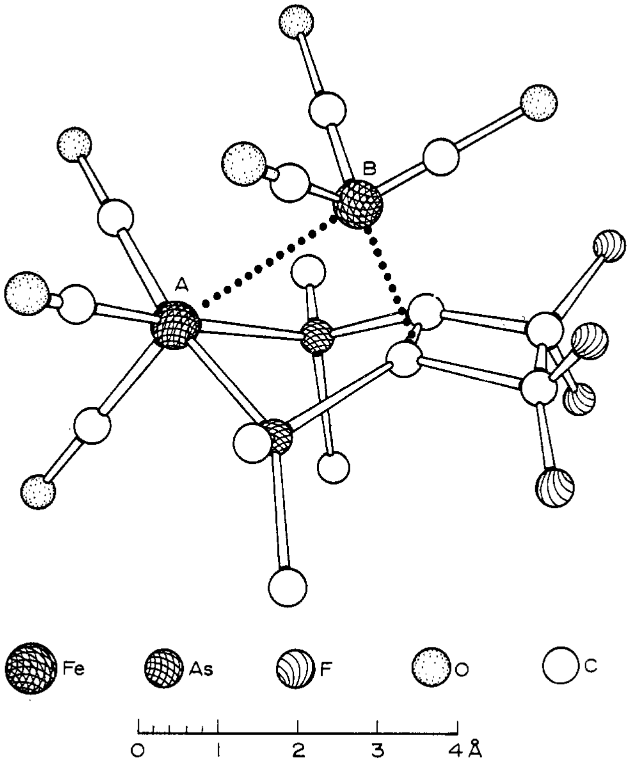
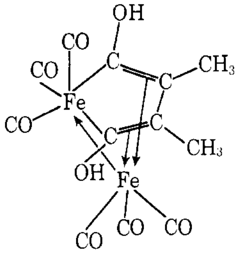


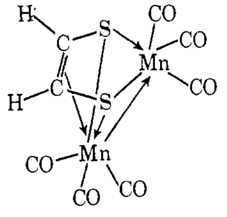
Figure 1.—Structure of (ffars)$Fe_2(CO)_6$.

bonyl compounds, can act as Lewis bases[6,7]; thus (ffars)$Fe_2(CO)_6$ can be regarded as a mixed compound (chelate)$Fe(CO)_3 \rightarrow$(olefin)$Fe(CO)_3$.

The structure of (ffars)$Fe_2(CO)_6$ is similar to that found for the ferracyclopentadiene complexes such as II[6c] obtained from the reaction of acetylenes with iron carbonyls and their derivatives[8] and to the dimanganese compound (III) reported by King and Eggers.[9]



II



III

Another unusual complex formed by ffars has the formula (ffars)$Fe_3(CO)_{10}$.[10] The compound is probably formed by displacing one terminal carbonyl group from each of the two equivalent iron atoms of $Fe_3(CO)_{12}$ to give a planar tricyclic molecule.

The purpose of the present paper is to report details of the preparation and properties of (ffars)$Fe_2(CO)_6$ and the related compounds (ffos)$Fe_2(CO)_6$ and ($f_6$fos)$Fe_2(CO)_6$($f_6$fos = IV).

Experimental Section

Infrared spectra were obtained using a Perkin-Elmer Model 457 instrument. Nmr spectra were run on Varian A-60 and HA-100 spectrometers. Chemical shifts are reported in ppm upfield from internal $CFCl_3$ (^{19}F spectra) and downfield from internal TMS (^1H spectra). Mass spectra were measured with an AEI MS-9 spectrometer with direct introduction of solid samples. The Mössbauer spectrometer consists of a velocity transducer which drives the source at constant acceleration, a gas-filled proportional counter for detection of the transmitted γ radiation, and a 400-channel analyzer for storing the spectrum. The analyzer is phase-locked to the transducer and operates in the time mode. The experiments employed a room-temperature source of ^{57}Co in a Pd matrix and were carried out in transmission geometry. The powdered absorbers were contained in a cell with Mylar windows, which could be refrigerated to liquid nitrogen temperature. Approximately a 1-mm thickness of sample was traversed by the γ radiation in all cases. The spectra were subsequently computer-fitted to Lorentzian line shapes. The Doppler velocity scale was frequently calibrated against the quadrupole splitting of an NBS standard single-crystal sodium nitroprusside absorber, and all isomeric shifts are reported relative to the center of the spectrum for this standard.

Microanalyses were done by Mr. P. Borda, Chemistry Department, University of British Columbia, and by Drs. F. Pascher and A. Pascher, Bonn, Germany.

The details given below in expt 2 are selected from a large number of related experiments. They give the conditions that have been found to result in the highest yields of the desired compounds.

(1) **Preparation of 1,2-Bis(diphenylphosphino)hexafluorocyclopentene ($f_6$fos, IV).**—Diphenylphosphine (9.3 g, 50 mmol) and octafluorocyclopentene (30 g, 141 mmol) were sealed together under vacuum in a Pyrex tube. The tube was shaken for 10 days at 20° during which time pale yellow crystals were produced. The tube was opened and the volatile contents were removed. The remaining solid was recrystallized from ether–acetone to give white $f_6$fos, mp 97–99° (19.3 g, 71% yield). *Anal.* Calcd for $C_{29}H_{20}F_6P_2$: C, 64.0; H, 3.7; F, 20.9. Found: C, 63.7; H, 4.0; F, 20.6.

(2) **Preparation of $LFe_2(CO)_6$ Complexes.** (a) **(ffos)$Fe_2(CO)_6$.**—Triiron dodecacarbonyl (0.8 g, 1.59 mmol) and ffos (0.4 g, 0.81 mmol) were refluxed in benzene (50 ml) under nitrogen with infrared monitoring. After 5.5 hr the solution was filtered and evaporated to dryness. Trituration with petroleum ether (bp 30–60°) followed by recrystallization from acetone–petroleum ether gave bright orange crystals of (ffos)$Fe_2(CO)_6$, mp ~220° dec (360 mg, 76%). *Anal.* Calcd for $C_{34}H_{20}F_4Fe_2O_6P_2$: C, 52.7; H, 2.6; F, 9.8; P, 8.0; Fe, 14.5. Found: C, 52.9; H, 2.7; F, 10.4; P, 7.7; Fe, 15.0.

(b) **($f_6$fos)$Fe_2(CO)_6$.**—Diiron enneacarbonyl (2.4 g, 6.6 mmol) and $f_6$fos (0.8 g, 1.5 mmol) were refluxed in cyclohexane (50 ml) under nitrogen for 10 hr. The solution was evaporated to dryness and the residue was chromatographed on Florisil. The separation of the three main products of the reaction by eluting with petroleum ether–benzene mixtures was not good and rechromatography and/or recrystallization (acetone–hexane) of the appropriate fraction yielded orange crystals of ($f_6$fos)$Fe_2(CO)_6$, mp 226–228° with darkening at ~210° (0.09 g, 8%). *Anal.* Calcd for $C_{35}H_{20}F_6Fe_2P_2O_6$: C, 51.0; H, 2.4; F, 13.9. Found: C, 51.0; H, 2.6; F, 13.7.

(c) **(ffars)$Fe_2(CO)_6$.**—Triiron dodecacarbonyl (1.9 g, 3.78 mmol) and ffars (1.0 g, 3.0 mmol) were sealed under vacuum in a Pyrex tube containing acetone (20 ml). The tube was irradiated using a 100-W ultraviolet lamp at a distance of 20 cm for 110 hr. The tube was opened and all volatiles were

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(6) *E.g.*, (a) D. M. Adams, D. J. Cook, and R. D. W. Kemmitt, *J. Chem. Soc., A*, 1067 (1968); (b) I. N. Nowell and D. R. Russell, *Chem. Commun.*, 817 (1967); (c) A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961).

(7) References 6a and b provide examples of compounds where a metal-metal *dative* bond is the sole link between the halves of a molecule. A statement is made by R. B. King and C. A. Eggers, *Inorg. Chem.*, **7**, 1214 (1968), that no cases are known where this occurs.

(8) W. Hübel in "Organic Syntheses *Via* Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Interscience Publishers, Inc., New York, N. Y., 1968, p 273.

(9) R. B. King and C. A. Eggers, *Inorg. Chem.*, **7**, 1214 (1968).

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

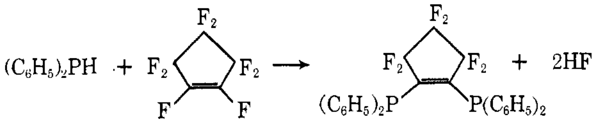
removed. The residue was extracted with petroleum ether, which removed a mononuclear complex, and then was chromatographed on Florisil eluting with petroleum ether–ether mixtures to yield (ffars)$Fe_3(CO)_{10}$[10] and orange (ffars)$Fe_2(CO)_6$, which sublimes at ~160° *in vacuo*, darkens in a sealed tube at ~235°, and does not melt below 300° (0.3 g, 21%). *Anal.* Calcd for $C_{14}H_{12}As_2F_4Fe_2O_6$: C, 27.4; H, 2.0; F, 12.4. Found: C, 27.7; H, 2.3; F, 12.1.

Nmr Data.—Fluorine-19 spectra (acetone solutions) of $f_6$fos show a multiplet of nine lines centered at 105.4 ppm (area 2) and a quintuplet of triplets (J = 6.2 and 0.7 Hz) at 132.7 ppm. Spectra of $f_6$fos$Fe_2(CO)_6$ show four regions of absorption: (a) unsymmetrical doublet (J = 242 Hz) of multiplets centered at 70.35 ppm; (b) unsymmetrical doublet (J = 240 Hz) of multiplets at 99.98 ppm; (c) unsymmetrical doublet (J = 236 Hz) of multiplets at 112.4 ppm; (d) unsymmetrical doublet (J = 234 Hz) of triplets ($J \simeq 6$ Hz) at 121.7 ppm. The [(a) + (b)]: [(c) + (d)] area ratio is 2:1. Spectra of (ffos)$Fe_2(CO)_6$ show four multiplets at (a) 86.95, (b) 88.88, (c) 103.9, and (d) 105.9 ppm. Multiplets (a) and (b) are mirror images as are (c) and (d). Spectra of (ffars)$Fe_2(CO)_6$ show four multiplets at (a) 94.74, (b) 96.67, (c) 107.1, and (d) 109.1 ppm. Multiplets (a) and (d) have the same outline as (b) and (c).

The ^1H spectrum of (ffars)$Fe_2(CO)_6$ in acetone-d_6 consists of two equal-area singlets at 1.16 and 2.45 ppm.

Discussion

The new ligand 1,2-bis(diphenylphosphino)hexafluorocyclopentene, $f_6$fos (IV), is produced in good yield from the room-temperature reaction between diphenylphosphine and perfluorocyclopentene. An analogous reaction is used to prepare ffos.[11] The easy displacement of both vinylic fluorine atoms is noteworthy.[12] The structure of $f_6$fos follows from its microanalysis and its ^{19}F nmr spectrum which consists of a multiplet (area 2) at 105.4 ppm and a quintuplet of triplets at 132 ppm (area 1). The chemical shifts are similar to those found for related systems.[12] Coupling of the two high-field fluorine atoms with the other four equivalent fluorine and two equivalent phosphorus atoms should give rise to the quintuplet of triplets.



IV

The complex (ffos)$Fe_2(CO)_6$ can be prepared in good yield and in the virtual absence of other products by treating ffos with triiron dodecacarbonyl. This complex is also the most characteristic product of reactions between ffos and the enneacarbonyl. In contrast both (ffars)$Fe_2(CO)_6$ and ($f_6$fos)$Fe_2(CO)_6$ are produced along with a number of other products from which they can be separated in only fair yield. The variations in structure between the related ligands ffars, ffos, and $f_6$fos are sufficient to cause marked differences in behavior when reacting under similar conditions. The different syntheses required to give optimum yields of the diiron complexes demonstrate this fact.

The ^1H nmr spectrum of (ffars)$Fe_2(CO)_6$ shows two singlet methyl resonances as expected from a consideration of the structure (Figure 1). The ^{19}F nmr spectra of all three complexes are complex as expected and analysis is hampered by the poor quality of the spectra due to low solubility.

The mass spectra of the complexes (Tables I and II) all exhibit a parent peak $LFe_2(CO)_6^+$, and all show a stepwise loss of six CO groups down to Fe_2L^+. The parent (P) and (P − CO) peaks are weak. Similar behavior is exhibited by III.[9] The loss of fluorine is a common feature of the fragmentation processes of many fluorocarbon derivatives[13] and is particularly prevalent in the spectrum of (ffars)$Fe_2(CO)_6$ (Table II). The loss of the neutral metal fluoride FeF_2 is also observed in the spectra of the three complexes which again is a feature of this type of compound.[13a,14]

TABLE I

MASS SPECTRAL DATA FOR (ffos)$Fe_2(CO)_6$ AND ($f_6$fos)$Fe(CO)_6$[a]

m/e		
(ffos)$Fe_2(CO)_6$	($f_6$fos)$Fe_2(CO)_6$	Ion
774	824	$LFe_2(CO)_6^+ \equiv P^+$
746	796	$(P - CO)^+$
718	768	$(P - 2CO)^+$
690	740	$(P - 3CO)^+$
662	712	$(P - 4CO)^+$
634	684	$(P - Fe(CO)_3)^+$, $(P - 5CO)^+$
606	656	$(P - Fe(CO)_4)^+$, $(P - 6CO)^+$
	646	$(P - 3CO - FeF_2)^+$
578	628	$(P - Fe(CO)_5)^+$
	618	$(P - 4CO - FeF_2)^+$
550	600	$(P - Fe(CO)_6)^+$
540	590	$(P - 5CO - FeF_2)^+$
512	562	$(P - 6CO - FeF_2)^+$
494	544	$(P - Fe_2(CO)_6)^+ \equiv L^+$
~453	503	$(P - 6CO - 2C_6H_5)^+$?
436	~486	$(L - F_2 - HF)^+$
	~468	$(P - 6CO - 2FeF_2)^+$
417	~467	$(L - C_6H_5)^+$
	429	$(L - C_6H_5 - 2F)^+$
	418	
	409	
360		
	391	$(L - 2C_6H_5 + H)^+$?
327		
	360	
309		$(L - P(C_6H_5)_2)^+$
	333	
	328	
	314	
	289	
	282	
233	233	
	213	
	183	

[a] Major or assignable peaks (above m/e 180).

The infrared spectra of the complexes are listed in Tables III and IV. The positions and intensities of the strong bands in the carbonyl stretching region are also illustrated in Figure 2. The expected six carbonyl bands are obtained and the spectra of the phosphorus compounds are very similar. The same pat-

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

(12) W. R. Cullen, *Fluorine Chem. Rev.*, in press.

(13) (a) R. B. King, *J. Am. Chem. Soc.*, **90**, 1429 (1968); (b) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967); (c) M. I. Bruce, *J. Organometal. Chem.* (Amsterdam), **10**, 95 (1967).

(14) R. B. King, *J. Am. Chem. Soc.*, **89**, 6368 (1967).

TABLE II

MASS SPECTRUM OF (ffars)$Fe_2(CO)_6$[a]

m/e	Ion	*m/e*	Ion
614	$LFe_2(CO)_6^+ \equiv P^+$	436	$(P - 5CO - F_2)^+$, $(P - 3CO - FeF_2)^+$
595	$(P - F)^+$	428 426	427 $(P - 6CO - F)^+$?
586	$(P - CO)^+$	418	$(P - Fe(CO)_5)^+$
567	$(P - CO - F)^+$	408	$(P - 6CO - F_2)^+$, $(P - 4CO - FeF_2)^+$
558	$(P - 2CO)^+$	390	$(P - Fe(CO)_6)^+$
539	$(P - 2CO - F)^+$	380	$(P - 5CO - FeF_2)^+$
530	$(P - 3CO)^+$	352	$Fe(L - F_2)^+$, $(P - 6CO - FeF_2)^+$
511	$(P - 3CO - F)^+$	334	$L^+ \equiv (P - Fe_2(CO)_6)^+$
502	$(P - 4CO)^+$	~324	$(P - Fe(CO)_5 - FeF_2)^+$
490		262	$(P - 6CO - FeF_2 - AsCH_3)^+$
483	$(P - 4CO - F)^+$	258	$(P - 6CO - 2FeF_2)^+$
474	$(P - 5CO)^+$, $(P - Fe(CO)_3)^+$	243	$(P - 6CO - 2FeF_2 - CH_3)^+$
464	$(P - 4CO - F_2)^+$, $(P - 2CO - FeF_2)^+$	206	$(P - 6CO - FeF_2 - AsCH_3 - Fe)^+$
454 456	455 $(P - 5CO - F)^+$?	153	Base peak $(P - 6CO - 2FeF_2 - As(CH_3)_2)^+$
446	$(P - 6CO)^+$, $(P - Fe(CO)_4)^+$		

[a] Major or assignable peaks (above *m/e* 150).

TABLE III

CARBONYL INFRARED STRETCHING FREQUENCIES OF $LFe_2(CO)_6$ COMPOUNDS[a]

(ffos)$Fe_2(CO)_6$	($f_6$fos)$Fe_2(CO)_6$	(ffars)$Fe_2(CO)_6$
2062 s	2063 s	2059 s
2024 vs	2026 vs	2022 vs
2001 s	2004 m	1992 s
1984 m	1985 m	1982 s
1971 m	1973 m	1965 w
1965 m	1968 m, sh	1950 m

[a] Cyclohexane solution (±3 cm^{-1}).

TABLE IV

INFRARED BANDS OF NEW COMPOUNDS[a]

(ffos)$Fe_2(CO)_6$	($f_6$fos)$Fe_2(CO)_6$	(ffars)$Fe_2(CO)_6$	$f_6$fos
1483 w	1486 w		1480 w
1437 w	1437 m	1312 vw, sh	1435 m
1297 w	1312 m	1294 w	1335 m
1137 w	1240 w	1275 vw, sh	1279 m
1108 m	1181 w	1105 w	1245 s
1087 w	1174 m	904 vw	1230 s
1002 vw	1119 m	594 vw	1190 s
874 w	1099 m		1144 s
840 vw	1082 m		1094 s
616 m	1006 m		1025 w
605 m	999 m, sh		1006 s
585 m	874 m		845 w
575 m	857 w, sh		725 w
	612 m		695 s
	596 m		
	584 m		
	572 m		

[a] $CHCl_3$ and CCl_4 solution; only bands below 1900 cm^{-1} are listed.

tern is obtained from (ffos)$Ru_2(CO)_6$.[15] Comparison of the infrared bands of the uncomplexed $f_6$fos with those of $f_6$fos$Fe_2(CO)_6$ (Table IV) shows little similarity and indicates that a considerable change in the structure of the ligand takes place on complex formation.

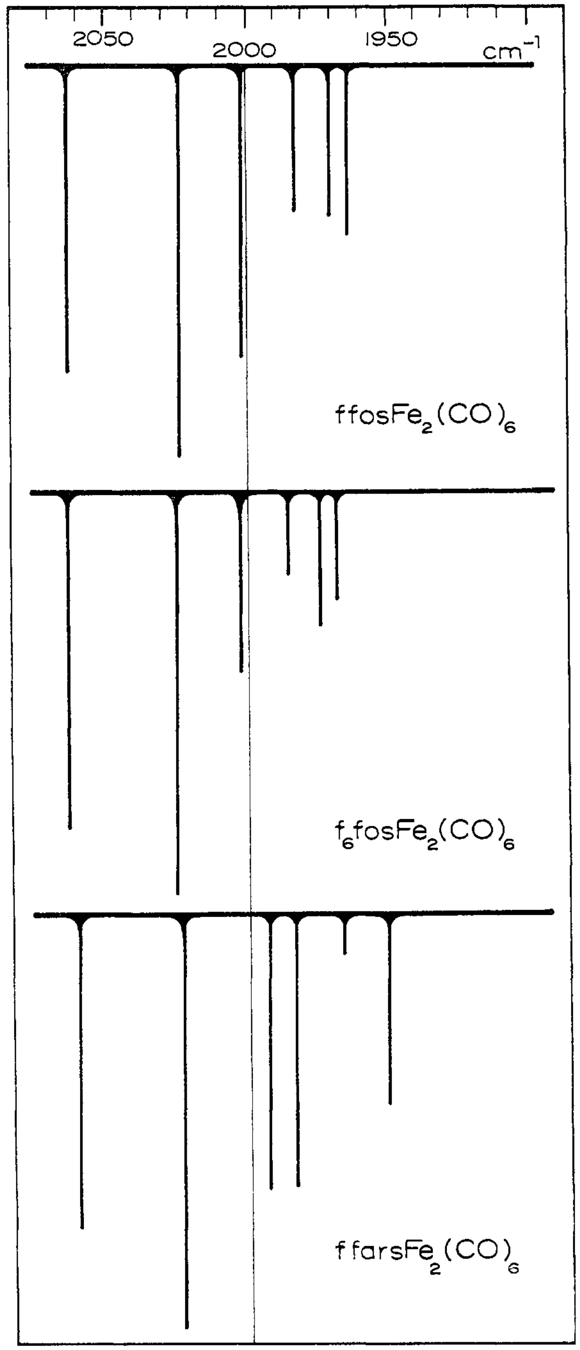

Figure 2.—Carbonyl absorption bands of $LFe_2(CO)_6$ compounds.

Similar changes occur in the spectra of the other ligands if the cyclobutene ring is involved in the bonding. If the ligand is acting only as a chelating group as in the compound (ffos)$Cr(CO)_4$, the spectrum of the free ligand is very similar to that of the complex.[1] The pattern of carbonyl bands of Figure 2 is different from that reported for the dimanganese compound III[9] (KBr disk: 2060 m, 2037 s, 1978 s, 1955 s, 1908 s cm^{-1}) and for a ferracyclopentadiene complex similar to II[16] ($Cl_2CHCHCl_2$ solution: 2079 s, 2042 vs, 2006 vs, 1998 vs, 1962 vw cm^{-1}).

The results presented so far indicate that the three diiron complexes have a structure not inconsistent

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(15) W. R. Cullen and D. A. Harbourne, unpublished results.

(16) H. D. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols, and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4749 (1960).

with that of Figure 1,[17] and further corroboration for this comes from a study of their Mössbauer spectra.

The complex (ffars)Fe$_2$(CO)$_6$ contains two bonded iron atoms, 2.88 Å apart. Iron atom A is octahedrally coordinated to three carbonyl groups and the two arsenic atoms, the sixth position being occupied by the Fe–Fe bond. The second iron atom (B) appears to have trigonal-bipyramidal coordination, the equatorial positions involving two carbonyl groups and a bond from the cyclobutene system, with the apical positions occupied by the third carbonyl group and the Fe–Fe bond. Even if one assumes that Fe^B is bonded to the two carbon atoms, rather than to the double bond, of the cyclobutene group (*vide infra*), it is clear from the known bond angles and distances[2] that the symmetry about Fe^B is considerably lower than that about Fe^A. These two inequivalent iron atoms give rise to four lines in the ^{57}Fe Mössbauer spectrum, shown in Figure 3, which also shows the spectra of the corresponding di-*t*-phosphine complexes. The solid curves represent least-squares computer fits to Lorentzian line shapes. Keeping in mind that, from the known molecular structure of (ffars)Fe$_2$(CO)$_6$, the quadrupole splitting for Fe^B should be appreciably greater than that for Fe^A, there are then three possible ways of assigning the spectral lines, *viz.:* (a) lines 1 and 2 to Fe^A, lines 3 and 4 to Fe^B (reading from left to right in Figure 3); (b) lines 1 and 3 to Fe^A, lines 2 and 4 to Fe^B; (c) lines 2 and 3 to Fe^A, lines 1 and 4 to Fe^B.

Assignment (a) can be ruled out on three grounds. First, this assignment requires both iron atoms to have only very slightly distorted octahedral symmetry (maximum splitting 0.43 mm sec^{-1}), which is not in accord with the X-ray data for the compound. Second, it leads to very large differences in isomeric shifts for the two iron atoms, whereas this parameter has been found to be fairly insensitive to formal oxidation state in low-spin iron compounds. Third, isomeric shifts for low-spin iron complexes have always been found to lie in the range 0.0–0.4 mm sec^{-1} (relative to sodium nitroprusside),[18] while this assignment would lead to typical values of about −0.28 and +0.79 mm sec^{-1}, respectively, for Fe^A and Fe^B.

On the basis of any one spectrum alone, assignment (b) cannot be dismissed with certainty, although it does imply that both iron atoms show very large and nearly equal distortions from octahedral symmetry, which does not seem plausible. However, the spectral shifts anticipated when the ligand is changed serve to eliminate this assignment as a possibility. Changing the ligand from ffars to ffos should result in a first-order effect on the isomeric shift for Fe^A and a considerably smaller effect on the shift for Fe^B. Furthermore, replacing the cyclobutene ring in ffos by the cyclopentene ring in f$_6$fos should result in very small changes in isomeric shift and quadrupole splitting for Fe^A and in the shift for Fe^B but could have an appreciable effect on the splitting for Fe^B. The only assignment which satisfies these criteria is (c) above, and we therefore conclude that lines 2 and 3 arise from Fe^A and lines 1 and 4 arise from Fe^B. The Mössbauer parameters derived from the spectra on the basis of this assignment are presented in Table V. δ is the isomeric shift (relative to sodium nitroprusside) and measures the total s-electron density at the iron nucleus. The quadrupole splitting Δ arises from the interaction between the electric field gradient at the iron nucleus and the nuclear quadrupole moment of the 14.4-keV level in ^{57}Fe. The parameter Γ is the full width at half-maximum of the resonance line.

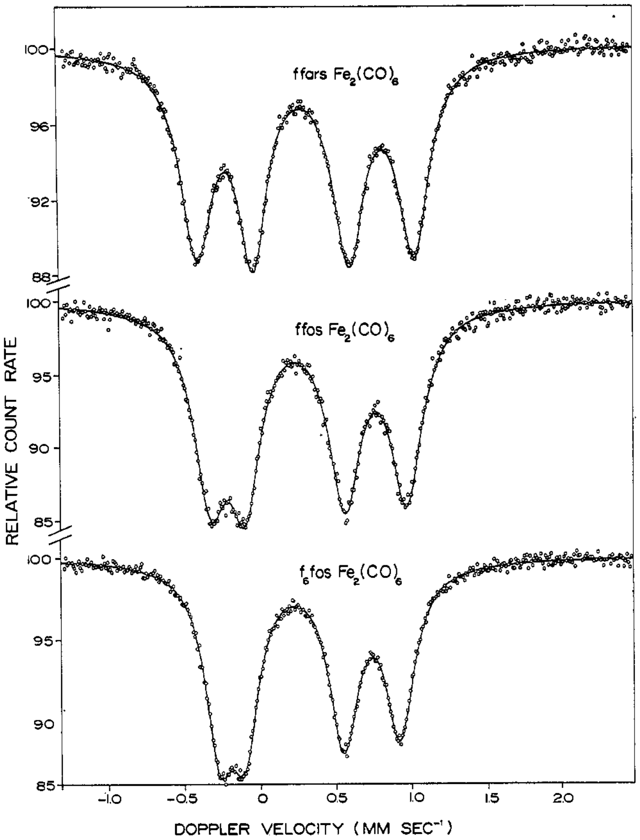

Figure 3.—Mössbauer spectra of LFe$_2$(CO)$_6$ compounds at 80°K.

Table V

Mössbauer Parameters for LFe$_2$(CO)$_6$ Compounds

Compound	Temp, °K	mm sec^{-1}			Iron atom
		$\delta^{a,b}$	Δ^a	Γ^a	
(ffars)Fe$_2$(CO)$_6$	80	0.28	0.64	0.25	A
		0.315	1.44	0.25	B
	295	0.21	0.70	0.25	A
		0.245	1.46	0.22	B
(ffos)Fe$_2$(CO)$_6$	80	0.23	0.66	0.26	A
		0.32	1.30	0.26	B
	295	0.16	0.68	0.27	A
		0.245	1.28	0.22	B
(f$_6$fos)Fe$_2$(CO)$_6$	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] Deviation ±0.01 mm sec^{-1}. [b] Relative to sodium nitroprusside.

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(17) Some crystals of a different morphology from that previously found for (ffars)Fe$_2$(CO)$_6$ were present in a sample of the complex prepared during the present investigation. These were separated by hand and found to have the same infrared and mass spectra as the bulk sample.

(18) L. May, Advances in Chemistry Series, No. 68, American Chemical Society, Washington, D. C., 1967, p 52.

In all three compounds Fe^B exhibits a larger value of the isomeric shift than does Fe^A, indicating a lower s-electron density at the former nucleus. It is tempting *a priori* to describe the Fe–Fe bonds 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. However, the Mössbauer results clearly show that there remains a deficiency in s-electron density at the Fe^B nucleus. Furthermore, the isomeric shifts for both iron atoms are considerably larger than those which have been observed in simple pentacoordinate iron carbonyl derivatives of the type $LFe(CO)_3$ (0.18–0.22 mm sec^{-1}),[19,20] in which the iron atom is clearly satisfying the effective atomic number rule. Of course, there are only 18 electrons donated to the two iron atoms in the present compounds, so this result is not unexpected.

The temperature dependence of the isomeric shifts is attributable to a second-order Doppler shift and has no chemical significance.

Note that replacement of the $(CH_3)_2As$ groups in ffars by the $(C_6H_5)_2P$ groups in ffos and $f_6$fos decreases the isomeric shift for Fe^A; *i.e.*, there is an increase in the s-electron density at this nucleus. This could be caused either by an increased 4s density or a decreased 3d density which would then lower the effective shielding of the s electrons from the nuclear charge and cause contraction of the s-electron wave functions. In simple chelate complexes of ffos and ffars, ffos appears to be the better π acceptor. It would therefore seem that the most likely explanation of the change in isomeric shift is a diminished 3d electron density about Fe^A arising from an increase in the metal-to-ligand back-π-donation.

One very interesting feature of the Mössbauer spectra of these compounds is the values of the quadrupole splittings observed for Fe^B. These are intermediate between the small splittings associated with distorted octahedral symmetry ($\lesssim$1.0 mm sec^{-1}) and the large splittings found for trigonal-bipyramidal configurations ($\sim$2.5 mm sec^{-1}). Splittings of this magnitude have been observed recently by Herber and coworkers[21] for $C_4H_4Fe(CO)_3$, $C_8H_8Fe(CO)_3$, and related compounds, in which the metal atoms are bonded to 1,3-diene systems. It has been suggested[22] that in such compounds, the iron-bonding orbitals adopt a quasi-octahedral configuration, with σ bonds to carbon atoms 1 and 4 of the 1,3-diene system and to the three carbonyl groups and a μ bond to the π system localized between carbon atoms 2 and 3 of the ring. On a similar basis,[23] Fe^B in the present compounds could be said to form six σ bonds: to Fe^A, to three carbonyl groups, and to two carbon atoms of the cyclobutene ring. This picture is consistent with the X-ray data for (ffars) $Fe_2(CO)_6$, in which the C—C distance (1.54 Å) in the cyclobutene ring is not significantly longer than the C=C length (1.51 Å).

There appears to be a definite trend in the quadrupole splitting of Fe^B as one changes the ligand from ffars to ffos to $f_6$fos. In the absence of detailed structural data for the latter two compounds, it is not feasible to attempt a detailed explanation of these effects. However, we might mention that the C–Fe^B–C angle in (ffars)$Fe_2(CO)_6$ is only 43°, and any widening of this angle in the phosphorus compounds, *e.g.*, by shortening the distance between Fe^B and the ring systems, would be expected to diminish the electric field gradient at Fe^B, thereby lowering the quadrupole splitting.

Finally, we should point out that the Mössbauer spectra of all three of these compounds show quite narrow lines. The line widths are appreciably smaller than those which have been reported for other iron carbonyl derivatives[20,24] and are not much greater than the minimum observable width of 0.19 mm sec^{-1}.

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