FLUOROALICYCLIC DERIVATIVES OF METALS AND METALLOIDS

W. R. Cullen

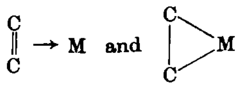
Chemistry Department, University of British Columbia, Vancouver, British Columbia, Canada

I. Introduction

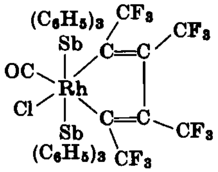
This article will be concerned with the preparation and properties of alicyclic fluorocarbon (fluoroalicyclic) derivatives of metals and metalloids. The discussion will be restricted to compounds containing the fluoroalicyclic ring sigma-bonded to elements other than carbon, nitrogen, oxygen, and the halogens, although inevitably the chemistry of some compounds from this latter group will need to be described. Complexes in which the metal or metalloid is part of a ring such as (**1**) (*160*) are excluded as are π complexes of fluoroalicyclic olefins which some authors regard as metallocyclopropanes as in (**2**) (*131*).*

---

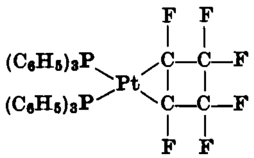
* The mode of bonding of olefins lies between the extremes represented by



(*130*). The latter is preferred by some workers (e.g., *24*, *131*) to describe the fluoroolefin case.



(1)



(2)

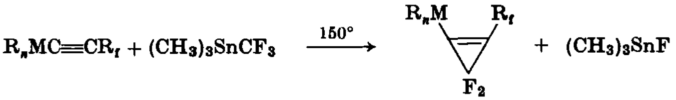
The general class of sigma-bonded fluorocarbon derivatives of metals and metalloids has been known for some time (*5*, *114*). Most of the early work was concerned with the chemistry of trifluoroiodomethane and the preparation of trifluoromethyl derivatives such as $(CF_3)_2Hg$ (*115*). Since then fluoroaliphatic derivatives of many transition metals have been prepared (*28*, *208*) and some interest has been shown in studying vinylic and acetylenic derivatives (*27*, *28*, *43*, *63*, *89*, *203*).

Some of the material presented in this review has been described previously (*62*). The present article is an updating of this work and, in particular, gives an account of the coordination complexes derived from fluoroalicyclic-bridged ditertiary phosphines and arsines.

II. Preparative Methods

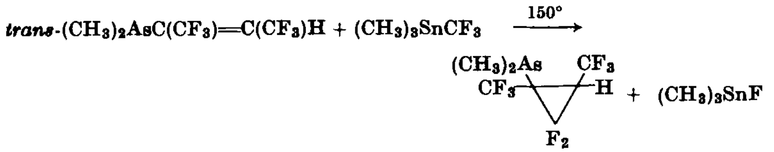
A. CARBENE AND CARBENOID ADDITIONS

The addition of a carbene ($R_2C:$) to a carbon–carbon double bond is a well-known source of cyclopropanes (*143*, *153*), and addition to a triple bond is a less extensively investigated route to cyclopropenes (*20*, *98*, *143*, *153*, *195*). Trimethyl(trifluoromethyl)tin acts as a source of difluorocarbene when heated in the gas phase at ~150°C (*45*). The carbene so produced adds stereospecifically to *cis*- and *trans*-butene-2, so it is probably in the singlet state (*87*, *153*). It also adds to vinylic and acetylenic derivatives of the Group IV and V elements to give the corresponding cyclopropene or cyclopropane derivative (*81*, *87*). Again these additions are probably stereospecific.



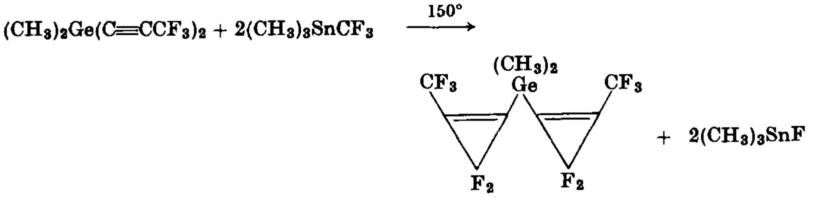
(1)

R = mainly CH_3, M = As, Si, Ge, Sn
R_f = mainly CF_3, also C_2F_5, and $CF(CF_3)_2$



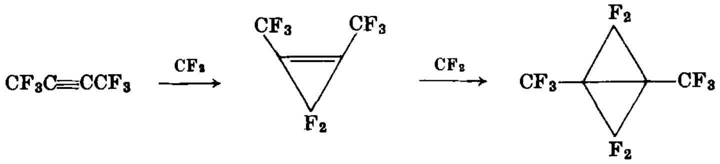
(2)

The yields in the thermal reactions [reactions (1) and (2)] are quite high, e.g., 84% in the case of $(CH_3)_3Ge\overline{C{=}C(CF_3)C}F_2$ but, not surprisingly, they are poor when addition of the carbene to a bisacetylide



(3)

is attempted. Further reaction of the cyclopropene products of reaction (1) with the carbene source does not seem to occur, even though Mahler (*161*) found that a bicyclobutane results when hexafluorobutyne-2 is heated with tris(trifluoromethyl)phosphorus difluoride. The phosphorus fluoride is another carbene source.



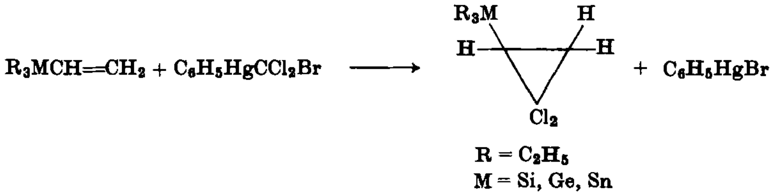
(4)

Other cyclopropyl derivatives, $(C_2H_5)_3M\overline{CHCH_2C}F_2$, have been obtained by reacting vinyl derivatives with a CF_2 source. In this investigation the carbene was generated by treating the trifluoromethyltin compound with sodium iodide (*198*).

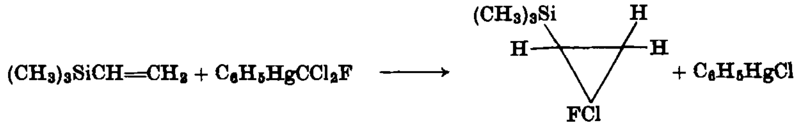
$$(CH_3)_3SnCF_3 + I^- \xrightarrow[80^\circ]{DME} (CH_3)_3SnI + CF_3^- \qquad (5)$$

$$CF_3^- \longrightarrow CF_2 + I^-$$

Seyferth and his co-workers have also extensively investigated mercurials as carbene sources (*194*), and have prepared dichloro- and chlorofluorocyclopropanes by either heating the mercurial with the Group IV vinyl derivative or by using an iodide displacement method as described in reaction (5) (*196*, *197*).

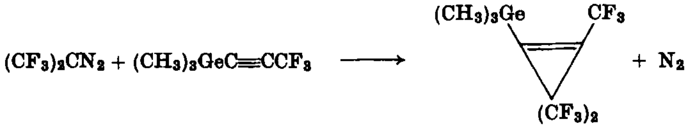


(6)

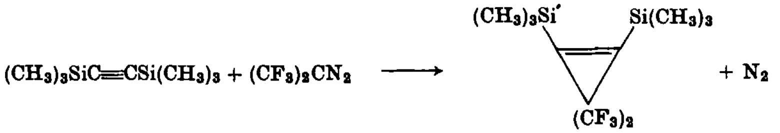


(7)

The reaction of nonfluorinated diazomethanes with unsaturated metallic species has received scant attention (*94*). In the fluorocarbon field it has been found that bis(trifluoromethyl)diazomethane, $(CF_3)_2CN_2$ (*129*), reacts with alkynyl derivatives to afford cyclopropenes (*79*, *88*).

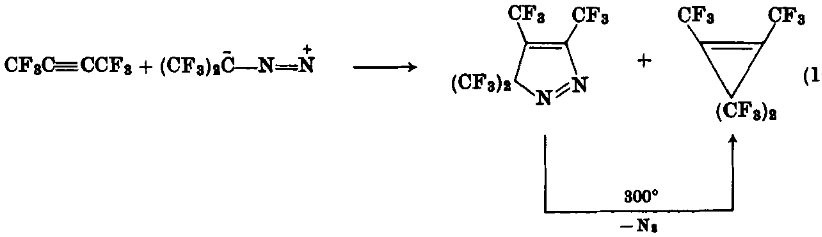


(8)



(9)

The product of reaction (8) can also be prepared by reacting the alkyne with bis(trifluoromethyl)diazirine, $(CF_3)_2\overline{C{-}N{=}N}$ (*88*). The yield of the bistrimethylsilyl derivative, the only known cyclopropene with two metalloid substituents, is low. It is possible that the free carbene $[(CF_3)_2C\!:]$ is involved in these reactions. An alternative path would allow 1,3-addition to form an isopyrazole which would then eliminate nitrogen, either thermally or photo-chemically, to give the cyclopropene. This is found in the thermal reaction of the diazomethane with hexafluorobutyne-2 (*88*).

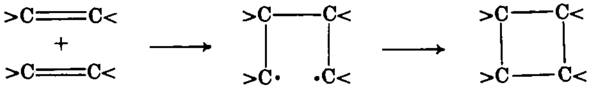


(10)

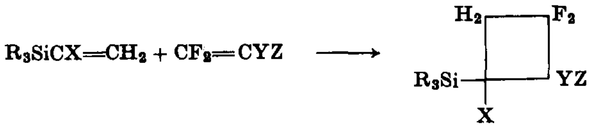
B. CYCLOADDITION REACTIONS

1. *The* [2 + 2] *Reaction*

Although the concerted [2 + 2] cycloaddition reaction of olefins to give a cyclobutane is disallowed (*218*), the reaction can still take place via a diradical intermediate (*7*, *181*, *187*, *206*). So far only silicon derivatives have been prepared by this procedure (*21*, *144*, *179*, *207*).



(11)



(12)

X = H (mainly), Cl
Y = F (mainly), Cl
Z = Cl (mainly), F

Reaction takes place at about 200°C and a free radical inhibitor is often added to improve yields which, on the whole, are quite good. Cyclization occurs in the sense shown in reaction (12). When geometric isomers are possible, for example, if X = Z = Cl, these are produced in approximately equal amounts. However, one isomer predominates when R = X = Z = Cl and Y = F (*80*).* It seems that the silyl groups activate the double bond with respect to addition (*179*), possibly by stabilizing the radical intermediate.

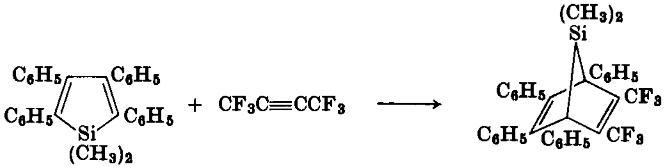
The related [2 + 2] addition of an acetylene to an olefin to give a cyclobutene is known for fluorocarbon systems (e.g., *161*). However, attempts to react fluoroalkynyl derivatives of metals such as $(C_2H_5)_3GeC{\equiv}CCF_3$ with fluoroolefins have not been successful (*81*).

2. *The* [2 + 4] *Reaction*

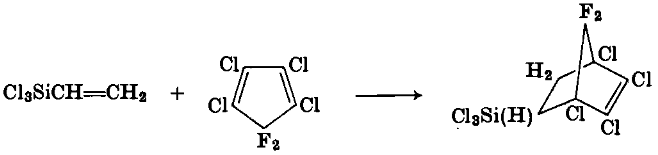
This cycloaddition reaction, the Diels–Alder reaction, is a thermal symmetry-allowed addition (*218*). It is a commonly studied reaction of fluorocarbons (e.g., *3*, *193*) and has been used to prepare hydrocarbon derivatives of metals and metalloids (e.g., *32*, *128*); however, only a few fluoroalicyclic derivatives of germanium and silicon have been obtained by this route (*145*, *184*).

---

* The cyclization of $CH_2{=}CHCl$ with $CF_2{=}CFH$ is apparently stereospecific (*181*).



(13)



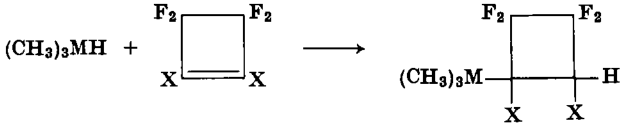
(14)

The germanium analog of the product of reaction (13) can probably be prepared by the same method. Reaction (14) is known for a variety of vinylsilanes and best yields are obtained if an Si–H bond is present.

C. Hydride Additions

1. *Additions without Elimination*

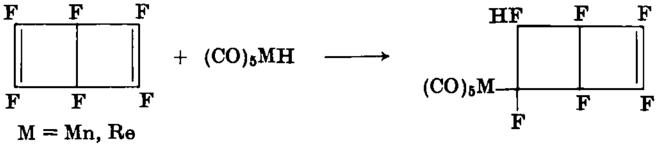
Addition of hydrides to fluoroolefins has been a fruitful source of fluorocarbon derivatives of many elements (*5*, *28*, *114*, *208*). In the case of fluoroalicyclic olefins the product is usually that which would be obtained from an "addition–elimination" sequence (*q.v.*). However, some of the adducts are stable. Thus, trimethylsilane, -germane, and -stannane add to fluorocyclobutenes to yield cyclobutanes (*82*, *136*).



(15)

$M = Ge; X = F, Cl$
$M = Si, Sn; X = F$

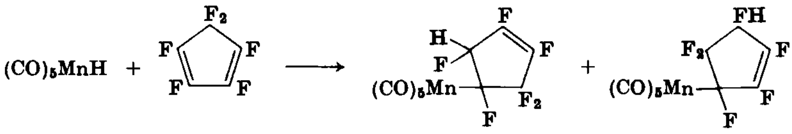
Some thiols react similarly (*65*, *186*), as do pentacarbonylmanganese and pentacarbonylrhenium hydrides (*16*, *50*).



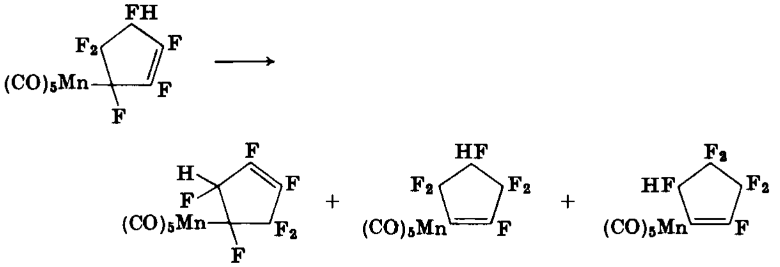
$M = Mn, Re$

(16)

The nuclear magnetic resonance spectra of the adducts of reaction (15) suggest that cis hydride addition occurs (*82*). However, pentacarbonylmanganese hydride apparently adds trans to hexafluorocyclopentadiene (*121*).


(17)

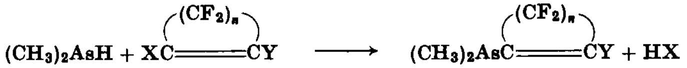
The 1,4-adduct is the major product of this reaction at –78°, but it is unstable and rearranges to the 1,2-adduct and cyclopent-1-enylmanganese derivatives on warming to 20°.


(18)

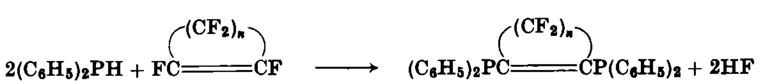
In the overall reaction the yield of pentacarbonyl-σ-(5*H*-hexafluorocyclopent-1-enyl)manganese is much lower (~10%) than that of the other two products of reaction (18).

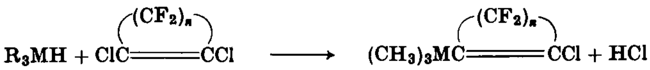
2. *Additions with Elimination*

This route has been a major source of fluoroalicyclic derivatives as summarized in the following equations (*39*, *40*, *44*, *56*, *65–67*, *69*, *75*, *82*, *124*, *136*, *165*, *168*, *185*, *186*, *200*, *201*).

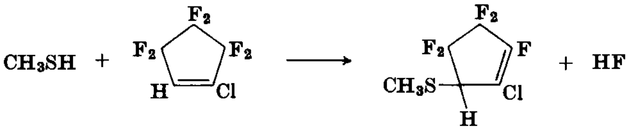

$$(CH_3)_2AsH + XC\overset{(CF_2)_n}{=\!=\!=}CY \longrightarrow (CH_3)_2AsC\overset{(CF_2)_n}{=\!=\!=}CY + HX \qquad (19)$$

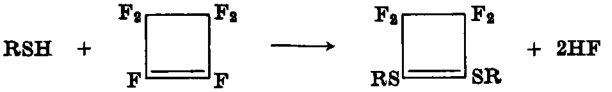
$Y = H, Cl, F, C_2H_5, As(CH_3)_2$; $X = Cl, F$

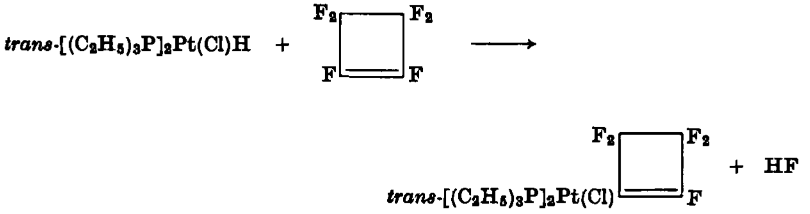

$$2(C_6H_5)_2PH + FC\overset{(CF_2)_n}{=\!=\!=}CF \longrightarrow (C_6H_5)_2PC\overset{(CF_2)_n}{=\!=\!=}CP(C_6H_5)_2 + 2HF \qquad (20)$$


$$R_3MH + ClC\overset{(CF_2)_n}{=\!=\!=}CCl \longrightarrow (CH_3)_3MC\overset{(CF_2)_n}{=\!=\!=}CCl + HCl \qquad (21)$$

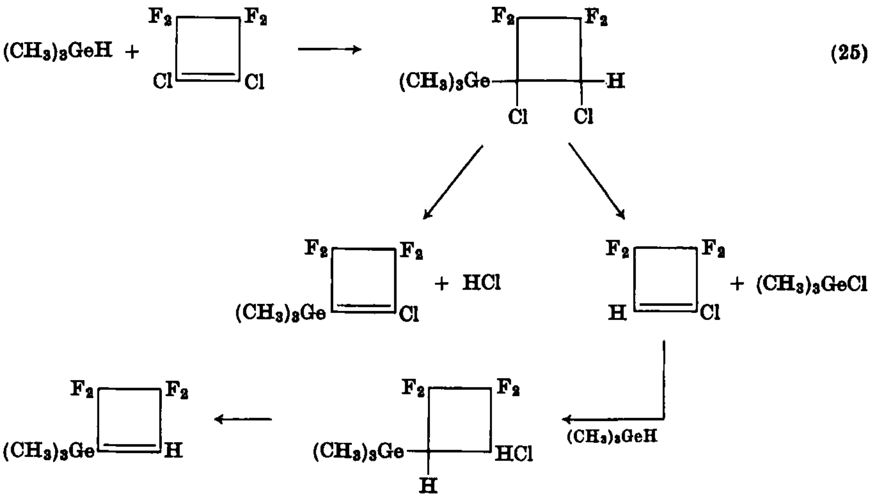
$M = Si, Ge$


(22)


(23)

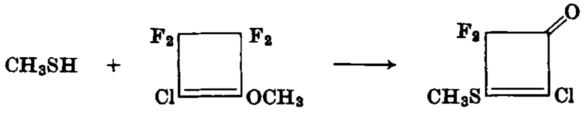

(24)

In the reactions of thiols, silanes, and germanes [reactions (21)–(23)] both 1,1-adducts and HX eliminated products are obtained suggesting that the former are precursors of the latter. In some cases elimination of hydrogen fluoride is preferred over hydrogen chloride so vinylic substitution need not be the end result as is shown in reaction (22). It should also be pointed out that elimination of metal halides can also occur and in the case of trimethylgermane the resulting reduced cyclobutene apparently reacts further (*82*).


(25)

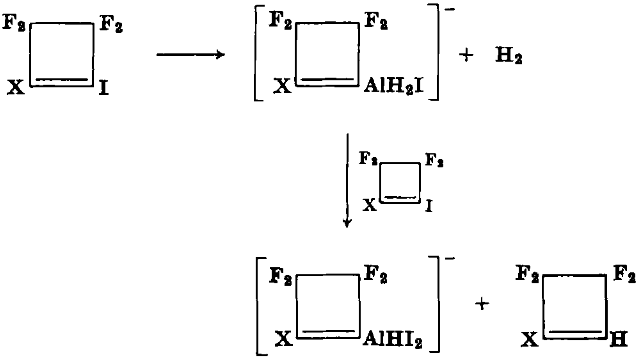
All the germanium-containing products were isolated in this investigation. The rate of the arsine reactions [reaction (19)] depends on the electronegativity of X and Y, but no intermediates were detected (*66*, *69*). The product reacts further with dimethylarsine to give a ditertiary arsine when X = Y = F and n = 2, 3, or 4 (*40*). Diphenylphosphine displaces both vinylic fluorine atoms [reaction (20)] to give the ditertiary phosphine (*67*, *75*, *200*), but monosubstitution is found when vinylic chlorine atoms are present and if the reaction is carried out in DMF (*200*, *201*). Dialkylphosphines have a greater tendency to give monosubstituted products (*65*). Mixed derivatives are available by reacting the arsine products of reaction (19) (Y = F) with diphenylphosphine (*40*, *56*). The ease of these substitution reactions decreases as the ring size increases, a result which may be related to ring strain (*200*, *202*).

When the ring has a methoxy substituent, reaction with a thiol or a secondary amine gives a cyclobutenone (*67*, *102*).



(26)

An addition–elimination sequence is believed to take place when fluorocyclobutenes containing a vinylic iodine atom are reduced by lithium aluminum hydride (*30*).



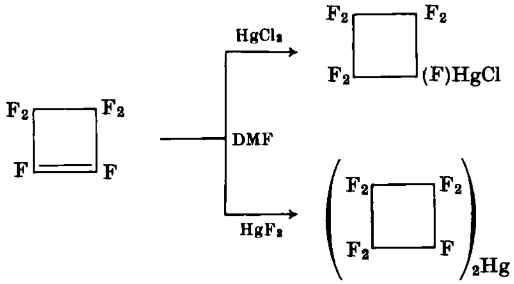
(27)

The first intermediate is formed by attack of the eliminated hydrogen iodide on the initially formed $R_fAlH_3^-$.

Reactions such as reaction (24) (*44*) involving transition metal hydrides have been little investigated. It seems that manganese pentacarbonyl hydride does not react with perfluorocyclopentene or the products of reaction (18) (*121*).

D. METAL–FLUORIDE ADDITIONS

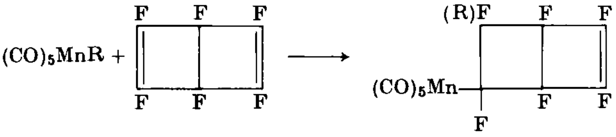
The addition of metal fluorides to fluoroolefins and acetylenes is a useful source of fluorocarbon derivatives (*103*, *170*), but the reaction has had limited application to cyclic fluoroolefins (*104*).



(28)

E. Metal–Alkyl and Metal–Aryl Additions

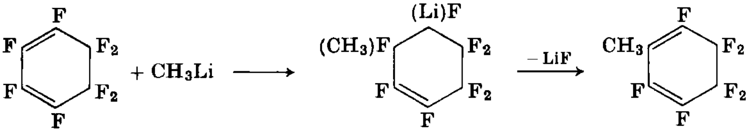
In the general fluorocarbon field only compounds with Mn–R and Pt–R bonds (R = alkyl or aryl group) have been extensively investigated with respect to their addition reactions with olefins and acetylenes (*43*, *167*, *217*). Two additions to hexafluoro(Dewar)benzene have been described (*16*).



(29)

R = CH_3, C_6H_5

Lithium derivatives have been postulated as the intermediates in the reaction of lithium alkyls with fluoroolefins or diradicals (e.g., *35*, *47*, *199*). (See also reaction (57) in Section III.)



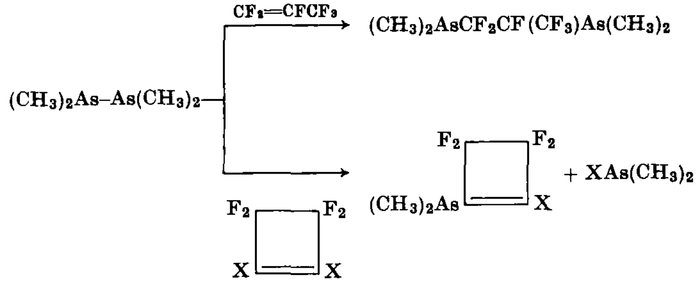
(30)

Similar additions followed by elimination of metal halide are believed to be involved in the reduction of cyclic fluoroolefins with lithium aluminum hydride (e.g., *47*) and alkali metal alkoxides (e.g., *46*). Thus, these reactions can be regarded as involving unstable aluminum and alkali metal fluoroalicyclic derivatives.

F. REACTIONS WITH COMPOUNDS CONTAINING METAL–METAL BONDS

In this section the phrase "metal–metal bond" is used to include such diverse reagents as $(CH_3)_2As\text{–}As(CH_3)_2$, C_6H_5SCu, and $(\pi\text{-}C_5H_5)Fe(CO)_2Na$.

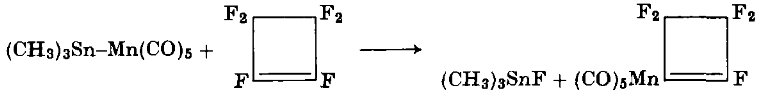
Tetramethyldiarsine readily adds to fluoroolefins and fluorocarbonacetylenes—a reaction that is a useful source of chelating ditertiary arsines (*61*, *77*, *86*). However, when cyclic fluoroolefins are used the product is that which would be expected from an addition–elimination sequence (*69*).



(31)

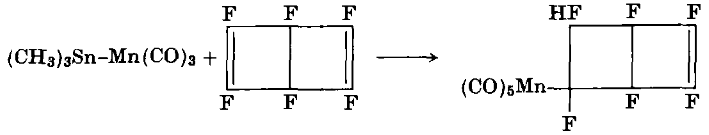
X = Cl, F

Hexamethylditin does not react with fluorocyclobutenes (*82*), but the Sn–Mn bond in trimethyltin(pentacarbonyl)manganese is more easily cleaved (*15*). Trimethyltin fluoride is eliminated in a reaction analogous to reaction (31).



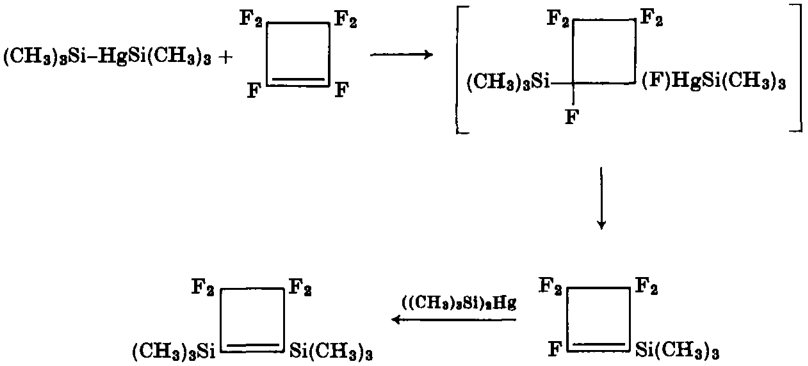
(32)

A saturated product is obtained from the reaction of the same tin–manganese compound with hexafluoro(Dewar)benzene (*16*).



(33)

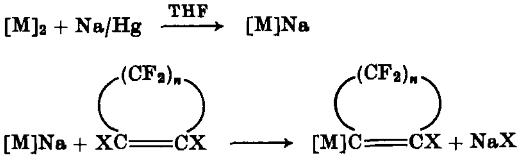
When perfluorocyclobutene and bis(trimethylsilyl)mercury are irradiated, the products are trimethylsilyl fluoride, mercury, and cyclobutenyl derivatives of silicon (*122, 123*).



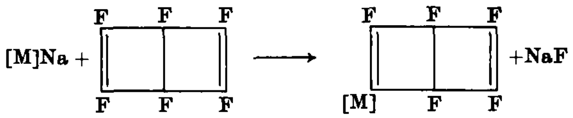
(34)

These reactions are believed to proceed through adducts like the one shown. Similar intermediates have been detected in additions to acylic fluoroolefins.,

Reactions involving metal carbonyl anions have been the most fruitful means of obtaining fluoroalicyclic derivatives of the transition metals. The tetrahydrofuran (THF) solutions of the anion are treated with the fluoroolefin and monosubstitution takes place in good yield (*6, 16, 26, 50, 148*).



(35)



(36)

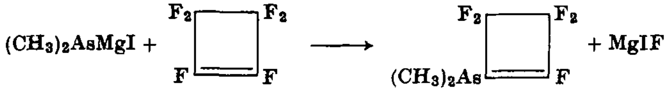
$M = (\pi\text{-}C_5H_5)Fe(CO)_2, (CO)_5Mn, (CO)_5Re, (C_6H_5)_3P(CO)_4Mn$

Disubstitution does not occur. In one investigation (*26*) the saturated

1,2-tetrachlorocyclobutane was used; the product was the same as from reaction (35), but the yields were much lower.

Although the sodium derivative of di-*n*-butylphosphite failed to react with 1-chloroheptafluorocyclopentene at 20°C (*124*) an arsino-Grignard reagent gave the expected product when treated with perfluorocyclobutene. This is only of academic interest since the hydride precursor to the Grignard reagent also reacts to give the same product [cf. reaction (19)] (*69*).

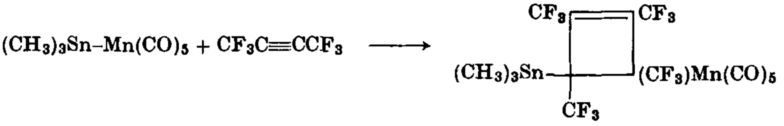
$$(CH_3)_2AsH + CH_3MgI \longrightarrow (CH_3)_2AsMgI + CH_4$$



(37)

Copper derivatives RSCu ($R = C_6H_5$, $C_6H_5CH_2$) have been used to prepare disubstituted fluoroalicyclic derivatives from 1,2-dichlorocycloolefins (*120*).

Clark and co-workers (*15*) have suggested that the reaction of hexafluorobutyne-2 with trimethyltin(pentacarbonyl)manganese gives a product which can be regarded as the adduct of the Sn–Mn compound with the dimer of the butyne [a cyclobutadiene, cf. reaction (49)].

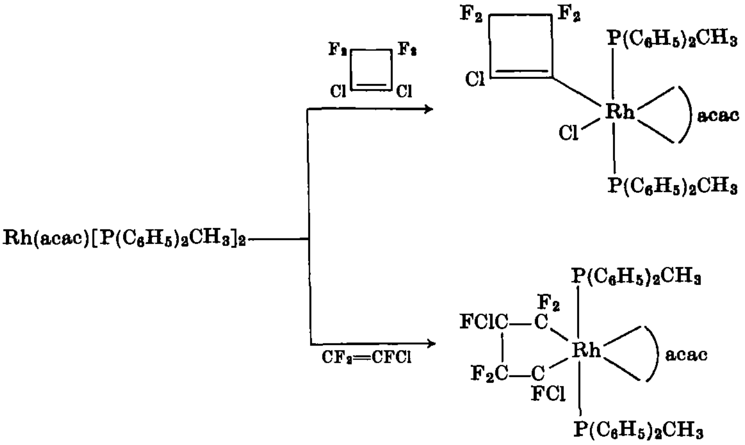


(38)

However, it is possible that an adduct with the butyne is first formed which then undergoes a [2 + 2] cycloaddition with more butyne.

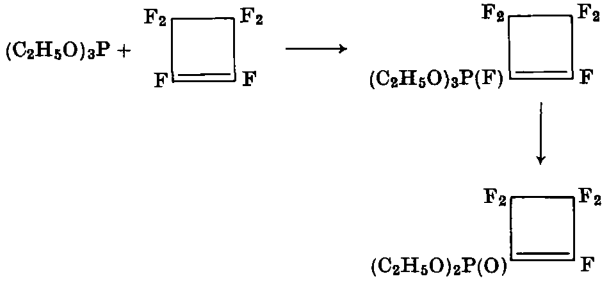
G. Oxidative Addition Reactions

In the transition metal field the oxidative addition of, say, alkyl halides to derivatives of metals with a d^8 configuration has been exhaustively studied (*49*). However, there is only one report (*173*) of a reaction of this type leading to a fluoroalicyclic derivative. Fluoroolefins usually act as two electron donors or dimerize to give metallocyclopentane rings as is also shown in reaction (39).



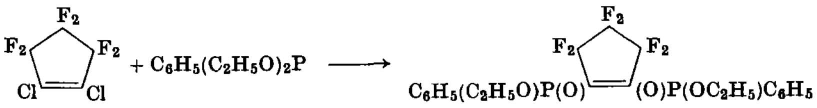
(39)

Triethylphosphite interacts with hexafluorocyclobutene to give a five-coordinate phosphorus compound, which on heating undergoes an Arbusov reaction to the phosphonate (*155*).

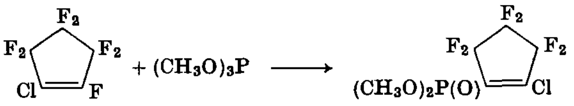


(40)

Presumably intermediates of this sort are involved when other phosphites react with fluorocycloolefins (*124–127, 154, 155*). The following are typical examples.



(41)

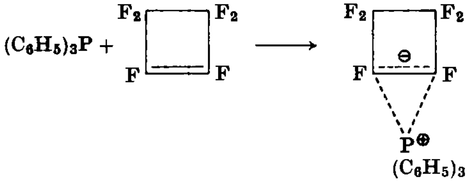


(42)

Frank (*124–127*) found that disubstitution occurs when 1,2-dichloroolefins are involved, but that monophosphonates can be obtained from

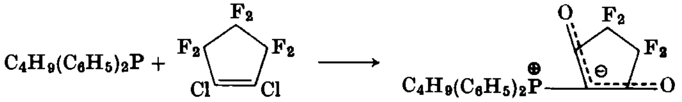
1-chloro-2-fluoroolefins. The vinylic chlorine atom of the product of reaction (42) can be replaced by further treatment with phosphite.

A 1 : 1 adduct which can be formulated as a nonclassical dipolar species is formed when triphenylphosphine and perfluorocyclobutene interact (*202*).



(43)

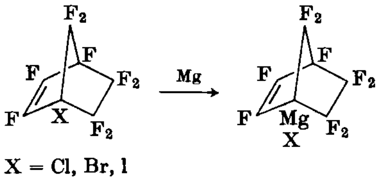
The intermediate is hydrolyzed to a phosphobetaine. Other alicyclic fluoroolefins react with tertiary phosphines in acetic acid/water solution to give phosphobetaines directly, presumably via an initially formed 1,1-adduct.



(44)

H. Direct Reaction with a Metal

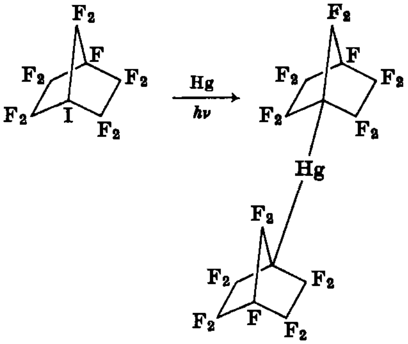
Apart from vinylic Grignard reagents, magnesium derivatives are not well known in acyclic fluorocarbon chemistry (*5*, *114*). However, a number of fluoroalicyclic Grignard reagents derived from bicyclic systems are accessible by direct reaction of magnesium with the appropriate halogen derivative (*33*–*36*).



(45)

Saturated analogs of the products of reaction (45) are known, as are derivatives with hydrogen at the other bridgehead position. A saturated bicyclic derivative with two MgBr groups, one at either bridgehead position, has been reported.

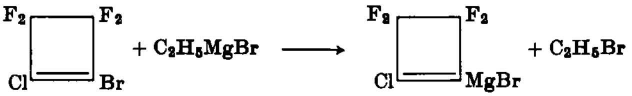
Although the reaction of trifluoroiodomethane with mercury and other elements was one of the first to be studied in this field of chemistry (*5*, *114*), the corresponding fluoroalicyclic derivatives have been little investigated in this respect. Park and his co-workers (*178*) have obtained uncharacterized products from the reaction of $I\overline{C{=}CClCF_2C}F_2$ with mercury. Bis(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury is obtained when 1-iodoundecafluorobicyclo[2,2,1]heptane and mercury react under the influence of ultraviolet light (*35*).



(46)

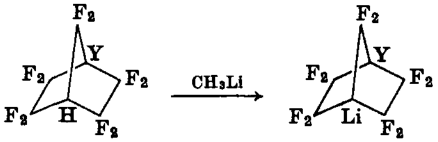
I. Exchange Reactions

These have been used to prepare magnesium and lithium fluoroalicyclic derivatives. Halogen exchange affords cyclobutenyl and cyclopentenyl derivatives (*179*, *180*, *182*, *203*). Electropositive halogens normally need to be present for these reactions, otherwise substitution occurs.* However, a recent report (*177*) describes how even 1,2-dichlorofluorocycloolefins are lithiated by *n*-butyllithium.



(47)

Hydrogen exchange with methyllithium affords lithium derivatives of cyclobutene, cyclopentene, and cyclohexene (*37*). This method also yields lithium derivatives of the bicyclic systems studied by Tatlow and co-workers (*33–35*, *199*).



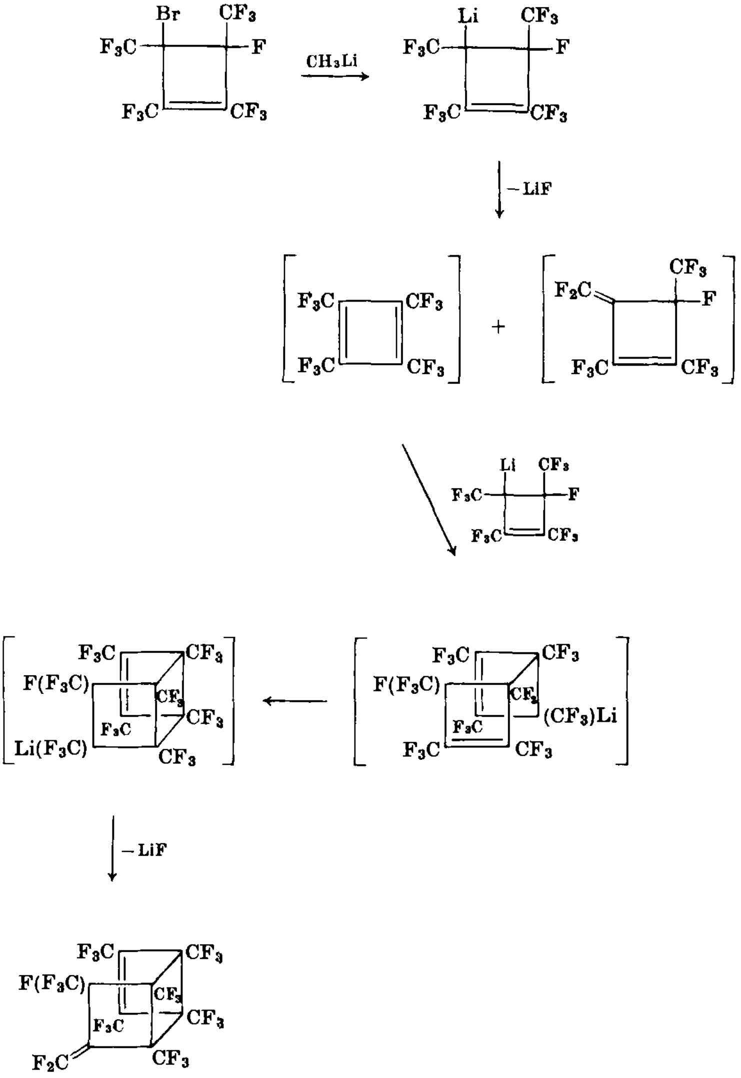
Y = F, H, CF_3

(48)

---

* Presumably substitution takes place via an addition–elimination process which would involve the formation of magnesium fluoroalicyclic intermediates (see Section II, E).

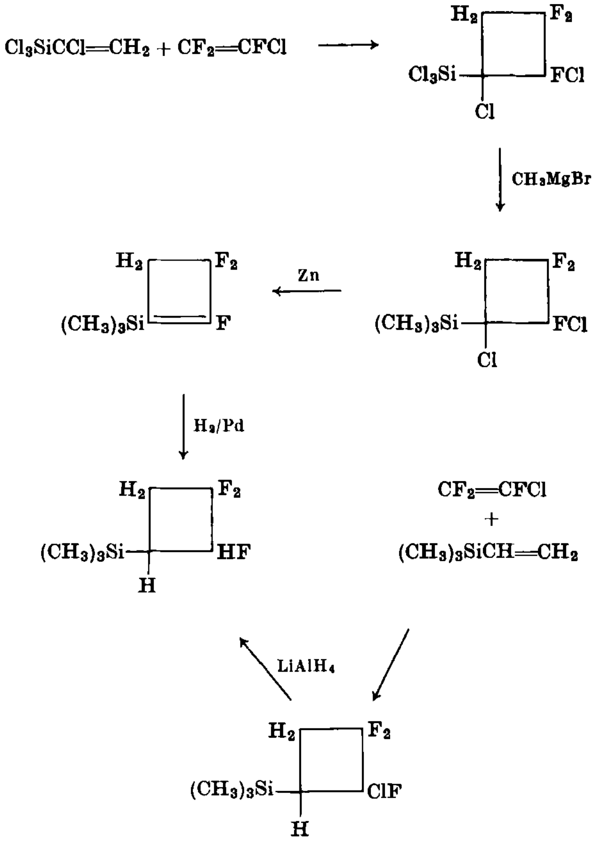
An unstable lithium derivative is probably involved as an intermediate in the synthesis of the unstable tetrakis(trifluoromethyl)-cyclobutadiene (*169*). The cyclobutadiene was not isolated, but its existence was inferred from the products actually obtained. For example,



(49)

J. PREPARATION BY MODIFICATION OF EXISTING FLUOROALICYCLIC DERIVATIVES

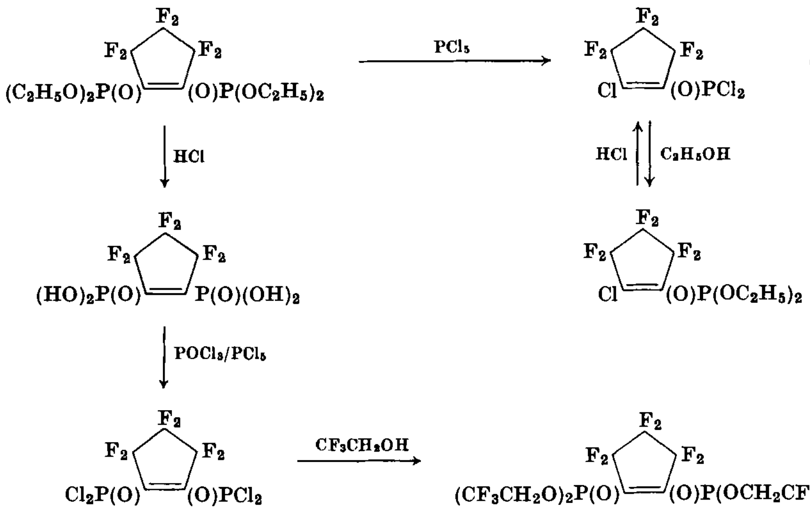
Park and co-workers (*179*) established the direction of their [2 + 2] cycloaddition reactions (Section II,B,1) by a series of interconversions, some of which are shown in the scheme below.



(50)

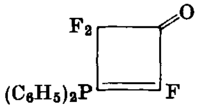
Base-assisted elimination of hydrogen chloride from a silylcyclobutane has also yielded a cyclobutene (*144*).

Frank (*124–127*) found that the phosphonate products of reactions such as reactions (41) and (42) also undergo a number of reactions which have synthetic potential [reaction (50a)]. The initial cleavage by PCl_5 was developed in order to obtain monophosphonates. These, as shown above [reaction (41)], are also available by treating phosphites with 1-chloro-2-fluorocycloolefins.

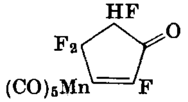


(50a)

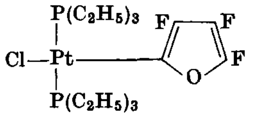
As previously described [reaction (44)], phosphobetaines are obtained from the hydrolysis of some phosphorus compounds (*202*). The butenone (**3**) seems to be one of the products obtained when tetraphenyldiphosphine is heated with perfluorocyclobutene (*65*).



(**3**)



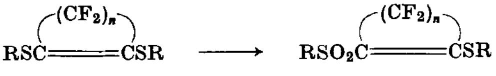
(**4**)



(**5**)

A similar hydrolysis product (**4**) can be isolated from the reaction described by reactions (17) and (18) (*121*). Cherwinski and Clark (*39*) have found that heating *trans*-$[(C_2H_5)_3P]_2PtCl(\overline{C{=}CFCF_2C}F_2)$ with water in the presence of silicon tetrafluoride produces the cationic carbonyl salt *trans*-$\{[(C_2H_5)_3P]_2PtCl(CO)\}^+SiF_5^-$ (*42*) together with a compound of formula *trans*-$[(C_2H_5)_3P]_2PtCl(C_4F_3O)$. The latter could be a butenone analogous to (**3**), but spectroscopic evidence favors the structure (**5**).

Oxidation of bis-sulfides with potassium permanganate affords sulfones in good yield (*120*).

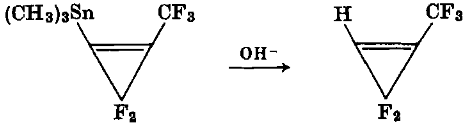


$$\overbrace{RSC{=\!=\!=}CSR}^{(CF_2)_n} \longrightarrow \overbrace{RSO_2C{=\!=\!=}CSR}^{(CF_2)_n} \qquad (51)$$

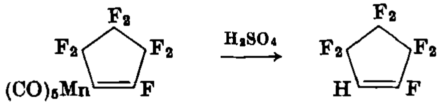
$n = 2, 3, 4$; R = aliphatic or aromatic

III. Other Chemical Properties

On the whole, the properties of the fluoroalicyclic derivatives resemble those of their better known acyclic analogs (*5*, *114*). Thus, hydrolysis usually results in liberation of the fluorocarbon group (e.g., *6*, *87*) (see the preceding Section II, for some exceptions).

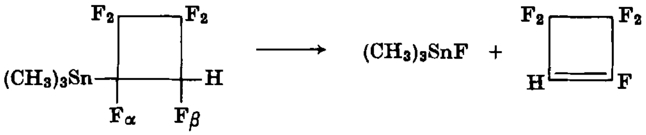


(52)



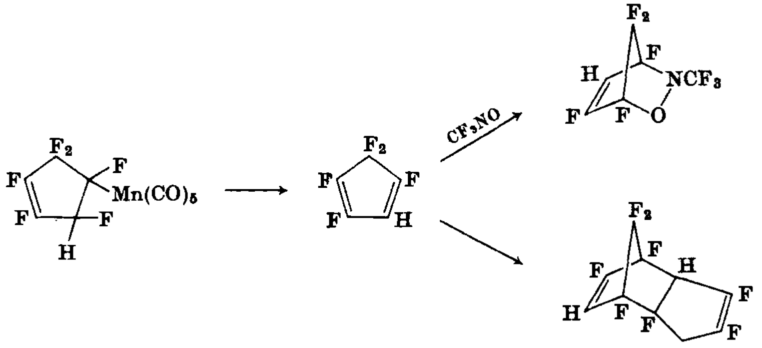
(53)

As previously mentioned in connection with the preparation of cyclopropenes (Section II,A), trimethyl(trifluoromethyl)tin acts as a difluorocarbene source when heated, the other product being trimethyltin fluoride (*45*). Although other acyclic fluorocarbon–tin derivatives appear to be more stable (*85*), the 1,1-adduct of trimethyltin hydride and perfluorocyclobutene slowly decomposes at 20° as follows (*82*):



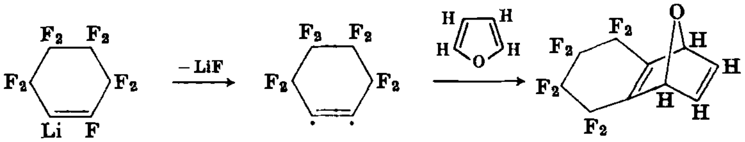
(54)

The initial hydride addition is believed to take place cis to the double bond, thus the mechanism of decomposition is possibly abstraction of F_α by the tin atom to form a carbene followed by hydrogen migration to yield the cyclobutene. Both α and β elimination have been proposed for similar reactions involving silicon compounds (e.g., *12*, *95*) and in the reactions described by reactions (54) and (25) no distinction between these two possibilities can be made at the moment. A β elimination is believed to take place when one of the products of reaction (18) is heated. The resulting unstable diene can be trapped with CF_3NO, otherwise it dimerizes (*121*).



(55)

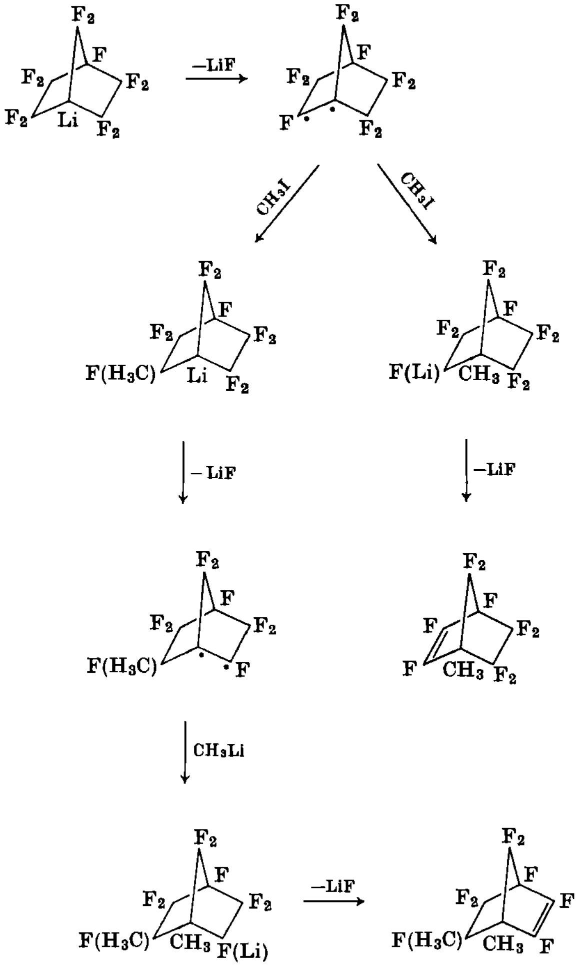
The thermal stability of other fluoroalicyclic derivatives of Groups IV and V and the transition metals is quite high and even the cyclopropenes are stable. Apart from the mercury compounds, the derivatives of other elements exist only in solution and most are unstable. Here again there is a rough parallel with their acyclic analogs. The lithium and magnesium compounds, in particular, have a tendency to eliminate metal halide (*34*, *35*, *37*, *199*, *203*), often with the transient existence of cyclohexyne and bridgehead olefin intermediates (both may be equally well represented as diradicals). A related sequence (49) has previously been mentioned.



(56)

The diradicals can be trapped by, for example, furan as in reaction (56). In other cases their existence is inferred from the products obtained from, for example, their thermal decomposition in the presence of methyllithium as in reaction (57). Note that these addition–elimination sequences suggest the formation of a number of new lithium intermediates. The stability of 1-lithio derivatives such as the initial reactant of (57) is a function of the group at the other bridgehead position. This stability is in the order F < H < CF_3, which is not the order of acidity found in the 1*H* species (*199*).

Apart from these eliminations the lithium and magnesium fluoroalicyclic derivatives react normally with the usual reagents such as aldehydes, carbon dioxide, and halogens (*34*, *35*, *177*, *199*) and, thus, offer a very convenient route to other derivatives. Many of these reactions are not possible in hydrocarbon chemistry. In some cases reaction of 1*Li*-4*H*-decafluorobicyclo[2.2.1]heptane leads to 1,4-disubstituted products. This is believed to be due to lithium–halogen and lithium–hydrogen exchange (*34*).



(57)

The manganese pentacarbonyl derivatives $(CO)_5Mn\overline{C{=}CF(CF_2)_nC}F_2$ ($n = 2$, 3) react with triphenylphosphine to give both cis and trans isomers of $[(C_6H_5)_3P](CO)_4Mn\overline{C{=}CF(CF_2)_nC}F_2$ (*6*, *148*), whereas reaction of the perfluoroolefins with $[(C_6H_5)_3P](CO)_4Mn^-$ yields only the trans compounds.

IV. Physical Properties

The transition metal derivatives are all solids; those of the main group elements are mainly liquids. The only physical properties of the compounds which have been studied to any extent are their infrared and nuclear magnetic resonance (NMR) spectra which have proved to be useful in characterizing the derivatives.

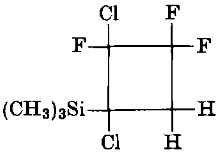
The infrared spectra of the cyclopropenes $R_nMC{=}C(R_f)CF_2$ show a strong band in the region 1758–1733 cm^{-1}. This can be assigned to $\nu(C{=}C)$; however, it involves considerable contributions from normal skeletal modes and substituent vibrations (*48*, *216*). When the cyclopropene has CF_3 groups in the 3-position, $\nu(C{=}C)$ is increased. For example $(CH_3)_3GeC{=}C(CF_3)C(CF_3)_2$ absorbs at 1837 cm^{-1} (*88*) and the bistrimethylsilyl compound $(CH_3)_3SiC{=}C(Si(CH_3)_3)C(CF_3)_2$ [reaction (9)] has one of the highest frequencies noted for this absorption (*79*), in spite of the observation (*211*) that electropositive groups in the vinylic position lower the frequency.

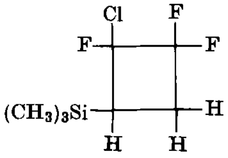
The monosubstituted derivatives $R_nMC{=}CFCF_2CF_2$ have $\nu(C{=}C)$ in the region 1623–1662 cm^{-1} and this does not change much with increase in ring size. The same is true for the chloro compounds $R_nMC{=}CCl(CF_2)_nCF_2$ which have $\nu(C{=}C)$ at a lower frequency (~1575 cm^{-1}). The unsubstituted perfluorocycloolefins have $\nu(C{=}C)$ at higher frequencies, e.g., $FC{=}CF(CF_2)_2CF_2$ absorbs at 1754 cm^{-1}. Thus, the presence of an absorption at 1745 cm^{-1} in one of the products of reaction (18) is good evidence for the proposed 1,2-addition.

Symmetrically substituted compounds such as the diphosphonates and the ditertiary arsines and phosphines show little double-bond absorption. The intensity of the absorption increases somewhat when the substitution is unsymmetrical (*40*).

Little can be said about other regions of the infrared spectra. The most intense features are the C–F vibrations which, within a particular series of compounds, have a characteristic pattern. The presence of a vinylic fluorine atom is usually indicated by a strong absorption at the high-energy end (~1370 cm^{-1}) of the C–F stretching region.

The NMR spectra of all the derivatives are as expected and can often be interpreted on a first-order basis. Exceptions to this are the silylcyclobutanes. Cyclobutanes can be either bent or planar (e.g., *38*, *163*, *219*). As a result of a study of the NMR spectra of fluorocyclobutanes Lambert and Roberts (*156*) suggested that two types of conformational equilibria are possible in solution at 30°, planar ⇌ bent and bent ⇌ bent, but in both cases bulky groups preferentially occupied "equatorial" positions. The NMR spectra of other fluorocyclobutanes have also been interpreted in terms of conformational equilibria (e.g., *116, 138, 174, 181*). The spectra of the silylcyclobutanes (**6**) and (**7**) have been studied with the aid of heteronuclear decoupling (*80*).

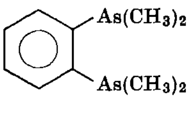

(**6**)

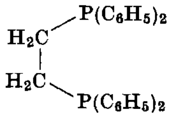

(**7**)

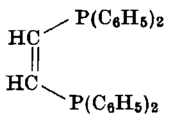
If certain assumptions are made, for example, that $^{3}J_{\mathrm{HF}}$ couplings follow a Karplus type of dependence, it follows that (**7**) exists predominantly in the conformer having the bulky trimethylsilyl group equatorial. The trimethylsilyl methyl groups apparently couple with the fluorine atoms in the ring only when the trimethylsilyl and fluorine groups are cis to each other. However, when this information is used to establish the preferred conformation of (**6**) an axial preference of the trimethylsilyl group is indicated. These results indicate the difficulty of interpreting the spectra of cyclobutanes and although the NMR spectra of the 1,1-adducts of reaction (15) indicate that addition is cis to the double bond, this is by no means certain (*82*).

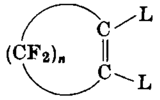
V. Coordination Complexes

The complexing abilities of ditertiary arsines and phosphines such as (**8**) (diars) and (**9**) (diphos) have been much investigated (*17, 31, 100, 137, 162*). However, until recently analogs with unsaturated bridging groups such as (**10**), which could conceivably also use their double bond in complex formation, were unknown and unstudied. Several groups are now working in this area (*1, 10, 117, 118, 151, 159*). The fluoroalicyclic bridged ditertiary arsines and phosphines (**11**) and their unsymmetrical analogs (**12**) whose preparations have been described in Section II,C,2


(**8**)

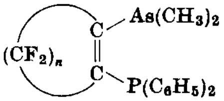

(**9**)


(**10**)



(11)

(11a) L = $(CH_3)_2As$, $n = 2$, **f$_4$fars**
(11b) L = $(CH_3)_2As$, $n = 3$, **f$_6$fars**
(11c) L = $(CH_3)_2As$, $n = 4$, **f$_8$fars**
(11d) L = $(C_6H_5)_2P$, $n = 2$, **f$_4$fos**
(11e) L = $(C_6H_5)_2P$, $n = 3$, **f$_6$fos**
(11f) L = $(C_6H_5)_2P$, $n = 4$, **f$_8$fos**



(12)

(12a) $n = 2$, **f$_4$AsP**
(12b) $n = 3$, **f$_6$AsP**
(12c) $n = 4$, **f$_8$AsP**

also have an unsaturated bridging group. Other interesting features of these molecules are the electronegative bridging groups which could enhance any π-acceptor properties of the ligands (*54*, *100*),* and the possibility of varying the "bite" of the ligand, i.e., the direct donor-to-donor distance, by varying the ring size.

The fluorocarbon bridged ligands (**11**) and (**12**) interact with metal halides and metal carbonyls to give a variety of products in which the ligand is monoligate, biligate, triligate, or even rearranged, and these complexes are described in the next sections. It should be pointed out that where more extensive studies have been made the products actually isolated are very dependent on the reaction conditions. Thus, the reaction of f_4AsP (**12a**) with $Fe(CO)_5$ at 80° yields $f_4AsPFe(CO)_4$, at 150° $f_4AsPFe_2(CO)_6$, and under ultraviolet irradiation $f_4AsPFe_2(CO)_8$. Reaction of the same ligand with $Fe_3(CO)_{12}$ yields as major products $f_4AsPFe_3(CO)_{10}$, $f_4AsPFe_3(CO)_9$, and $f_4AsPFe_2(CO)_6$, or $(f_4AsP)_2Fe_2(CO)_4$ and $(f_4AsP)_2Fe(CO)_3$ depending on the ratio of reactants (*40*).

A. MONOLIGATE COMPLEXES

In spite of the presence of two potential donor atoms on the fluorocarbon-bridged ligands (**11**) and (**12**) and their similarity to the hydrocarbon-bridged analogs (**8**) and (**9**), there is a surprising tendency of some of the former class to yield complexes in which they are monoligate.

---

* This makes the assumption that in a coordination complex the bond between the phosphorus (or arsenic) atom and the metal has two components: (*i*) a sigma component arising from donation of the lone pair on the phosphorus (or arsenic) to a suitable acceptor metal orbital and (*ii*) a synergic back donation from filled metal orbitals (of mainly *d* character) into vacant orbitals of mainly *d* character on the donor atom. This back-bonding concept is a useful model for rationalizing a number of results, although it is by no means universally accepted (e.g., *2*, *210*, *220*).

This is especially true for derivatives containing the cyclobutene ring and may be an indication that the bite of the ligand, which would be expected to be at maximum for the small ring and for compounds with $(CH_3)_2As$ groups because of the greater exocyclic angles and As–C bond distances, is such as to discourage chelation. However, as will be pointed out below, the bite of a ligand is very dependent on the type of complex formed and, hence, the geometry cannot be the only reason for the reluctance of, say, $f_4$fars (**11a**) to chelate.

When a petroleum ether solution of $f_4$fars and $Fe(CO)_5$ is irradiated with ultraviolet light, a yellow complex $f_4farsFe(CO)_4$ is obtained (*74*). Mild reaction conditions also afford $f_4fosFe(CO)_4$, $f_4AsPFe(CO)_4$, and in low yield $(f_4AsP)_2Fe(CO)_3$ and $f_6AsPFe(CO)_4$ (*40*, *72*, *74*). The (L–L)Fe-$(CO)_4$* derivatives have infrared spectra similar to the three-band pattern reported for compounds such as $(C_6H_5)_3PFe(CO)_4$ (*53*), which is indicative of apical substitution in a trigonal bipyramid. The parent pentacarbonyl has this trigonal-bipyramidal structure (*8*, *101*). In the cases where (L–L) = $f_4$fos, f_4AsP, and f_6AsP, the asymmetry of the ligand results in an overall C_s symmetry for the molecule and an extra band appears presumably because of splitting of the E mode in a C_{3v} spectrum (*74*). In the case of $f_4AsPFe(CO)_4$ it is apparent that it is the phosphine end of the molecule that is coordinated, since the NMR spectrum of the complex shows that the chemical shift of the $(CH_3)_2As$ moiety is virtually unaltered on complexing. The free ligand has an absorption at 1.33 ppm and the complex at 1.25 ppm.† If coordination through the arsenic occurred the resonance would shift downfield by ~0.5 ppm (*10*, *74*, *176*). This is seen in the spectrum of $f_4farsFe(CO)_4$, where the free ligand absorbs at 1.36 ppm and the complex at 1.44 ppm [the "free" $(CH_3)_2As$ group] and 1.90 ppm. Similar considerations indicate that $f_6AsPFe(CO)_4$ is P-bonded as is $(f_4AsP)_2Fe(CO)_3$. The infrared spectrum of the latter compound can be interpreted in terms of a trigonal-bipyramidal structure with two apical phosphine substituents (*40*, *53*).

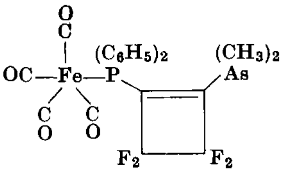
A recent X-ray study of $f_4AsPFe(CO)_4$ (*109*) confirms that its structure is as shown in (**13**) with the ligand coordinated through the phosphorus atom. There is no significant difference between axial and equatorial iron–carbon bond lengths [1.74(2) Å] and the iron atom is dis-

---

* In this account (L–L) represents a ditertiary arsine or phosphine such as (**11**) and, when appropriate, a mixed ligand such as (**12**).

† In this chapter NMR chemical shifts are given in ppm downfield from internal TMS. Mössbauer parameters are derived from spectra run at 80°K. Isomer shifts, δ, and quadrupole splittings, Δ, are quoted in mm sec^{-1}. Isomer shifts for iron compounds are given relative to sodium nitroprusside.

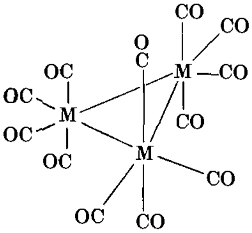
placed 0.025 Å from the plane of the equatorial groups toward the axial carbonyl group.



(13)

The Mössbauer spectra of these and related five-coordinate iron complexes consist of a widely split quadrupole doublet as expected for a single iron atom in a noncubic field (*134, 215*). At 80°K the isomer shifts of these compounds lie in the narrow range of $\delta = 0.16$–0.23 mm sec^{-1} and the quadrupole splittings, Δ, lie in the range 2.12–2.83 mm sec^{-1}. The compounds with $(CH_3)_2As$ groups coordinating show greater shifts than those containing $(C_6H_5)_2P$ indicating that phosphorus is a better π acceptor than arsenic. As a result the spectrum of $f_4AsPFe_2(CO)_8$, (**18**), shows two doublets (Fe^A, $\delta = 0.21$, $\Delta = 2.83$; Fe^B, $\delta = 0.19$, $\Delta = 2.18$ mm sec^{-1}) and the one with the greater isomer shift, Fe^A, can be assigned to the iron atom bonded to the arsenic atom (*40*).

Triosmium dodecarbonyl (**14**) (M = Os), like its ruthenium analog (*164*), has a triangular arrangement of osmium atoms with each metal atom approximately octahedrally coordinated by four carbonyl groups and the other two osmium atoms (*51*). The stability of the $M_3(CO)_{12}$ skeleton increases in the series M = Fe < Ru < Os,* and a number of derivatives are known in which a carbonyl group has been replaced



(14)

by a tertiary phosphine or arsine without rupture of the Os_3 skeleton (*97*). Both yellow $f_4fosOs_3(CO)_{11}$ and $f_8fosOs_3(CO)_{11}$ are obtained

---

* $Fe_3(CO)_{12}$ has a different structure with bridging carbonyl groups (**20**) (*212*).

under vigorous conditions by displacement of one, presumably equatorial, carbonyl group (*55*).

The ditertiary phosphine diphos (**9**) reacts with (π-C_5H_5)Fe(CO)$_2$ Sn(CH_3)$_3$ under ultraviolet irradiation with displacement of both carbonyl groups (*152*). Under similar conditions f$_6$fos displaces only one carbonyl group from the same compound and its triphenyltin analog (*84*).

$$(\pi\text{-}C_5H_5)Fe(CO)_2\text{–}SnR_3 + f_6fos \xrightarrow{h\nu} (\pi\text{-}C_5H_5)Fe(CO)(f_6fos)\text{–}SnR_3 \qquad (58)$$

$$R = CH_3,\ C_6H_5$$

The solid state structure of the trimethyltin compound is shown in Fig. 1

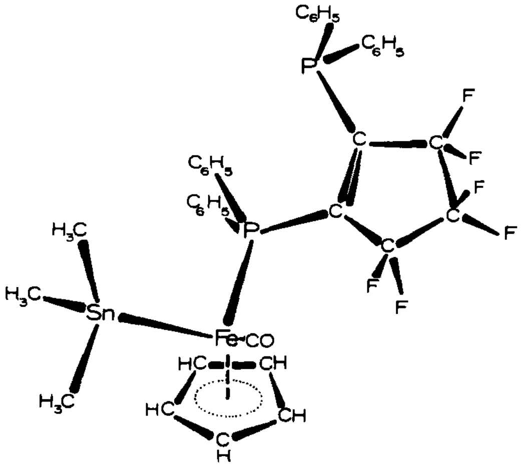


FIG. 1. The structure of (π–C_5H_5)Fe(CO)(f$_6$fos)Sn(CH_3)$_3$. (*112*).

(*112*), although rotamers appear to be present in solutions of this type of derivative (*152*) [see also (*23*, *147*)]. The ligand is clearly monodentate with a P- - -P separation of 3.60(1) Å. The fluorocarbon ring is in an envelope conformation and the coordination is approximately tetrahedral round the tin atom, and octahedral round the iron assuming that the π-C_5H_5 ring occupies three coordination sites. The Fe–Sn distance of 2.562(4) Å is not significantly different from the sum of the covalent radii, although assigning radii to metals in low oxidation states is a hazardous undertaking, and the conclusion can be made that there is little π-character to the metal–metal bond. This same conclusion has been reached from X-ray studies on the parent molecules (π–C_5H_5)-Fe(CO)$_2$SnR$_3$ (*29*, *132*, *133*) and from spectroscopic studies on their derivatives (*85*) (see also *119*). It should be pointed out that many workers favor a π-bonded model for metal–metal bonds especially those involving the lighter Group IV elements (e.g. *13*).

B. BILIGATE MONOMETALLIC (CHELATE) COMPLEXES

1. *Chelate Complexes Derived from the Group VI Hexacarbonyls*

The reaction of the Group VI hexacarbonyls, or their derivatives, with ditertiary arsines and phosphines to give the compounds $(L\text{–}L)M(CO)_4$ has been the subject of many investigations (*31*, *100*). The fluorocarbon-bridged ligands also give complexes of the same stoichiometry (*59*, *68*, *70*). The complete series $f_n$fos$M(CO)_4$ is known for $n = 2$, 4, or 6 and M = Cr, Mo, or W in addition to $f_4$fars$M(CO)_4$, where M = Cr or Mo. As usual, the tungsten compounds require more forcing conditions for their preparation. An interesting feature of the complexes $f_6$fos$M(CO)_4$ is their ability to form solvates of formula $f_6$fos$M(CO)_4 \cdot \frac{1}{2}S$, where S = benzene, cyclohexane, or chloroform, and where the solvent is quite strongly held. One of the main reasons for preparing these compounds was to study their carbonyl infrared spectra and the following conclusions have been made.

(*i*) Since the spectra of diphos$M(CO)_4$ and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2M(CO)_4$ are similar, the electronegative $>C{=}C<$ group with its sp^2-hybridized carbon atoms has little effect on the donor–acceptor properties of the ligand.

(*ii*) Since the spectra of $f_n$fos$M(CO)_4$ are approximately the same for a given M, differences in properties of the $f_n$fos ligands are mainly due to geometric rather than electronic effects.

(*iii*) Since the spectra of the $f_n$fos complexes have bands at higher wavenumber than those of the diphos complexes, the electronegative bridging groups cause the phosphorus atoms to be better π acceptors (*or worse σ donors*).

In addition, the spectra of the $f_6$fos complexes have one band more than expected for a molecule with C_{2v} symmetry. This has been explained as follows (*70*). The complex $f_6$fos$M(CO)_4$ contains two five-membered rings which will be puckered (see Figs. 1 and 2), and it is possible that the combination of these two rings would give rise to two distinct isomers ["chair" and "boat" (*105*)] which could have a long enough lifetime in solution to be detected by infrared spectroscopy. The lifetime of any one isomer must be short since the ^{19}F NMR spectrum of the complex is almost identical with that of the free ligand.* An "extra" band is also seen in the spectrum of $f_6$fos$Fe(CO)_3$ (*74*).

---

* The NMR spectra indicate that the ligands are chelated.

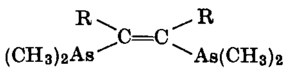
2. *Chelate Complexes Derived from Manganese and Rhenium Carbonyls*

Dimanganese decacarbonyl and $f_4$fos interact to give a complex which is probably best formulated as $(CO)_5Mn{-}Mn(CO)_3f_4$fos with the ligand chelated to one manganese atom (*59*). However, an alternative formulation involving ligand cleavage is possible (cf. Fig. 11 and Section V,E). The chelated carbonyl halide derivatives $f_4$fars$M(CO)_3X$ have also been synthesized. In the case of the iodides these were obtained by warming the biligate bimetallic complexes $f_4$fars$[M(CO)_3I]_2$ (see Section V,C,2). This reaction involves considerable redistribution of ligands and is rather surprising in view of the usual reluctance of $f_4$fars to chelate.

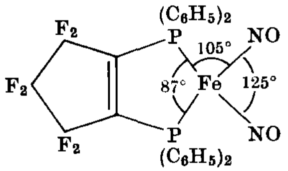
3. *Chelate Complexes Derived from Iron and Ruthenium Carbonyls*

Chelate complexes of formula $(L{-}L)Fe(CO)_3$ [$(L{-}L) = f_4$fos, $f_6$fos, $f_8$fos, f_4AsP, f_6AsP] are obtained from most reactions involving iron carbonyls and the fluorocarbon-bridged ligands (*40*, *72*, *74*). Similar compounds are obtained from diars and diphos (*73*). The NMR spectra of these complexes indicate that the symmetry of the ligands is unaltered on complexing which suggests a C_{2v} structure with the ligand occupying two equatorial positions of a trigonal bipyramid. Thus, the L–Fe–L angle would be about 120° on a rigid model. It is apparent from the structures that have been determined that this angle should be closer to 90° (*105*, *139*). Indeed the structure of $f_6$fos$Fe(NO)_2$ (**16**) (*139*) is considerably distorted from one with tetrahedral angles round the iron atom (*vide infra*). Thus, geometrical requirements seem to favor aplical-equatorial substitution, and this is the structure found in an X-ray investigation of diars$Fe(CO)_3$ (*22*). If this were the structure of diars$Fe(CO)_3$ in solution then two arsenic–methyl environments would be seen in the NMR spectrum. However, the spectrum is a singlet in the $As{-}CH_3$ region down to −80°C which suggests that this molecule and the related $(L{-}L)Fe(CO)_3$ compounds are undergoing positional exchange (*14*, *172*), probably by the "turnstile" mechanism (*209*), where the ligands (L–L) rotate so as to exchange axial and equatorial arsenic atoms.

It is significant that $f_4$fars does not form the chelate complex $f_4$fars$Fe(CO)_3$ even though the closely related ligands (**15**) ($R = CF_3$) and



(**15**)



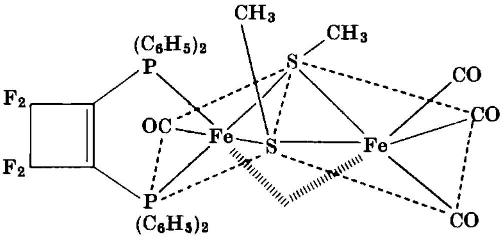
(**16**)

f_4AsP do (*40*, *61*). This suggests that geometric factors may be operating especially since in the phosphine series the ease of formation of $f_n$fosFe$(CO)_3$ increases as n increases (using yields obtained under comparable conditions as indicators) (*72*).

The corresponding complexes of ruthenium are known for $f_4$fos and $f_8$fos. They have similar properties to the iron analogs, but are less stable (*71*). Osmium analogs are unknown (*55*).

Reaction of $f_4$fars with iron dicarbonyl dinitrosyl results in displacement of only one carbonyl group even though other ligands give the chelate $f_n$fosFe$(NO)_2$ complexes ($n = 4$, 6, or 8) in good yield (*58*). The Mössbauer spectra of these Fe^{-2}, d^{10} derivatives, show little variation in δ(Fe) with ligand, and point charge calculations indicate that the ligand strength of $f_n$fos is approximately the same as triphenylphosphine (*58*). The crystal structure of $f_6$fosFe$(NO)_2$ shows some interesting features (**16**) (*139*). The ligand is in an envelope conformation, although here again this is not seen in the solution ^{19}F NMR spectrum. The nitrosyl groups are linear, but the P–Fe–P angle is only 87°, whereas the N–Fe–N angle is 125°. Thus, the ligand seems to prefer to chelate with a P–Fe–P angle of ~90°. The bite of the ligand is 3.084(3) Å which will be discussed later. Mingos and Ibers (*171*) have recently reported the structure of the isoelectronic ion $[(C_6H_5)_3P)_2Ir(NO)_2]^+$. Here there is a large angle (154°) between *nonlinear* nitrosyl groups.

The "folded book" structure of $Co_2(CO)_8$ (*204*) is also found in the iron complexes $[Fe(CO)_3SR]_2$ (*91*, *149*). The compound with $R = CH_3$ exists as two isomers syn and anti depending on the orientation of the $S\text{–}CH_3$ groups in the bridge. Under mild conditions $f_n$fos ($n = 4$, 8) displaces two carbonyl groups from the syn/anti mixture to yield products which have two different iron environments (*57*). The Mössbauer spectra indicate that one iron atom is little changed from the parent molecule, but the other is increased in isomer shift considerably (Table I), so it is probable that the ditertiary phosphines are chelated. The chemical shift difference between the two *S*-methyl resonances in the NMR spectrum indicates that the products have the anti *S*-methyl arrangement. The structure proposed for the $f_4$fos derivative is (**17**).



(17)

TABLE I

Spectroscopic Data for some $[Fe(CO)_3SCH_3]_2$ Derivatives[a]

Compound	Mössbauer δ(Fe)	Mössbauer Δ(Fe)	NMR δ(S–CH_3)
anti-$[Fe(CO)_3SCH_3]_2$	0.29	0.88	1.61, 2.12
anti-$[Fe_2(CO)_5(SCH_3)_2P(C_6H_5)(CH_3)_2]$	0.28	1.15	1.12, 1.80
	0.29	1.70	
$f_4$fos$[Fe(CO)_2SCH_3]_2$[b]	0.33	1.01	—
$f_4$fars$[Fe(CO)_2SCH_3]_2$[b]	0.36	1.08	1.57, 1.71
$f_4$fos$[Fe(CO)_2SCH_3]_2$[c]	0.28	1.14	0.85, 1.80
	0.40	0.47	—

[a] See footnote on p. 348.

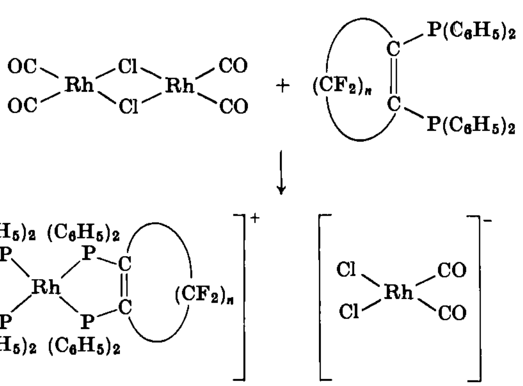
[b] The ligand is bridging.

[c] The ligand is chelating.

Equatorial–axial substitution is more likely because monosubstitution by $C_6H_5P(CH_3)_2$ leads to a compound apparently with a plane of symmetry since the NMR spectrum shows that the *P*-methyl groups are equivalent (*57*). The carbonyl infrared spectra of these $f_n$fos derivatives are similar to that of the diphos complex which is also believed to be chelated (*96*).

4. *Chelate Complexes Derived from $[Rh(CO)_2Cl]_2$ and Other Metal Halides*

Reaction of the ditertiary phosphines $f_n$fos($n = 4, 6$) with the chlorine-bridged dimer $[Rh(CO)_2Cl]_2$ yields a product which can be regarded as the result of unsymmetrical cleavage of the dimer (*83*). A 1 : 4 ratio of reactants affords $[(f_n\text{fos})_2Rh]^+Cl^-$ and in this case $n = 4, 6$, or 8.



(59)

Similar products are obtained by reaction of other hydrocarbon-bridged ditertiary arsines and phosphines such as (**10**) (*159*), but diphos behaves differently (*142*, *192*). The structures of the anion and cation products of reaction (59) were first proposed on the basis of their spectroscopic properties, and were later verified by an X-ray investigation (*105*). The structure of the cation $[(f_6fos)_2Rh]^+$ is shown in Fig. 2. Like the anion the cation has approximately the square-planar geometry around the central atom expected for a Rh^I (d^8) derivative. The cation is actually twisted slightly so that it is not superimposable on its mirror image. This twisting probably occurs to accommodate the anion which lies perpendicular to the plane of the cation with the two cis chlorine atoms closer to two trans phosphorus atoms in the cation. A similar structure has been found for the cation $[(diphos)_2Rh]^+$ (*135*).

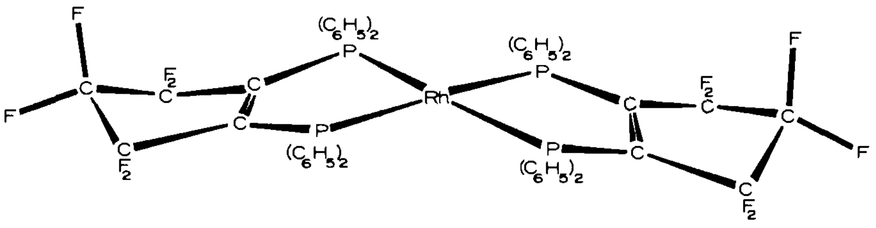


FIG. 2. The structure of $[(f_6fos)_2Rh]^+$ (*105*).

The bite of the ligand in Fig. 2 is 3.111(8) Å which is considerably shorter than that found when the same ligand is monodentate (*112*) (Fig. 1) but is similar to that found for $f_6fosFe(NO)_2$, 3.084(3) Å (*139*). These results show that the bite of a ligand can be very much dependent on the bonding situation and, hence, caution is needed when the concept is being used to rationalize chemical results.

One of the features of Rh^I derivatives is their ability to undergo oxidative addition (*49*). The electronegative bridging groups of $[(f_nfos)_2Rh]^+$ seem to inhibit this reaction and hydrogen chloride has been successfully added only to $[(f_4fos)_2Rh]^+$ (*83*).

Hydrocarbon-bridged ligands such as diars (**8**) have the ability to form chelate complexes with a wide variety of metals in a variety of oxidation states (*31*, *100*, *137*, *162*). In preliminary investigations (*68*, *69*, *99*) it has been found that the fluorocarbon-bridged ligands are reluctant to react with salts of the first-row transition metals. Although compounds of formula $diarsMX_2$ ($M = Zn, Cd$, or Hg) are well established (*157*), only the $HgCl_2$ derivative is known for f_4fars and f_4fos. Other chelate complexes of the heavier metals have been isolated including

$f_4$farsPdCl_2 and $(f_4\text{fars})_2RhCl_3$. The reaction of both $f_4$fos and $f_4$fars with Pt^{II} derivatives is complex and seems to resemble the behavior of the related ligand (**15**) (R = H) which gives bridged complexes (*9*).

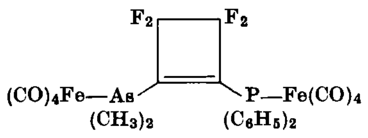
C. BILIGATE BIMETALLIC COMPLEXES

In these complexes the ditertiary arsine or phosphine is acting in a bridging bis-monoligate fashion.

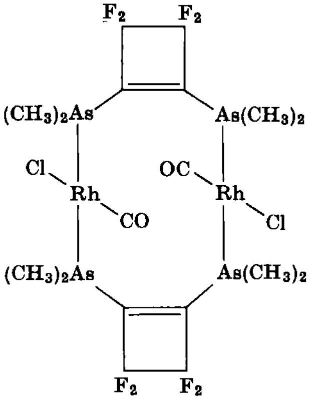
1. *Bridging Two Atoms not Otherwise Connected*

When a solution of $f_4$fars and an iron carbonyl is irradiated with ultra-violet light, one of the products is $f_4\text{fars}Fe_2(CO)_8$ (*72*, *74*). Similar conditions produce $f_4AsPFe_2(CO)_8$ (*40*) and the analogous complexes of diars and diphos are known (*73*). There are numerous examples in the literature where it has been postulated that a ligand bridges two metal carbonyl moieties and this is the confirmed structure of diars$[(\pi\text{-}CH_3C_5H_4)Mn(CO)_3]_2$ (*11*). The spectroscopic properties of these $Fe_2(CO)_8$ derivatives are compatible with bridged structures similar to that shown for $f_4AsPFe_2(CO)_8$ (**18**) with substitution taking place in the apical position. Again these complexes are almost certainly not rigid in solution (see also Sections V,A and B above).

When $f_4$fars is treated with $[Rh(CO)_2Cl]_2$, a red complex is obtained (*83*) which has been assigned the structure (**19**) on the basis of its spectroscopic properties and its similarity to the previously known compounds



(**18**)

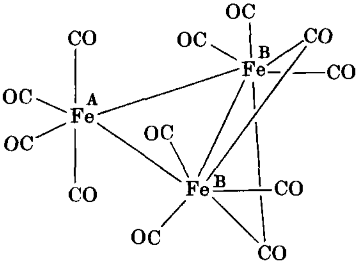


(**19**)

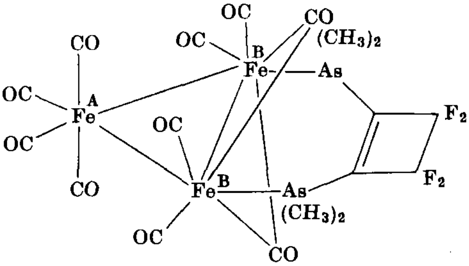
$[(C_6H_5)_2ECH_2E(C_6H_5)_2Rh(CO)Cl]_2$ (*158*, *159*). It is worth noting that $f_n$fos ligands give chelate complexes under the same conditions as in reaction (59). Thus, changing the donor atoms is sufficient to change the type of product. It had been suggested (*159*) that the length of the bridging chain in the ligands $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ determines whether the complexes would be bridged or chelated.

2. *Bridging Two Atoms Otherwise Connected*

Most reactions of $Fe_3(CO)_{12}$ involve rupture of the basic skeleton (**20**)



(20)



(21)

(*212*).* However, some monodentate ligands have been found to displace one or more carbonyl groups from the basic skeleton. Examples include $(C_6H_5)_3PFe_3(CO)_{11}$ (*4, 92, 93*) and $(C_6H_5P(CH_3)_2)_3Fe_3(CO)_9$ (*166*), where the ligands are equatorial, i.e., they lie in the Fe_3 plane. Irradiation of a mixture of $f_4$fars and $Fe_3(CO)_{12}$ yields $f_4$fars$Fe_3(CO)_{10}$ in low yield (*72, 76*). The spectroscopic properties of this molecule, singlet ^1H and ^{19}F NMR resonances, and simple infrared spectrum in the carbonyl stretching region indicate a symmetrical structure. The Mössbauer spectrum shown in Fig. 3 is very similar to that of $Fe_3(CO)_{12}$. The centre peak associated with the unique Fe^A atom (**20**) (approximately octahedrally coordinated and therefore unsplit) is little changed in the complex. The two outer peaks arising because of quadrupole splitting of the absorption due to the two equivalent Fe^B atoms are slightly shifted to more positive velocities suggesting that the ligand has displaced a terminal carbonyl group from each Fe^B. This structure (**21**) was subsequently confirmed by an X-ray investigation (*188*). The $f_4$fars ligand in the solid state is not quite coplanar with the Fe_3 triangle, but presumably it is in solution to account for the spectroscopic properties. Otherwise, the Fe_3 fragment is little altered from that of the parent $Fe_3(CO)_{12}$. It should be noted that bands in the bridging carbonyl stretching region of the infrared spectrum of $f_4$fars$Fe_3(CO)_{10}$ are weak, just as are those of $Fe_3(CO)_{12}$ itself. Thus,

---

* The structure in solution is subject to debate (*76, 183, 212*).

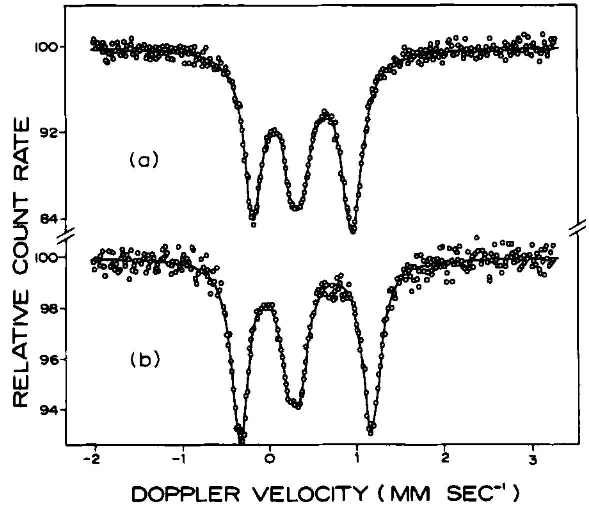


FIG. 3. The Mössbauer spectra at 80°K of (a) $Fe_3(CO)_{12}$ and (b) $f_4$fars$Fe_3(CO)_{10}$.

it is not necessary to postulate a different structure in solution for $Fe_3(CO)_{12}$ to explain the low intensity. The only similar complex so far isolated is $f_4AsPFe_3(CO)_{10}$, which is formed in high yield (87%) when f_4AsP and $Fe_3(CO)_{12}$ are refluxed in cyclohexane solution for 45 min (*40*). Its spectroscopic properties are very similar to those of $f_4$fars$Fe_3(CO)_{10}$. There is probably a connection between the formation of a (L–L)$Fe_3(CO)_{10}$ derivative and the reluctance of (L–L) to form the chelate complexes (L–L)$Fe(CO)_3$ (see Section V,B).

The structures of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ contain no bridging carbonyl groups (**14**) and their stability is greater than that of $Fe_3(CO)_{12}$. Consequently it is not surprising to find that both $f_4$fars and $f_4$fos react with $Ru_3(CO)_{12}$ to afford red (L–L)$Ru_3(CO)_{10}$ complexes on ultraviolet irradiation (*71*). More vigorous conditions (cyclohexane reflux) give $(L–L)_2Ru_3(CO)_8$. It may be significant that $f_6$fos which seems to be a better chelating ligand, does not form any Ru_3 complexes. No complex was isolated when $f_4$fars was treated with $Os_3(CO)_{12}$ presumably because of the vigorous reaction conditions needed; however, $f_4$fos gave $f_4$fos$Os_3(CO)_{10}$ and $(f_4fos)_2Os_3(CO)_8$ (*55*). The carbonyl infrared spectra of the Os_3 complexes are very similar to those of the corresponding Ru_3 derivatives and, hence, they are probably isostructural. The spectroscopic properties of $f_4$fars$Ru_3(CO)_{10}$ suggested that the molecule has high symmetry and a ligand-bridged structure was proposed which was subsequently verified by X-ray studies (*189*). A similar bridged structure was proposed and found for $(f_4fars)_2Ru_3(CO)_8$ (*190*) (Fig. 4). The ruthenium triangle is maintained in both Ru_3 structures, but equatorial substitution by the arsine distorts the molecule considerably in the solid. The solution spectroscopic properties indicate higher symmetry and, thus, the molecule is either flexing in solution or the distortion is due to crystal packing. It is interesting that in both structures the Ru–Ru bonds which involve ruthenium atoms with the greatest number of carbonyl groups are shorter than the others. Thus, in $f_4farsRu_3(CO)_{10}$ there are two bonds of length 2.831(3) Å and one (the bridged one) of length 2.856(6) Å, while in the $Ru_3(CO)_8$ derivative one Ru–Ru bond is 2.785(4) Å and the other two bridged ones are 2.853(3) Å. This can be ascribed to replacing a carbonyl group by a poorer π acceptor.

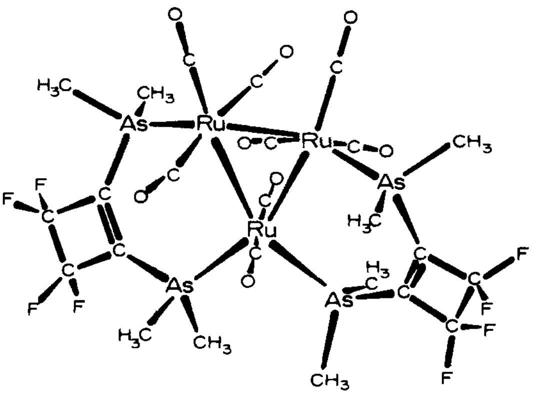
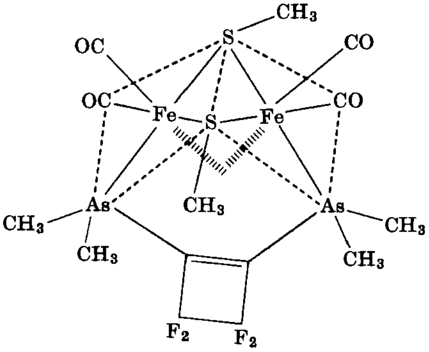


FIG. 4. The structure of $(f_4fars)_2Ru_3(CO)_8$ (*190*).

It is well established that dicobalt octacarbonyl exists in solution as an equilibrium mixture (approximately 1 : 1) of carbonyl bridged and nonbridged forms (*18*, *175*). The bridged structure is found in the solid state (*204*). Many tertiary phosphine and arsine derivatives show this same tendency (*31*); however, some, e.g., $[(C_4H_9)_3PCo(CO)_3]_2$, exist in solution and the solid state in the nonbridged form (*146*). The ligands f_4fars, f_6AsP, and f_nfos, ($n = 4$, 6, or 8) react easily with dicobalt octacarbonyl to displace two moles of carbon monoxide and give complexes of formula $(L\text{–}L)Co_2(CO)_6$ (*56*). The carbonyl infrared spectra of these complexes are simple, and show the presence of bridging carbonyl groups. Two types of spectra are obtained. In the f_4fars, f_6AsP, and f_4fos derivatives the two frequencies associated with the bridging carbonyl groups are separated by ~56 cm^{-1}; in the $f_6$fos and $f_8$fos derivatives the frequency difference is much smaller (~12 cm^{-1}). These results lead to the suggestion that the $f_4$fars-type complexes were formed by displacement of two terminal carbonyl groups; one from each cobalt atom as shown in Fig. 5. Indeed, this is the X-ray determined structure of $f_4farsCo_2(CO)_6$ (*140*), and the same structure is assumed for the $f_4$fos and f_6AsP analogs. The $f_6$fos and $f_8$fos derivatives are believed to have a similar bridged structure, only here the ligand is situated trans to the Co–Co bond so that the bridging and terminal carbonyl groups are cis to the ligand which would account for the similarity of the asymmetric and symmetric bridging carbonyl stretching frequencies.

Similar bridged products are obtained when the acetylene-bridged complex $Co_2(CO)_6C_6H_5C{\equiv}CH$ is treated with $f_4$fars and $f_4$fos.

Under xylene reflux $f_4$fos and $f_4$fars react with the syn/anti mixture of $[Fe(CO)_3SCH_3]_2$ to give $(L\text{–}L)[Fe(CO)_2SCH_3]_2$ (*57*). The Mössbauer spectra of the products (see Table 1) indicate that the two iron atoms are equivalent and that they are monosubstituted. The NMR spectrum shows that the As–CH_3 groups of the $f_4$fars complex are inequivalent and the *S*-methyl groups have chemical shifts characteristic of the syn isomer. Therefore, the bridged structure (**22**) is proposed for these molecules whose infrared spectra are very similar to that of $(C_6H_5)_2PCH_2P(C_6H_5)_2[Fe(CO)_2SCH_3]_2$, which is also believed to be bridged (*96*).



(**22**)

It is interesting to note that $f_4fos[Fe(CO)_2SCH_3]_2$ also exists as a chelated isomer (see Section V,B) and this is one of the two instances where a ligand gives isomers whose structure depends on whether it is bridged or chelated. The other example is afforded by the compound $(f_4AsP)_2Fe_2(CO)_4$ (*40*), which is a derivative of $f_4AsPFe_2(CO)_6$ (cf. Fig. 9 and Section V,D) in which the second ligand bridges the two Fe atoms or is chelated to one iron atom (Fe^A). The bridged isomer is obtained by reacting excess f_4AsP with $Fe_3(CO)_{12}$ or by irradiating a mixture of $f_4AsPFe_2(CO)_6$ and f_4AsP. The latter method also gives the chelated isomer (*40*, *108*). A related complex $(f_4AsP)(f_6AsP)Fe_2(CO)_4$, obtained from $f_6AsPFe_2(CO)_6$, seems to exist only in the bridged form.

The cobalt clusters $RCCo_3(CO)_9$ ($R = CH_3$, CF_3), which are not carbonyl bridged in the solid state (*205*), react with $f_4$fars to give the substitution product $f_4farsCH_3CCo_3(CO)_7$ and the rearranged product $f_4farsCo_4(CO)_8$ (*56*), respectively (the fate of the fluorocarbon residue is unknown). The bridging carbonyl groups seen in the solution infrared spectrum are present in the solid state structure of $f_4farsCH_3CCo_3(CO)_7$ (Fig. 6) (*106*). However, the bridging carbonyl groups present in solutions of the $Co_4(CO)_8$ complex are *absent* in the solid state (Fig. 7) (*107*). The skeleton of the latter structure is similar to that of $Ir_4(CO)_{12}$ (*214*), but both $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ are carbonyl-bridged in the solid state (*52*, *213*). Some terminal carbonyl groups of $(f_4fars)_2Co_4(CO)_8$ are weakly interacting with adjacent cobalt atoms. This feature has been found in a number of structures determined recently (e.g., *41*).

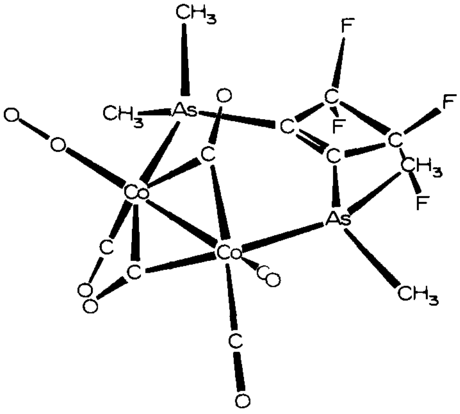


FIG. 5. The structure of $f_4farsCo_2(CO)_6$ (*140*).

In the known structure of $CH_3CCo_3(CO)_8P(C_6H_5)_3$ (*25*) the phosphine has displaced an equatorial carbonyl group (with respect to the Co_3 plane) and the complex is unbridged like the parent $CH_3CCo_3(CO)_9$. However, bridging carbonyl groups are present in solutions of this phosphine derivative. In the structure shown in Fig. 6 the ligand has displaced two carbonyl groups from axial positions.

Under mild conditions $f_4$fars, $f_6$fars, and $f_4$fos react with $M_2(CO)_{10}$ ($M = Mn$, Re) to give bridged derivatives such as $f_4farsMn_2(CO)_8$ (*59*, *78*). Other hydrocarbon-bridged bidentate ligands apparently afford chelate complexes $(L\text{–}L)M(CO)_3$ or $(L\text{–}L)M_2(CO)_8$ (*141*, *191*). The spectroscopic properties of the $f_4$fars derivative are in agreement with the solid state structure (Fig. 8) (*60*). Here the Mn–Mn bond is longer than in

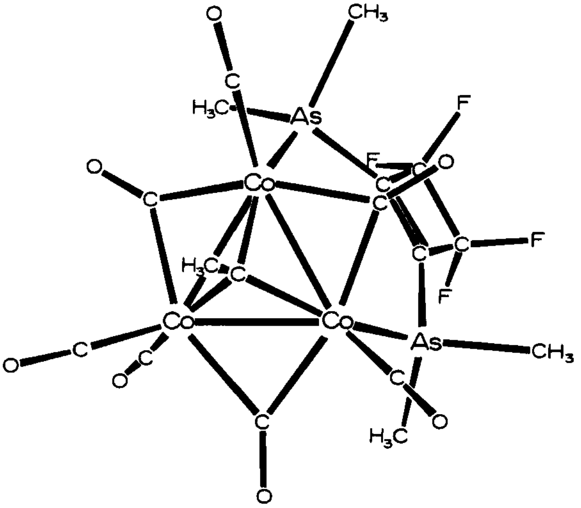


FIG. 6. The structure of $f_4farsCH_3CCo_3(CO)_7$ (*106*).

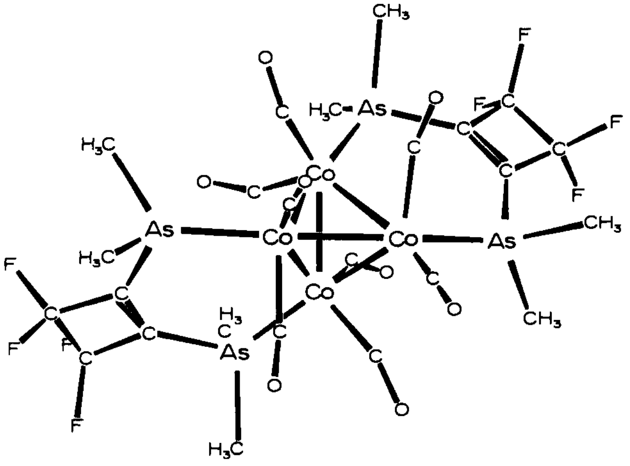


FIG. 7. The structure of $(f_4fars)_2Co_4(CO)_8$ (*107*).

the parent carbonyl (*90*). The carbonyl groups are staggered. Reaction of the bridged (L–L)$Mn_2(CO)_8$ (*59*, *78*) derivatives with iodine results in easy cleavage of the M–M bond and the bridged derivatives (L–L)-$[Mn(CO)_4I]_2$ are obtained. The structure has been confirmed in the case of the $f_4$fars compound; the two $Mn(CO)_4I$ moieties which are coordinated to separate $-As(CH_3)_2$ groups lie on opposite sides of the cyclobutene plane. The iodine atoms are cis to the arsenic (*60*).

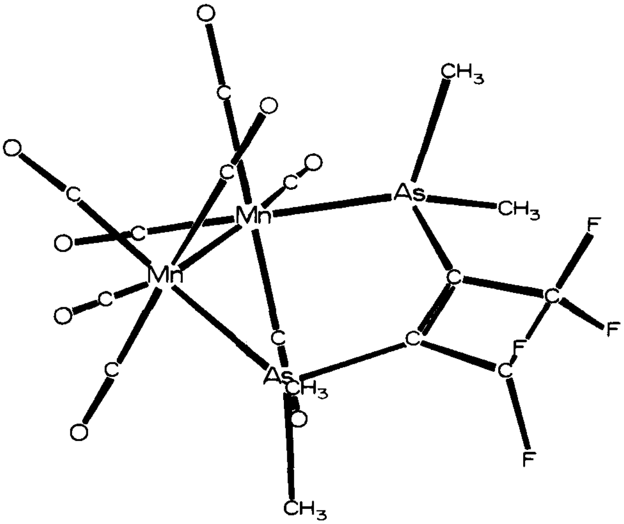


FIG. 8. The structure of $f_4farsMn_2(CO)_8$ (*60*).

D. TRILIGATE BIMETALLIC COMPLEXES

Ligands such as (**10**) and (**15**) with unsaturated bridging groups can, in principle, act as triligate groups by donating electron pairs from the two Group V atoms and the double bond. In practice this is realized only when the ligand is fluorocarbon-bridged, although not necessarily fluoroalicyclic since the complex (L–L)$Fe_2(CO)_6$ where (L–L) = (**15**) ($R = CF_3$) is of this type (*61*). The first complex in this class, $f_4farsFe_2(CO)_6$, had its crystal structure determined by accident [it was believed to be $f_4farsFe(CO)_3$ (*99*)]. The result is seen in Fig. 9 (*113*). One iron atom Fe^A is approximately octahedrally coordinated by two arsenic atoms and three carbonyl groups; the other by the double bond of the cyclobutene group, by three carbonyl groups, and by Fe^A which is acting as a donor. Thus, the coordination around Fe^B can be regarded as either a distorted

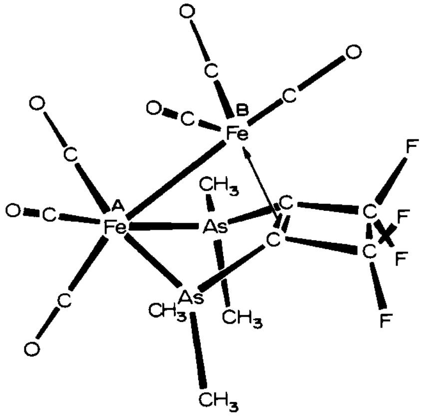


FIG. 9. The structure of $f_4farsFe_2(CO)_6$ (*113*).

trigonal bipyramid with the double bond occupying one site or a distorted octahedron with the two carbon atoms occupying two sites.* In any case the symmetry of Fe^B is lower than that of Fe^A.

This compound was eventually isolated and characterized from the reaction of $f_4$fars with $Fe_3(CO)_{12}$ (*75*), which has proven to be the best way of preparing the other complexes $(L–L)Fe_2(CO)_6$ [$(L–L) = f_4$fos, $f_6$fos (*75*), f_4AsP, f_6AsP (*40*), $f_6$fars, $f_8$fars (*64*)]. It is probably significant that in $f_4farsFe_2(CO)_6$ (Fig. 9) the bonding of the double bond of the cyclobutene ring to Fe^B allows the bite of the ligand to decrease enough for both arsenic atoms to coordinate to one iron atom (cf. the nonexistence of $f_4farsFe(CO)_3$, Section V,B). A feature of the preparation of the $f_n$fos and f_nAsP compounds is that the yields decrease as the ring size is increased (compounds with $n = 8$ are unknown), which was taken as an indication that as the ring became less strained there was less tendency for the double bond to coordinate to Fe^B. However, the preparation of $f_6$fars and $f_8$fars derivatives in good yield (*64*) suggests that ring strain is not the only factor and that possibly steric hindrance plays some part. Similar compounds are obtained from $Ru_3(CO)_{12}$ (*71*) for $f_4$fars, $f_4$fos, and $f_6$fos and from $Os_3(CO)_{12}$ (*55*) for $f_4$fos.

Of all the types of complexes formed between the Group VIII carbonyls and the fluorocarbon ligands the series $f_4fosM_2(CO)_6$ is the only complete one for M = Fe, Ru, or Os. Their ease of preparation decreases in the order M = Fe > Ru > Os, which is expected in view of the stability of the parent $M_3(CO)_{12}$ species. The spectroscopic properties

---

* See the footnote on p. 323.

of all these compounds are very similar and, hence, they all have the same basic structure (*55*).

The iron complexes have been most investigated and it has been found that the Mössbauer spectrum of, for example, $f_4farsFe_2(CO)_6$, consists of two doublets which can be assigned mainly on the basis of symmetry around the Fe atoms. The parameters are listed in Table II (*40*, *75*). Note that Fe^A, the more symmetrical, has a lower quadrupole splitting than Fe^B, and that the isomer shift of Fe^A is less than that of Fe^B indicating that the *s* electron density at Fe^A is greater than Fe^B. Also note that replacement of a $(CH_3)_2As$ group by a $(C_6H_5)_2P$ group causes a decrease in isomer shift at Fe^A, presumably due to the better π-acceptor properties of the phosphorus-containing moiety, and that when f_4fos is replaced by f_4AsP only Fe^A changes.

TABLE II

MÖSSBAUER PARAMETERS FOR $(L\text{–}L)Fe_2(CO)_6$ AND RELATED COMPLEXES[a]

Complexes	$\delta(Fe)$	$\Delta(Fe)$	Assignment[b]
$f_4farsFe_2(CO)_6$	0.28	0.64	Fe^A
	0.32	1.44	Fe^B
$f_4fosFe_2(CO)_6$	0.23	0.66	Fe^A
	0.32	1.30	Fe^B
$f_4AsPFe_2(CO)_6$	0.27	0.83	Fe^A
	0.31	1.45	Fe^B
$[(C_6H_5)_3P]f_4AsPFe_2(CO)_5$	0.36	0.56	Fe^A
	0.30	1.38	Fe^B
$(f_4AsP)^c(f_4AsP)Fe_2(CO)_4$	0.36	1.21	Fe^A
	0.36	1.21	Fe^B
$(f_4AsP)^d(f_4AsP)Fe_2(CO)_4$	0.50	0.61	Fe^A
	0.28	1.07	Fe^B

[a] See footnote on p. 348.
[b] See Fig. 9.
[c] The ligand is bridging.
[d] The ligand is chelating (*108*).

Also listed in Table II are parameters for some derivatives of $(L\text{–}L)Fe_2(CO)_6$. These are obtained as follows, where $(L\text{–}L)'$ can be bridging or chelating.

$$(L\text{–}L)Fe_2(CO)_6 + (L\text{–}L)' \xrightarrow[h\nu]{\text{acetone}} (L\text{–}L)'(L\text{–}L)Fe_2(CO)_4 \qquad (60)$$

Monosubstitution by $(C_6H_5)_3P$ apparently takes place on Fe^A as judged by the increase in $\delta(Fe^A)$. When (L–L)′ is a bridging ligand, only a two line spectrum is obtained and the isomer shifts of both Fe^A and Fe^B are thus essentially the same although increased over those of the unsubstituted complex.

E. Decomposition Products of Coordination Complexes

When $f_4farsFe_3(CO)_{10}$ (**21**) is heated in cyclohexane solution, the major product is a compound of formula $f_4farsFe_3(CO)_9$. On further heating, this loses its fluorocarbon group to yield $As_2(CH_3)_2CH_2Fe_3(CO)_9$ (*76*). The spectroscopic properties of the first $Fe_3(CO)_9$ derivative indicate that the molecule has little symmetry. The X-ray determined structure shown in Fig. 10 (*111*) indicates that an $As(CH_3)_2$ moiety has been displaced from the ligand. The structure consists of four dissimilar iron atoms and one arsenic atom which form a distorted square plane. One Fe^A–Fe^B bond is very long, 2.917(5) Å. The cyclobutene "double bond" of length 1.44 Å is situated 2.00 Å from Fe^B. In $f_4farsFe_2(CO)_6$ (Fig. 9) the double bond has a length of 1.51 Å and is situated 1.90 Å from Fe^B, implying a stronger bond in this case. Rearrangement of the ligand also occurs when $f_4AsPFe_3(CO)_{10}$ is heated to give the stable complex $f_4AsPFe_3(CO)_9$ (*40*). The carbonyl infrared spectrum of this $Fe_3(CO)_9$

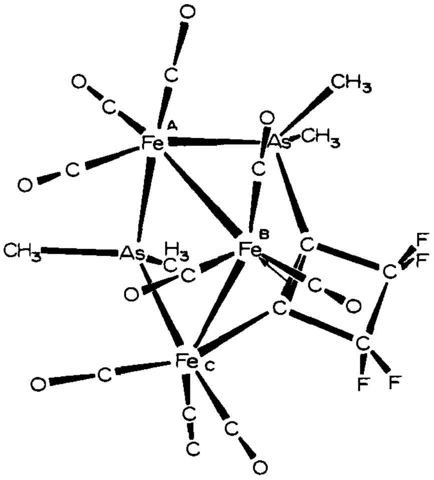


FIG. 10. The structure of $f_4farsFe_3(CO)_9$ (*111*).

derivative is very similar to that of the $f_4$fars complex suggesting a similar structure. This has now been confirmed by an X-ray investigation (*108a*) and the structure is essentially the same as in Fig. 9 except that a $(C_6H_5)_2P$ group replaces the $(CH_3)_2As$ group bonded to the cyclobutene ring.

Displacement of an $As(CH_3)_2$ group also occurs when $f_4farsMn_2(CO)_8$ (Fig. 8) is refluxed in xylene solution. The isomeric product was first believed to have the ligand chelating rather than bridging; however, the solid state structure is shown in Fig. 11. The two manganese atoms are approximately octahedrally coordinated and bridged by the displaced $As(CH_3)_2$ moiety (*60, 78, 110*) and again a transition metal–fluorocarbon bond is formed. Both isomers of the rhenium analogs $(L\text{-}L)Re_2(CO)_8$ [(L–L) = $f_4$fars, $f_6$fars] have also been isolated (*60, 78*).

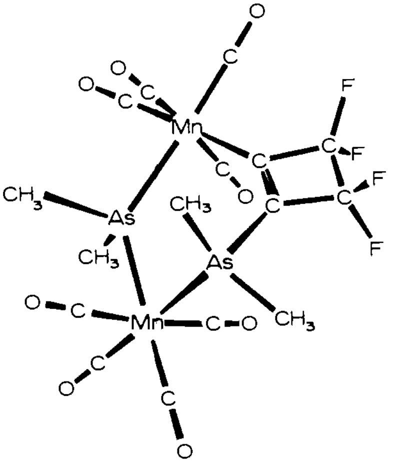


FIG. 11. The structure of the isomer of $f_4farsMn_2(CO)_8$ (cf. Fig. 8) (*110*).

Perhaps the most remarkable ligand transformation occurs when solutions containing $f_4farsCo_2(CO)_6$ (Fig. 5) are heated. One unstable product has the formula $f_4farsCo_2(CO)_5$ and is believed to have a structure analogous to that of $f_4farsFe_2(CO)_6$ (*56*); another, obtained in low yield has the empirical formula $(f_4fars)_2Co_4(CO)_9$ (2H?). The structure is shown in Fig. 12 (*110*). The molecule has a twofold axis. Again $(CH_3)_2As$ groups have been displaced, but this time the cyclobutene rings have united to form a bicyclobutyl system. The two carbonyl-bridged cobalt atoms are apparently one electron short of a "closed shell" configuration and it is possible that the sixth coordination position around each is occupied by a hydrogen atom.

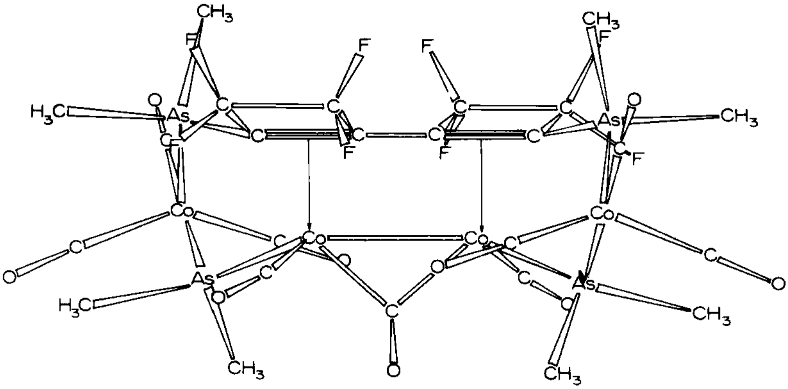


FIG. 12. The structure of $(f_4fars)_2Co_4(CO)_9$ (2H?) (*110*).

There are few examples of hydrocarbon ligands undergoing this type of modification on complex formation. However, this is not to say that they do not occur. Bosnich and co-workers (*19*) have described that a compound originally reported as $[(diars)_3Ni][ClO_4]_2$ is, in fact, $[(diars)(triars)Ni][ClO_4]_2$ $\{triars = CH_3As[C_6H_4As(CH_3)_2\text{-}o]_2\}$, where rearrangement of diars has occurred. Reaction of diars with iron carbonyls also seems to result in fragmentation of the ligand (*73*).

ACKNOWLEDGMENTS

The author is indebted to his many graduate students, postdoctoral fellows, and colleagues in Vancouver who have contributed so significantly to much of the work described in this review. The financial support of the National Research Council of Canada is gratefully acknowledged. The figures which were drawn by Beatrix Krizsan are reproduced with permission of Dr. J. Trotter and Dr. F. W. B. Einstein and the Chemical Society, London, the American Chemical Society, and the editors of *Inorganica Chemica Acta*, and the *Canadian Journal of Chemistry*.

REFERENCES

1. Aguiar, A. M., Mague, J. T., Aguiar, H. J., Archibald, T. G., and Prejean, G., *J. Org. Chem.* **33**, 1681 (1968).
2. Allen, F. H., and Pidcock, A., *J. Chem. Soc. A* 2700 (1968).
3. Anderson, L. P., Feast, W. J., and Musgrave, W. K. R., *J. Chem. Soc. C* 211 (1969).
4. Angelici, R. J., and Siefert, E. E., *Inorg. Chem.* **5**, 1457 (1966).
5. Banks, R. E., "Fluorocarbons and Their Derivatives." Oldbourne Press, London, 1964.
6. Banks, R. E., Haszeldine, R. N., Lappin, M., and Lever, A. B. P., *J. Organometal. Chem.* **29**, 427 (1971).

7. Bartlett, P. D., Montgomery, L. K., and Seidel, B., *J. Amer. Chem. Soc.* **86**, 616 (1964).
8. Beagley, B., Cruickshank, D. W. J., Pinder, P. M., Robiette, A. G., and Sheldrick, G. M., *Acta Crystallogr. Sect. B* **25**, 737 (1969).
9. Bennett, M. A., Erskine, G. J., and Wild, J. D., *Inorg. Chim. Acta* **2**, 379 (1969).
10. Bennett, M. A., and Wild, J. D., *J. Chem. Soc. A* 545 (1971).
11. Bennett, M. J., and Mason, R., *Proc. Chem. Soc.* 395 (1964).
12. Bell, T. N., Haszeldine, R. N., Newlands, M. J., and Plumb, J. B., *J. Chem. Soc.* 2107 (1965).
13. Berry, A. D., Corey, E. R., Hagen, A. P., MacDiarmid, A. G., Saalfeld, F. E., and Wayland, B. B., *J. Amer. Chem. Soc.* **92**, 1940 (1970).
14. Berry, R. S., *J. Chem. Phys.* **32**, 933 (1960).
15. Bichler, R. E. J., Booth, M. R., and Clark, H. C., *Inorg. Nucl. Chem. Lett.* **3**, 71 (1967).
16. Booth, B. L., Haszeldine, R. N., and Tucker, N. I., *J. Organometal. Chem.* **11**, P5 (1968).
17. Booth, G., *Advan. Inorg. Chem. Radiochem.* **6**, 1 (1964).
18. Bor, G., *Spectrochim. Acta* **19**, 2065 (1963).
19. Bosnich, B., Nyholm, R. S., Pauling, P. J., and Tobe, M. L., *J. Amer. Chem. Soc.* **90**, 4741 (1968).
20. Breslow, R., Eicher, T., Krebs, A., Peterson, R. A., and Posner, J., *J. Amer. Chem. Soc.* **87**, 1320 (1965).
21. British Patent 760,201 (1956).
22. Brown, D. A., and Bushnell, G. W., *Acta Crystallogr.* **22**, 296 (1967).
23. Brown, D. A., Lyons, H. J., and Manning, A. R., *Inorg. Chim. Acta* **4**, 428 (1970).
24. Browning, J., Green, M., and Stone, F. G. A., *J. Chem. Soc. A* 453 (1971).
25. Brice, M. D., Penfold, B. R., Robinson, W. T., and Taylor, S. R., *Inorg. Chem.* **9**, 362 (1970).
26. Bruce, M. I., Jolly, P. W., and Stone, F. G. A., *J. Chem. Soc. A* 1602 (1966).
27. Bruce, M. I., and Stone, F. G. A., *in* "Preparative Inorganic Reactions," (W. L. Jolly, ed.) Vol. 4, p. 177. Wiley, New York, 1968.
28. Bruce, M. I., and Stone, F. G. A., *Angew. Chem. Int. Ed. Engl.* **7**, 747 (1968).
29. Bryan, R. F., *J. Chem. Soc. A* 192 (1967).
30. Burton, D. J., and Mettille, F. J., *Inorg. Nucl. Chem. Lett.* **4**, 9 (1968).
31. Calderazzo, F., Ercoli, R., and Natta, G., *in* "Organic Synthesis Via Metal Carbonyls" (I. Wender and P. Pino, eds.) Vol. 1, p. 1. Wiley (Interscience), New York, 1967.
32. Callot, H. J., and Benezra, C., *Chem. Commun.* 485 (1970).
33. Campbell, S. F., Leach, J. M., Stephens, R., and Tatlow, J. C., *Tetrahedron Lett.* 4269 (1967).
34. Campbell, S. F., Leach, J. M., Stephens, R., Tatlow, J. C., and Wood, K. N., *J. Fluorine Chem.* **1**, 103 (1971/72).
35. Campbell, S. F., Leach, J. M., Stephens, R., and Tatlow, J. C., *J. Fluorine Chem.* **1**, 85 (1971/72).
36. Campbell, S. F., Stephens, R., and Tatlow, J. C., *Tetrahedron* **21**, 2997 (1965).
37. Campbell, S. F., Stephens, R., and Tatlow, J. C., *Chem. Commun.* 151 (1967).
38. Chang, C. H., Porter, R. F., and Bauer, S. H., *J. Mol. Struct.* **7**, 89 (1971).
39. Cherwinski, W. J., and Clark, H. C., *J. Organometal. Chem.* **29**, 451 (1971).

40. Chia, L. S., M.Sc. Thesis, University of British Columbia, 1971.
41. Churchill, M. R., and Veidis, M. V., *Chem. Commun.* 529 (1970).
42. Clark, H. C., Corfield, P. W. R., Dixon, K. R., and Ibers, J. A., *J. Amer. Chem. Soc.* **89**, 3360 (1967).
43. Clark, H. C., and Puddephatt, R. J., *Inorg. Chem.* **9**, 2670 (1970).
44. Clark, H. C., and Tsang, W. S., *J. Amer. Chem. Soc.* **89**, 529 (1967).
45. Clark, H. C., and Willis, C. J., *J. Amer. Chem. Soc.* **82**, 1888 (1960).
46. Clayton, A. B., Collins, D., Stephens, R., and Tatlow, J. C., *J. Chem. Soc. C* 1177 (1971).
47. Clayton, A. B., Feast, W. J., Sayers, D. R., Stephens, R., and Tatlow, J. C., *J. Chem. Soc. C* 1183 (1971).
48. Closs, G. L., *Advan. Alicyclic Chem.* **1**, 53 (1966).
49. Collman, J. P., and Roper, W. R., *Advan. Organometal. Chem.* **7**, 53 (1968).
50. Cook, D. J., Green, M., Mayne, N., and Stone, F. G. A., *J. Chem. Soc. A* 1771 (1968).
51. Corey, E. R., and Dahl, L. F., *Inorg. Chem.* **1**, 521 (1964).
52. Corradini, P., and Sirigu, A., *Ric. Sci.* **36**, 188 (1966).
53. Cotton, F. A., and Parish, R. V., *J. Chem. Soc.* 1440 (1960).
54. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," 2nd ed. Wiley (Interscience), New York, 1966.
55. Crow, J. P., and Cullen, W. R., *Inorg. Chem.* **10**, 1529 (1971).
56. Crow, J. P., and Cullen, W. R., *Inorg. Chem.* **10**, 2165 (1971).
57. Crow, J. P., and Cullen, W. R., *Can. J. Chem.* **48**, 2948 (1971).
58. Crow, J. P., Cullen, W. R., Herring, F. G., Sams, J. R., and Tapping, R. L., *Inorg. Chem.* **10**, 1616 (1971).
59. Crow, J. P., Cullen, W. R., and Hou, F. L., *Inorg. Chem.* in press.
60. Crow, J. P., Cullen, W. R., Hou, F. L., Chan, L. Y. Y., and Einstein, F. W. B., *Chem. Commun.* 1229 (1971).
61. Crow, J. P., Cullen, W. R., Sams, J. R., and Ward, J. E. H., *J. Organometal. Chem.* **22**, C 29 (1970).
62. Cullen, W. R., *Fluorine Chem. Rev.* **3**, 73 (1969).
63. Cullen, W. R., and Bruce, M. I., *Fluorine Chem. Rev.* **4**, 79 (1969).
64. Cullen, W. R., and Chia, L. S., unpublished results.
65. Cullen, W. R., Dawson, D. S., and Dhaliwal, P. S., *Can. J. Chem.* **45**, 683 (1967).
66. Cullen, W. R., and Dhaliwal, P. S., *Can. J. Chem.* **45**, 719 (1967).
67. Cullen, W. R., Dhaliwal, P. S., and Stewart, C. J., *Inorg. Chem.* **6**, 2256 (1967).
68. Cullen, W. R., Dhaliwal, P. S., and Stewart, C. J., unpublished results.
69. Cullen, W. R., Dhaliwal, P. S., and Styan, G. E., *J. Organometal. Chem.* **6**, 364 (1966).
70. Cullen, W. R., Dong, D. F., and Thompson, J. A. J., *Can. J. Chem.* **47**, 4671 (1969).
71. Cullen, W. R., and Harbourne, D. A., *Inorg. Chem.* **9**, 1839 (1970).
72. Cullen, W. R., and Harbourne, D. A., unpublished results.
73. Cullen, W. R., and Harbourne, D. A., *Can. J. Chem.* **47**, 3371 (1969).
74. Cullen, W. R., Harbourne, D. A., Liengme, B. V., and Sams, J. R., *Inorg. Chem.* **8**, 1464 (1969).
75. Cullen, W. R., Harbourne, D. A., Liengme, B. V., and Sams, J. R., *Inorg. Chem.* **8**, 95 (1969).

76. Cullen, W. R., Harbourne, D. A., Liengme, B. V., and Sams, J. R., *Inorg. Chem.* **9**, 702 (1970).

77. Cullen, W. R., and Hota, N. K., *Can. J. Chem.* **42**, 1123 (1964).

78. Cullen, W. R., and Hou, F. L., unpublished results.

79. Cullen, W. R., and Hou, F. L., *Can. J. Chem.* **49**, 2749 (1971).

80. Cullen, W. R., Johnson, R. N., and Hall, L. D., unpublished work.

81. Cullen, W. R., and Leeder, W. R., *Inorg. Chem.* **5**, 1004 (1966).

82. Cullen, W. R., and Styan, G. E., *J. Organometal. Chem.* **6**, 633 (1966).

83. Cullen, W. R., and Thompson, J. A. J., *Can. J. Chem.* **48**, 1730 (1970).

84. Cullen, W. R., Sams, J. R., and Thompson, J. A. J., *Inorg. Chem.* **10**, 843 (1971).

85. Cullen, W. R., Sams, J. R., and Waldman, M. C., *Inorg. Chem.* **9**, 1682 (1970).

86. Cullen, W. R., and Styan, G. E., *J. Organometal. Chem.* **4**, 151 (1965).

87. Cullen, W. R., and Waldman, M. C., *J. Fluorine Chem.* **1**, 151 (1971/72).

88. Cullen, W. R., and Waldman, M. C., *Can. J. Chem.* **48**, 1885 (1970).

89. Cullen, W. R., and Waldman, M. C., *J. Fluorine Chem.* **1**, 41 (1971/72).

90. Dahl, L. F., and Rundle, R. E., *Acta Crystallogr.* **16**, 419 (1963).

91. Dahl, L. F., and Wei, C. H., *Inorg. Chem.* **2**, 328 (1963).

92. Dahm, D. J., and Jacobson, R. A., *J. Amer. Chem. Soc.* **90**, 5106 (1968).

93. Dahm, D. J., and Jacobson, R. A., *Chem. Commun.* 496 (1966).

94. Davidsohn, W., and Henry, M. C., *J. Organometal. Chem.* **5**, 29 (1966).

95. Davidson, I. M. T., Eaborn, C., and Lilly, M. N., *J. Chem. Soc.* 2624 (1964).

96. de Beer, J. A., Haines, R. J., Greatrex, R., and Greenwood, N. N., *J. Organometal. Chem.* **27**, C33 (1971).

97. Deeming, A. J., Johnson, B. F. G., and Lewis, J., *J. Chem. Soc. A* 897 (1970).

98. Dehmlow, E. V., *J. Organometal. Chem.* **6**, 296 (1966).

99. Dhaliwal, P. S., Ph.D. Thesis, University of British Columbia, 1966.

100. Dobson, G. R., Stolz, I. W., and Sheline, R. K., *Advan. Inorg. Chem. Radiochem.* **8**, 1 (1966).

101. Donohue, J., and Caron, A., *J. Phys. Chem.* **70**, 603 (1966).

102. Dreier, F., Duncan, W., and Mill, T., *Tetrahedron Lett.* 1951 (1964).

103. Dyatkin, B. L., Mochalina, E. P., and Knunyants, I. L., *Fluorine Chem. Rev.* **3**, 45 (1969).

104. Dyatkin, B. L., Sterlin, S. R., Martynov, B. I., and Knunyants, I. L., *Abstr. 6th Int. Symp. Fluorine Chem. Durham*, p. A31 (1971).

105. Einstein, F. W. B., and Hampton, C. R. S. M., *Can. J. Chem.* **49**, 1901 (1971).

106. Einstein, F. W. B., and Jones, R. D. G., *Inorg. Chem.* **11**, 395 (1972).

107. Einstein, F. W. B., and Jones, R. D. G., *J. Chem. Soc. A* 3359 (1971).

108. Einstein, F. W. B., and Jones, R. D. G., *Inorg. Chem.*, in press.

108a. Einstein, F. W. B., and Jones, R. D. G., unpublished results.

109. Einstein, F. W. B., and Jones, R. D. G., *J. Chem. Soc. Dalton* 442 (1972).

110. Einstein, F. W. B., Jones, R. D. G., MacGregor, A. C., and Cullen, W. R., unpublished results.

111. Einstein, F. W. B., Pilotti, A. M., and Restivo, R., *Inorg. Chem.* **10**, 1947 (1971).

112. Einstein, F. W. B., and Restivo, R., *Inorg. Chim. Acta* **5**, 501 (1971).

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

114. Emeléus, H. J., "The Chemistry of Fluorine and its Compounds," Academic Press, New York, 1969.

115. Emeléus, H. J., and Haszeldine, R. N., *J. Chem. Soc.* 2948, 2953 (1949).
116. Ernst, R. R., *Mol. Phys.* **16**, 241 (1969).
117. Erskine, G. J., *Can. J. Chem.* **47**, 2699 (1969).
118. Feltham, R. D., Metzger, H. G., and Silverthorn, W., *Inorg. Chem.* **7**, 2003 (1968).
119. Fenton, D. E., and Zuckerman, J. J., *J. Amer. Chem. Soc.* **90**, 6226 (1968).
120. Ferretti, A., and Tesi, G., *Chem. Ind. (London)* 1987 (1964).
121. Fields, R., Green, M., Harrison, T., Haszeldine, R. N., Jones, A., and Lever, A. B. P., *J. Chem. Soc. A* 49 (1970).
122. Fields, R., Haszeldine, R. N., and Hubbard, A. F., *Chem. Commun.* 647 (1970).
123. Fields, R., Haszeldine, R. N., Hubbard, A. F., and Palmer, P. J., *Abstr. 6th Int. Symp. Fluorine Chem. Durham*, p. A15 (1971).
124. Frank, A. W., *J. Org. Chem.* **31**, 1917 (1966).
125. Frank, A. W., *J. Org. Chem.* **30**, 3663 (1965).
126. Frank, A. W., *J. Org. Chem.* **31**, 1521 (1966).
127. Frank, A. W., *J. Org. Chem.* **31**, 1920 (1966).
128. Freeburger, M. E., and Spialter, L., *J. Org. Chem.* **35**, 652 (1970).
129. Gale, D. M., Middleton, W. J., and Krespan, C. G., *J. Amer. Chem. Soc.* **87**, 657 (1965).
130. Green, M. L. H., "Organometallic Compounds", Vol. 2. Methuen, London, 1968.
131. Green, M., Osborn, R. B. L., Rest, A. J., and Stone, F. G. A., *J. Chem. Soc. A* 2525 (1968).
132. Greene, P. T., and Bryan, R. F., *J. Chem. Soc. A* 2261 (1970).
133. Greene, P. T., and Bryan, R. F., *J. Chem. Soc. A* 1696 (1970).
134. Greenwood, N. N., *Chem. Brit.* **3**, 56 (1967).
135. Hall, M. C., Kilbourn, B. T., Taylor, K. A., *J. Chem. Soc. A* 2539 (1970).
136. Haluska, L. A., U.S. Patent 2,800,494 (1957).
137. Harris, C. M., and Livingston, S. E., *in* "Chelating Agents and Metal Chelates" (F. P. Dwyer and D. P. Meller, eds.), p. 130. Academic Press, New York, 1964.
138. Harris, R. K., and Robinson, V. J., *J. Mag. Res.* **1**, 362 (1969).
139. Harrison, W., and Trotter, J., *J. Chem. Soc. A* 1542 (1971).
140. Harrison, W., and Trotter, J., *J. Chem. Soc. A* 1607 (1971).
141. Hieber, W., and Freyer, W., *Chem. Ber.* **93**, 462 (1960).
142. Hieber, W., and Kummer, R., *Chem. Ber.* **100**, 148 (1967).
143. Hine, J., "Divalent Carbon." Ronald Press, New York, 1964.
144. Holbrook, G. W., Gordon, A. F., and Pierce, O. R., *J. Amer. Chem. Soc.* **82**, 825 (1960).
145. Hota, N. K., and Willis, C. J., *J. Organometal. Chem.* **15**, 89 (1968).
146. Ibers, J. A., *J. Organometal. Chem.* **14**, 423 (1968).
147. Jetz, W., and Graham, W. A. G., *J. Amer. Chem. Soc.* **89**. 2773 (1967).
148. Jolly, P. W., Bruce, M. I., and Stone, F. G. A., *J. Chem. Soc.* 5830 (1965).
149. King, R. B., *J. Amer. Chem. Soc.* **84**, 2460 (1962).
150. King, R. B., and Egger, C. A., *Inorg. Chim. Acta* **2**, 33 (1968).
151. King, R. B., Kapoor, R. N., and Pannell, K. H., *J. Organometal. Chem.* **20**, 187 (1969).
152. King, R. B., and Pannell, K. H., *Inorg. Chem.* **7**, 1510 (1968).
153. Kirmse, W., "Carbene Chemistry." Academic Press, New York, 1964.

154. Knunyants, I. L., Pervova, E. Ya., and Tyuleneva, V. V., *Dokl. Akad. Nauk SSSR* **129**, 576 (1959).

155. Knunyants, I. L., Tyuleneva, V. V., Pervova, E. Ya., and Sterlin, R. N., *Izv. Akad. Nauk SSSR Ser. Khim.* 1797 (1964).

156. Lambert, J. B., and Roberts, J. D., *J. Amer. Chem. Soc.* **87**, 3884, 3891 (1965).

157. Lewis, J., Nyholm, R. S., and Phillips, D. J., *J. Chem. Soc.* 2177 (1962).

158. Mague, J. T., *Inorg. Chem.* **8**, 1975 (1969).

159. Mague, J. T., and Mitchener, J. P., *Inorg. Chem.* **8**, 119 (1969).

160. Mague, J. T., and Wilkinson, G., *Inorg. Chem.* **7**, 542 (1968).

161. Mahler, W., *J. Amer. Chem. Soc.* **84**, 4600 (1962).

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

163. Margulis, T. N., *J. Amer. Chem. Soc.* **93**, 2193 (1971).

164. Mason, R., and Rae, A. I. M., *J. Chem. Soc. A* 778 (1968).

165. McBee, E. T., Turner, J. J., Morton, C. J., and Stefani, A. P., *J. Org. Chem.* **30**, 3698 (1965).

166. McDonald, W. S., Moss, J. R., Raper, G., Shaw, B. L., Greatrex, R., and Greenwood, N. N., *Chem. Commun.* 1295 (1969).

167. Mitchell, C. M., and Stone, F. G. A., *Proc. 4th Int. Conf. Organometal. Chem. Bristol,* E5 (1969).

168. Mill, T., Rodin, J. O., Silverstein, R. M., and Woolf, C., *J. Org. Chem.* **28**, 836 (1963).

169. Miller, W. T., Hummel, R. J., and Pelosi, L. F., *Abstr. 6th Int. Symp. Fluorine Chem., Durham, 1971,* p. A30 (1971).

170. Miller, W. T., Snider, R. H., and Hummel, R. J., *J. Amer. Chem. Soc.* **91**, 6533 (1969).

171. Mingos, D. M. P., and Ibers, J. A., *Inorg. Chem.* **9**, 1105 (1970).

172. Muetterties, E. L., *Accounts Chem. Res.* **3**, 266 (1970).

173. Mukhedkar, A. J., Mukhedkar, V. A., Green, M., and Stone, F. G. A., *J. Chem. Soc. A* 3166 (1970).

174. Newmark, R. A., Apai, G. R., and Michael, R. O., *J. Mag. Res.* **1**, 418 (1969).

175. Noack, K., *Spectrochim. Acta* **19**, 1925 (1963).

176. Nyholm, R. S., Snow, M. R., and Stiddard, M. H. B., *J. Chem. Soc.* 6564 (1965).

177. Park, J. D., Bertino, C. D., and Nakata, B. T., *J. Org. Chem.* **34**, 1490 (1969).

178. Park, J. D., Choi, S. K., and Romine, H. E., *J. Org. Chem.* **34**, 2521 (1969).

179. Park, J. D., Groves, J. D., and Lacher, J. R., *J. Org. Chem.* **25**, 1628 (1960).

180. Park, J. D., and McMurtry, R. J., *Tetrahedron Lett.* 1301 (1967).

181. Park, J. D., Michael, R. O., and Newmark, R. A., *J. Org. Chem.* **34**, 2525 (1969).

182. Park, J. D., and Nakata, B. T., *Abstr. 154th Meeting Amer. Chem. Soc., Chicago, 1967.*

183. Poliakoff, M., and Turner, J. J., *J. Chem. Soc. A* 654 (1971).

184. Ponomarenko, V. A., and Snegova, A. D., *Izv. Akad. Nauk SSSR Otd. Khim. Nauk* 135 (1960).

185. Pruett, R. L., Barr, J. T., Rapp, K. E., Bahner, C. T., Gibson, J. D., and Lafferty, R. H., *J. Amer. Chem. Soc.* **72**, 3646 (1950).

186. Rapp, K. E., Pruett, R. L., Barr, J. T., Bahner, C. T., Gibson, J. D., and Lafferty, R. H., *J. Amer. Chem. Soc.* **72**, 3642 (1950).

187. Roberts, J. D., and Sharts, C. M., *Org. Reactions* **12**, 1 (1962).

188. Roberts, P. J., Penfold, B. R., and Trotter, J., *Inorg. Chem.* **9**, 2137 (1970).
189. Roberts, P. J., and Trotter, J., *J. Chem. Soc. A* 1479 (1971).
190. Roberts, P. J., and Trotter, J., *J. Chem. Soc. A* 3246 (1970).
191. Sacco, A., *Gazz. Chim. Ital.* **93**, 698 (1963).
192. Sacco, A., and Ugo, R., *J. Chem. Soc.* 3274 (1964).
193. Sargeant, P. B., *J. Amer. Chem. Soc.* **91**, 3061 (1969).
194. Seyferth, D., *Organometal. Chem. Rev.* **134**, 242 (1968).
195. Seyferth, D., and Damrauer, R., *J. Org. Chem.* **31**, 1660 (1966).
196. Seyferth, D., and Darragh, K. V., *J. Org. Chem.* **35**, 1297 (1970).
197. Seyferth, D., Jula, T. F., Dertouzos, H., and Pereyre, M., *J. Organometal. Chem.* **11**, 63 (1968).
198. Seyferth, D., Dertouzos, H., Suzuki, R., Mui, J. Y. P., *J. Org. Chem.* **32**, 2980 (1967).
199. Stephens, R., Tatlow, J. C., and Wood, K. N., *Abstr. 6th Int. Symp. Fluorine Chem., Durham,* p. A1 (1971).
200. Stockel, R. F., *Can. J. Chem.* **47**, 867 (1969).
201. Stockel, R. F., *Can. J. Chem.* **46**, 2625 (1968).
202. Stockel, R. F., Megson, F., and Beachem, M. T., *J. Org. Chem.* **33**, 4395 (1968).
203. Sullivan, R., Lacher, J. R., and Park, J. D., *J. Org. Chem.* **29**, 3664 (1964).
204. Sumner, G. G., Klug, H. P., and Alexander, L. E., *Acta Crystallogr.* **17**, 732 (1964).
205. Sutton, P. W., and Dahl, L. F., *J. Amer. Chem. Soc.* **89**, 261 (1967).
206. Tarrant, P., Johnson, R. W., and Brey, W. S., *J. Org. Chem.* **27**, 602 (1962).
207. Tarrant, P., and Oliver, W. H., *J. Org. Chem.* **31**, 1143 (1966).
208. Treichel, P. M., and Stone, F. G. A., *Advan. Organometal. Chem.* **1**, 143 (1964).
209. Ugi, I., Marquarding, D., Klusacek, H., Gillespie, P., and Ramirez, F., *Accounts Chem. Res.* **4**, 288 (1971).
210. Venanzi, L. M., *Chem. Brit.* **4**, 162 (1968).
211. Waldman, M. C., Ph.D. Thesis, University of British Columbia (1968).
212. Wei, C. H., and Dahl, L. F., *J. Amer. Chem. Soc.* **91**, 1351 (1969).
213. Wei, C. H., and Dahl, L. F., *J. Amer. Chem. Soc.* **88**, 1821 (1966).
214. Wei, C. H., Wilkes, G. R., and Dahl, L. F., *J. Amer. Chem. Soc.* **89**, 4792 (1967).
215. Wertheim, G. K., "Mössbauer Effect: Principles and Applications." Academic Press, New York, 1964.
216. Wilcox, C. F., and Craig, R. R., *J. Amer. Chem. Soc.* **83**, 3866 (1961).
217. Wilford, J. B., Treichel, P. M., and Stone, F. G. A., *Proc. Chem. Soc.* 218 (1963).
218. Woodward, R. B., and Hoffman, R., *Angew. Chem. Int. Ed. Engl.* **8**, 781 (1969).
219. Wright, J. S., and Salem, L., *Chem. Commun.* 1370 (1969).
220. Zumdahl, S. S., and Drago, R. S., *J. Amer. Chem. Soc.* **90**, 6669 (1968).