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ORGANOMETALLIC INTRAMOLECULAR-COORDINATION COMPOUNDS. RECENT ASPECTS IN THE STUDY OF SULFUR DONOR LIGANDS

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A. INTRODUCTION

Organometallic intramolecular-coordination compounds [1—4] are compounds with a ring system in which the metal has an intramolecular-coordinate bond with a donor atom as well as a covalent metal—carbon bond. These may be classified for the sake of convenience into the following four groups in accordance with their donor ligand atoms: (i) oxygen donor ligand such as carbonyl, alkoxy, aryloxy, etc., (ii) nitrogen donor ligand, (iii) carbon—carbon multiple bond donor ligand such as alkenyl, phenyl, etc., and (iv) other donor ligands such as sulfur, phosphorus, halogen, etc.

The author has reviewed the first group of compounds (particularly carbonyl group [1] as an oxygen donor) and the second group [2]. A great many articles on the third group of compounds have been reported. There are several reviews [5—9] which include intramolecular-coordination compounds in part. Recently, very general reviews covering all the groups have been published with the titles "Cyclometallated Compounds" [10] and "Cyclometallation Reaction [11].

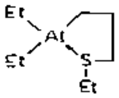
As sulfur belongs to the sixth group of the periodic table, it shows similar character to oxygen. However, while oxygen has 1s, 2s and 2*p* orbitals, sulfur has 3*d* orbitals in addition. Furthermore, the atomic radii and electronegativities of these atoms are different. Therefore a sulfur donor ligand is expected to show slightly different character from an oxygen donor ligand. Organometallic intramolecular-coordination compounds with oxygen or a sulfur donor ligand tend to form five-membered ring structures, but in other respects they show different characteristics.

The purpose of this review is (i) to show that organometallic intramolecular-coordination compounds with a sulfur donor ligand form mainly five-membered ring structures but with certain exceptions also form six-, four- and three-membered rings, and (ii) to discuss critically these compounds in comparison with other organometallic intramolecular-coordination compounds containing an oxygen or nitrogen donor ligand. An additional purpose is to stimulate further investigation in this area of research.

B. FIVE-MEMBERED RING COMPOUNDS

(i) Alkanethioethers

In 1955, Bähr and Müller [4] discovered organoaluminum organometallic intramolecular-coordination compounds. Both ether and amine compounds were reported. In the same year, they [12] synthesized thioether **1** having a sulfur atom in place of oxygen in the ether compound.



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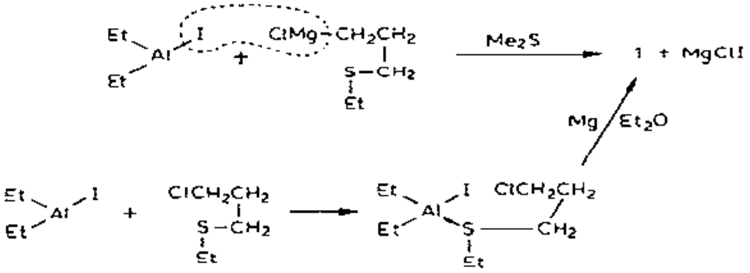

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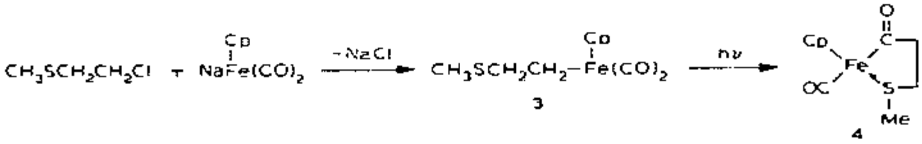
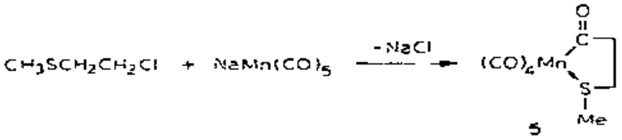
Since analytical instruments had not at that time been satisfactorily developed proof of intramolecular coordination was demonstrated by the two reaction routes, shown above. The structure of **1** is further confirmed by molecular weight (monomeric structure), elemental analysis and the destructive degradation.

Bähr and Thiele [13] further studied a similar compound having beryllium in place of aluminum in 1, and showed by using Stuart—Briegleb Models that the five-membered ring structure such as **1** can form with a strain-free configuration.

King and Bisnette [14,15] synthesized **4** and **5** which might have five-membered ring structures by the reaction of iron or manganese carbonyl compounds with halothioether.



Cp C_5H_5 $\nu C{=}O$ 1618 cm^{-1}

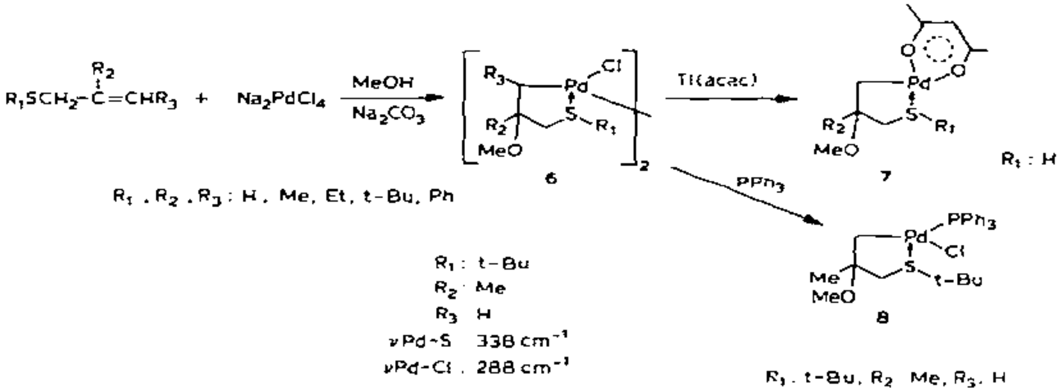


$\nu C{=}O$ 1631 cm^{-1}

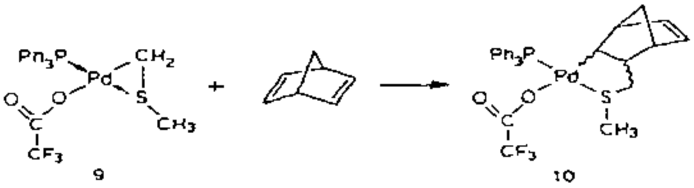
The condensation of 2-chloroethyl methyl sulfide with $NaFe(CO)_2C_5H_5$ gave an air sensitive liquid product, which is the ordinary type of alkyl iron compound **3** having an iron—carbon σ-bond and no iron—sulfur bond. Its IR spectrum exhibits no acyl carbonyl bands around 1600 cm^{-1}. Irradiation of **3** in benzene solution gave an orange crystalline solid. The IR spectrum of this orange solid is very different from that of **3**. It exhibits a single strong band in the metal carbonyl region at 1935 cm^{-1} and also a single strong band at 1618 cm^{-1}, the expected carbonyl frequency [16—18] for an acyl carbonyl group bonded to a transition metal. Structure **4** is preferred, where only one of the two carbonyl groups is clearly a terminal metal carbonyl and the other carbonyl group is an acyl carbonyl. This chelate-type ring formally donates three electrons to the metal atom. Two of these three electrons arise from the iron—sulfur dative bond and the third electron from the bond between the iron atom and the carbon atom of the acyl group.

The condensation of 2-chloroethyl methyl sulfide with $NaMn(CO)_5$ gave directly the chelate-type compound **5**. Complex **5** probably forms via a compound similar to **3** as intermediate; however, as the manganese compound has many electronegative carbonyl groups, and as the metal is very liable to bond with sulfur, the thioether group migrates to the carbonyl very readily, hence the condensation yields **5** in an apparent one-stage reaction.

Allylic sulfides react with palladium chloride in the presence of sodium carbonate to give di-μ-chloro-bis(3-alkyl- or phenylmercapto-2-methoxypropyl)dipalladium(II) **6**. Ishii and coworkers [19] showed direct evidence for metal—sulfur coordination by assigning IR spectra at 338 cm^{-1} and 288 cm^{-1} to the bridged Pd—Cl group. Compounds **6** react with thallium acetylacetonate or triphenylphosphine to give monomeric compounds **7** or **8** by the fission of the chloro-bridged bond of **6**.



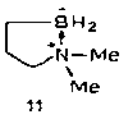
Okawara and coworkers [20] reported that the three-membered ring compound **9** reacts with 2,5-norbornadiene to give the *cis*-addition product **10**, which shows a doublet signal (J(P—H) = 4 Hz) (S—CH_3) in its proton resonance spectrum, direct evidence of Pd—S coordination. However, it is not certain at present whether insertion occurred through *endo*- or *exo*-addition. [Also see Section E]



S—CH_3 J(P—H) . 4 Hz

Dimethylallylamine [21] reacts with trimethylaminoborane in toluene to give a compound **11**. The IR spectrum indicates the presence of an N—B bond and the absence of a C—C double bond, and molecular weight determination indicates extensive association.

Reaction [22] of dimethyl sulfide-boran with allyl methyl sulfide in benzene gives compound **12** similar to **11**. Adams and coworkers presumed that the stability and distillable character of **12** is doubtless due to coordinate bonding of sulfur to boron.



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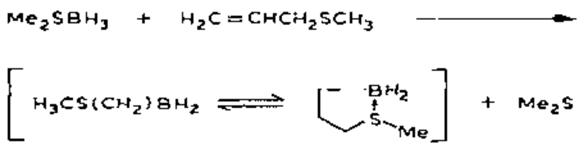

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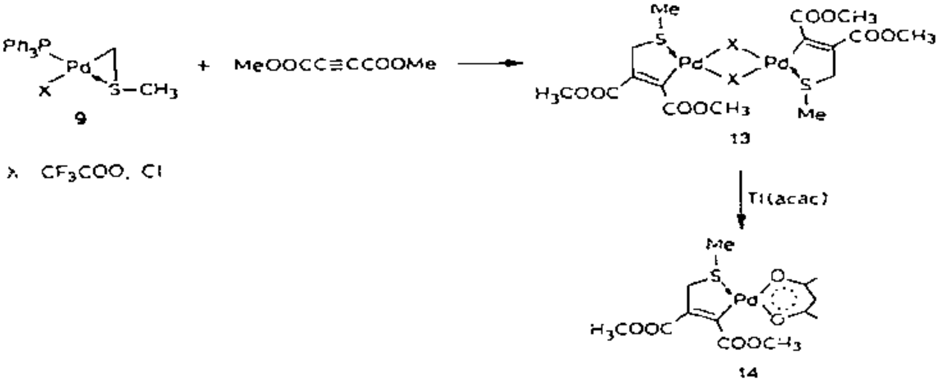
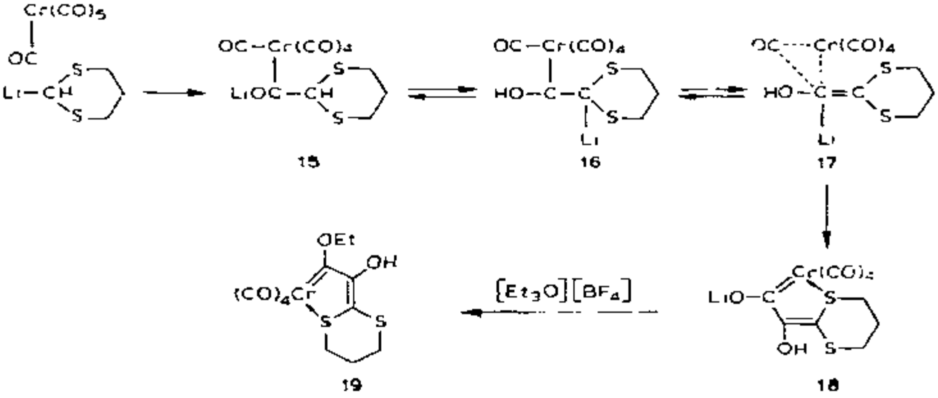
(ii) *Alkenethioethers*

Insertion [20] of an acetylenic compound into the organometallic intramolecular three-membered ring compounds **9** described above gave the corresponding *cis*-addition compounds **13**, which are trifluoroacetic acid- or chloro-bridged intramolecular alkenethioether dimers. Okawara and coworkers proposed the configuration of compounds **13** as shown below from molecular weight measurements, the appearance of the methylenic proton resonances as an AB pattern (δ 4.10 and 3.79 ppm J_{AB} = 16 Hz) and a strong IR band at 1650 cm^{-1} (X = CF_3COO) due to the bridging carboxylate groups. Compounds **13** can be converted to the compound **14** by the cleavage of the bridged bond with Tl(acac).



X: CF_3COO, Cl

Reaction [23] of chromium carbonyl with lithium cyclic dithioether and subsequent alkylation affords intramolecular alkenethioether **19**.



As shown above, this reaction proceeds via two carbonyl insertions, proton migration to give **18** and alkylation of **18** by $[Et_3O][BF_4]$ to give the stable metal—carbene complex **19** [24—27]. The mass spectrum of the com-

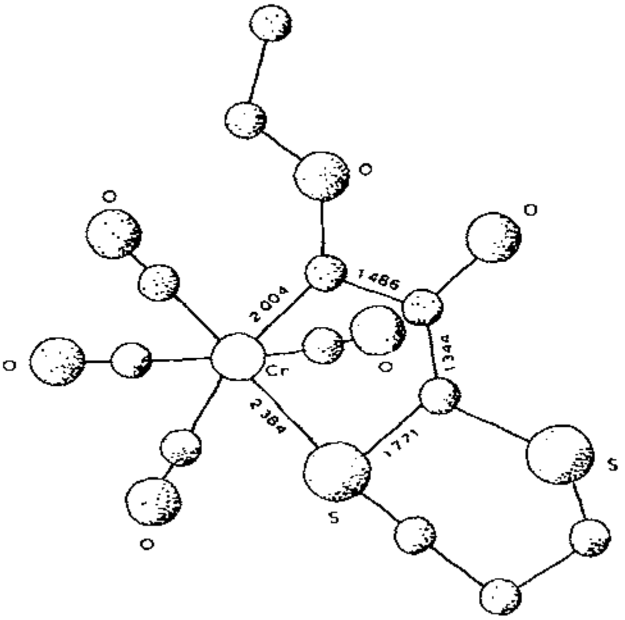
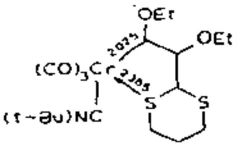


Fig. 1. The structure of *cis*[(ethoxy)-1,3-dithianylidene(hydroxy)methylcarbene-C,S]-tetracarbonylchromium(0) 19.

pound **19** showed the consecutive loss of four carbonyl groups from the molecular ion (*m/e* 368), and the IR spectrum indicates a *cis* $M(CO)_4L_2$ structure. The ^{13}C NMR spectrum [$(CD_3)_2CO$] indicated the presence of two sp^2-carbon atoms (δ 161.4 and 139.0 ppm) in addition to the carbene carbon (δ 313.3 ppm) among others. Final confirmation for the structure and stereochemistry of **19** was obtained from three-dimensional X-ray analyses [24,28] (Fig. 1).

The reaction of the cyclic dithioether chromium carbonyl complex with n-butyllithium in the presence of *t*-butyl isocyanate and subsequent alkylation produces the compound **20** [28,29]. *fac*-[1,3-Dithian-2-ylidene-(ethoxy)-methyl(ethoxy)carbene-C,S]-*t*-butylisocyanide]tricarbonyl chromium(0) **20** was shown to be similar to **19** by X-ray analysis.



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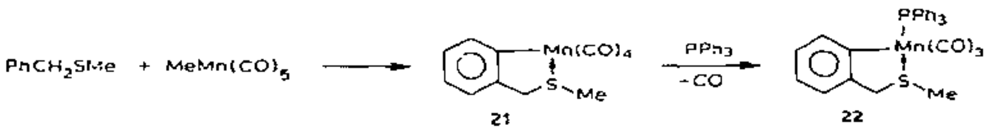
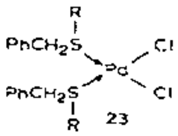
(iii) Benzylthioethers

Benzyl compounds easily orthometallate to give intramolecular-coordination compounds with a five-membered ring containing the electronegative group at the benzyl position, as in the case of benzylamines [2].



Ortho-metallation of benzylmethylthioether with methylmanganese carbonyl [30,31] easily gives the five-membered ring compound **21**, which in turn reacts with triphenylphosphine to give **22** with elimination of a carbonyl group. The structure of **22** is confirmed (Fig. 2) by a single crystal X-ray structural determination.

However, reaction between PhCH$_2$SR(R=Me [32], Ph [19]) and PdCl$_2$ or PdCl$_4^{2-}$ does not afford intramolecular coordination compounds, but yields PdCl$_2$(RSCH$_2$Ph)$_2$ **23**.



Ishii and coworkers [19] presumed the reason that the sulfur compounds above do not cyclometallate while the amine compounds [2] easily do is as follows. S→Pd coordination is so strong that electrophilic substitution at the phenyl group by palladium ion is inhibited and in this respect the sulfur atom is different from the nitrogen atom. However, the present author suggests an alternate reason why manganese carbonyl can *ortho*-metallate and palladium

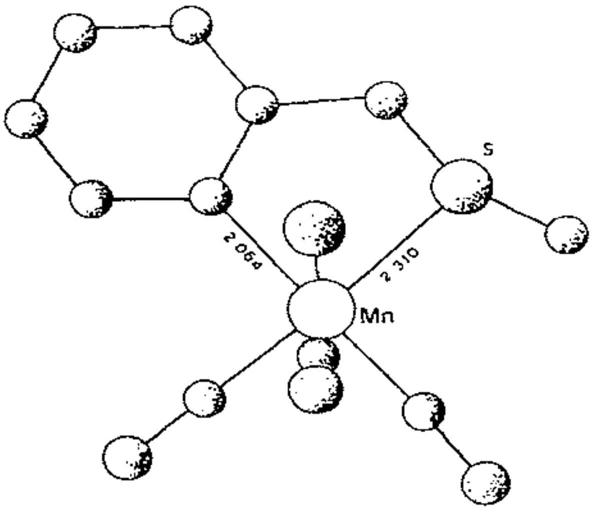
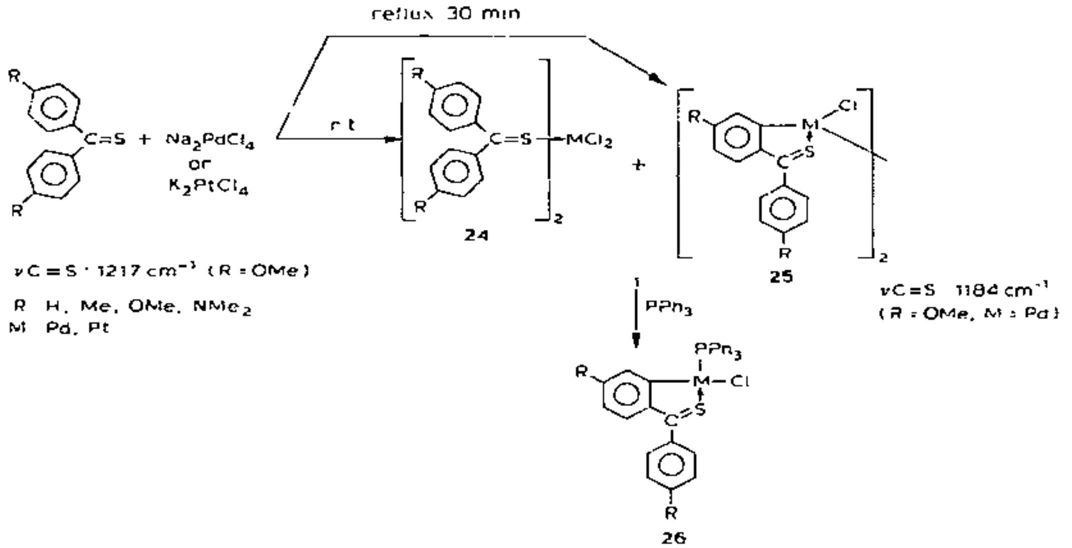


Fig. 2. The structure of (S-methylbenzyl-C,S)(tetracarbonyl)(triphenylphosphine)manganese 22.

chlorides can not. Namely as the manganese carbonyl compound has five electronegative carbonyl groups, and as the coordination of sulfur with Mn is so strong, the manganese metal is a stronger electrophile than palladium for attacking at the *ortho*-position.

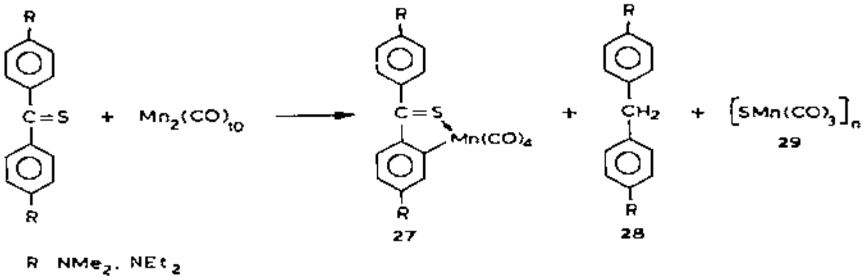
(iv) Thiobenzophenones

Alper et al. have investigated reactions between thiobenzophenones and many kinds of metal salts. In the reaction between benzylthioether and palladium compounds, the *ortho*-metallation reaction did not proceed. But the reaction [33] between thiobenzophenones and palladium or platinum compounds at room temperature afforded bis(thiobenzophenone)metal chlorides **24** and *ortho*-metallation compounds **25**: however, when a mixture of **24** and **25** was allowed to reflux in a methanol solution for 16 h **25** were obtained in high yield.

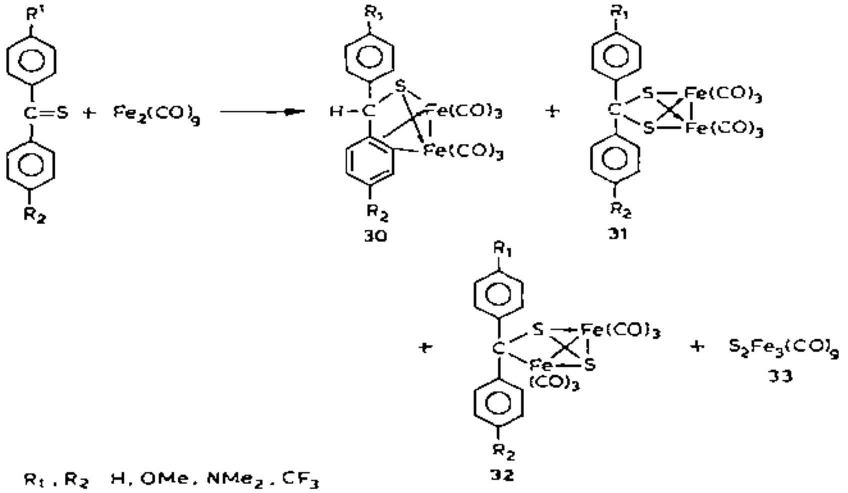


The present author presumes that the chlorides **24** are intermediates of the *ortho*-metallation products **25**, i.e., the *ortho*-metallation proceeds as follows: the first step, sulfur coordinates to the metal to form **24**, and the second step, the metal attacks the *ortho*-position as a nucleophile to form **25**. The intramolecular coordination of sulfur to the metal is assumed [33] because the IR spectrum of **25** shows ν(CS) absorption at 30 cm^{-1} lower frequency than those of the starting materials. The treatment of a mixture of **24** and **25** with triphenylphosphine affords **26** by ligand-exchange accompanied by the fission of the chloro-bridged bond of **25**.

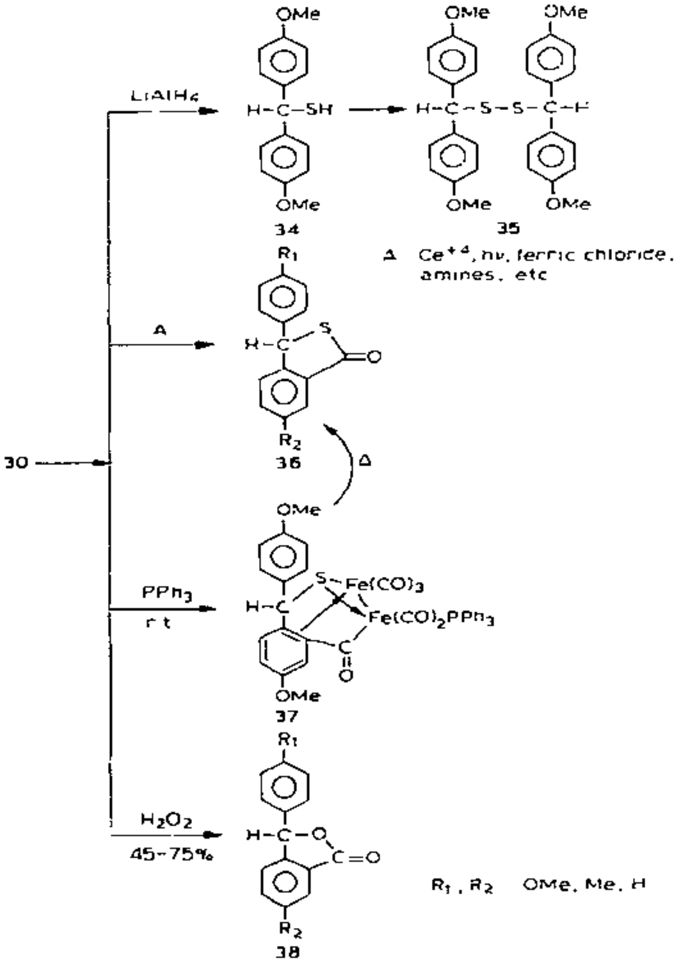
The reactions [34] of dimanganese decacarbonyl with thiobenzophenones afforded tetraphenylethylenes in high yields, but reactions with thiones containing the highly activated dialkylamino substituents afforded *ortho*-metallated complexes **27** with a sulfur-donor ligand. Alper [34] proposed the five-membered ring structure for **27** because the νCO frequencies at 2068—1927 cm^{-1} are analogous to the data obtained for five-membered ring *ortho*-manganated complexes with nitrogen-donor ligand derived from the Schiff bases [35] and benzo[h]quinone [36]. The reaction [37] of thiobenzophenones with dirhenium decacarbonyl also afforded *ortho*-metallated rhenium complexes having the sulfur-donor ligand similar to **27**.



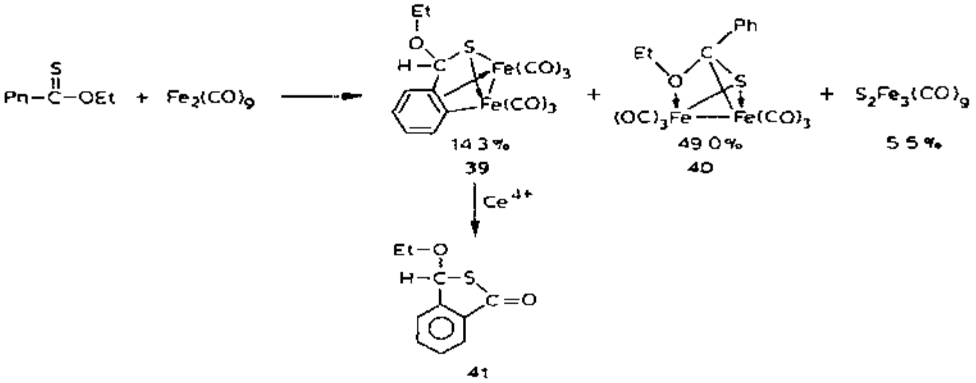
Alper et al. [38—47] also attempted many reactions of thiobenzophenones with diiron enneacarbonyl. In the reaction of diiron enneacarbonyl, the sulfur atom is assumed to bond to two iron atoms at the same time as to one ordinary σ-bond and one coordination bond, then the C=S double bond converts to a single bond to form compounds **30**. This reaction is also considered to be an *ortho*-metallation reaction involving one metal. Compound **30** has a five-membered ring structure containing one metal which is coordinately bound by sulfur with the other metal forming a bond with the π-orbital of the benzene ring. In addition to **30**, a small number of by-products **31—33** were obtained



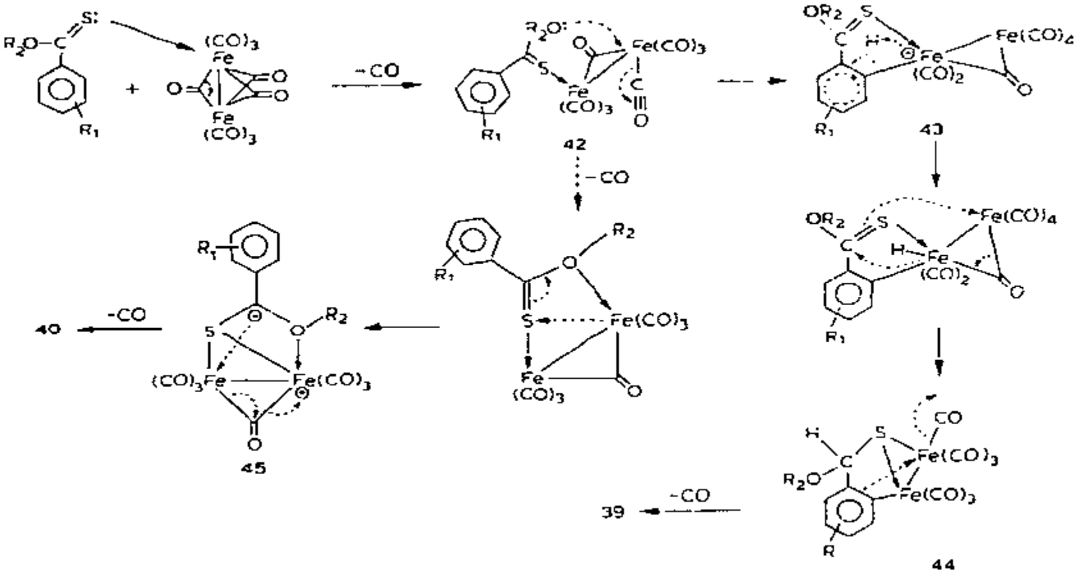
Reduction of one of the compounds **30** gave a mercaptan **34** which, on standing, was oxidized to form disulfide **35**. The *ortho*-metallated complexes **30** showed a great propensity for carbonyl insertion. This was demonstrated by the reactions of **30** with a variety of reagents in various conditions. For instance [38,39], thiolactone **36** is obtained in high yield when one of the complexes **30** was subject to treatment with ceric ammonium nitrate, ferric chloride, heating in ethanol, irradiation with UV light, amine, phosphine or SCN⁻. **30** was treated with triphenylphosphine under mild conditions in an attempt to isolate the carbonyl inserted organometallic complex **37** with two remaining iron atoms. The complex **37** was easily converted to a compound similar to **36** on heating. Hence, Alper et al. [38,39] presumed that **37** is an intermediate to **36** from **30**. Cleavage reaction of **30** by hydrogen peroxide [44] or *m*-chloroperbenzoic acid provided the lactones **38**.



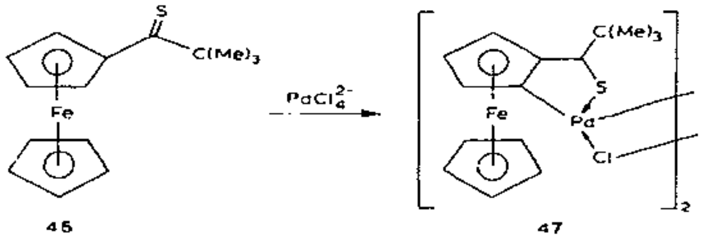
The reaction [46] of various *O*-ethyl aryl thioesters with enneacarbonyl afforded an *ortho*-metallated complex **39**; however, as the *O*-ethyl aryl thioester has an ether oxygen ligand besides sulfur, the above reaction also afforded the other bimetallation product **40** which has two kinds of coordinate bond (sulfur and oxygen to two metals). The complex **39** was also converted to thiolactone **41** by oxidative cleavage with ceric ammonium nitrate.



In the reaction [40] of diiron enneacarbonyl with *O*-alkyl thiobenzoates in place of *O*-ethyl aryl thioester, the ratio of *ortho*-metallated complexes similar to **39** to the O,S-donor complexes similar to **40** showed a marked increase in favor of the *ortho*-metallated complex in the case of a thioester containing the electron-donating methoxy substituent compared with that having the electron-withdrawing trifluoromethyl group. This trend supports the view that the *ortho*-metallation reaction proceeds by an electrophilic pathway. Increase in the effective bulk of the alkoxy group of the *O*-alkyl thiobenzoates has a dramatic effect on the product distribution. Only the *ortho*-metallated complex **39** was isolated in the reaction using the 1-adamantylmethyl thioester. A rationale for the above results can be given on the basis of the pathway outlined below.

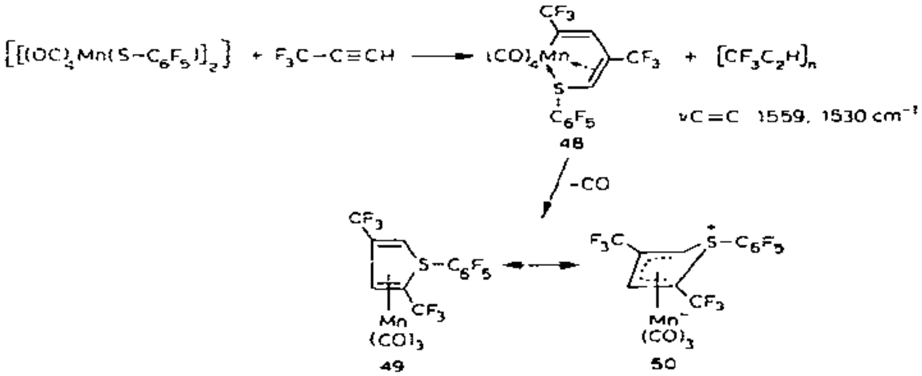


Moreover Alper [48] reported the reaction of thiopivaloylferrocene **46** with an equimolar amount of sodium tetrachloropalladate, to yield chloro-bridged *ortho*-metallated complex **47**.

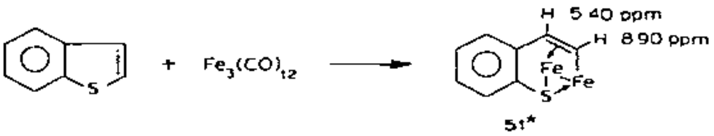


C. SIX-MEMBERED RING COMPOUNDS

The reaction [49] of complex $[[Mn(CO)_4(SC_6F_5)]_2]$ with trifluoropropyne afforded the complex **48**, which was obtained by insertion of a trifluoropropyne dimer into the Mn—S bond. The complex **48** has a six-membered ring structure containing a π-coordinate interaction with the olefinic double bond, whose IR spectrum shows absorption at 1559 and 1530 cm^{-1}. Thermal decarbonylation of **48** at 80°C gave in very low yield the complexes **49** or **50** having a heterocyclic sulfur-containing ring η-bonded to $Mn(CO)_3$ group.



Triiron dodecacarbonyl [50,51] reacted with thianaphthene to give binuclear iron carbonyl **51** which has a six-membered ring structure involving one iron atom. Analysis of **51** seemed to support a formulation $C_8H_6SFe_2(CO)_5$ rather than $C_8H_6SFe_2(CO)_6$. The structure of **51** is proposed by King et al. [50] on the basis of IR and NMR data.



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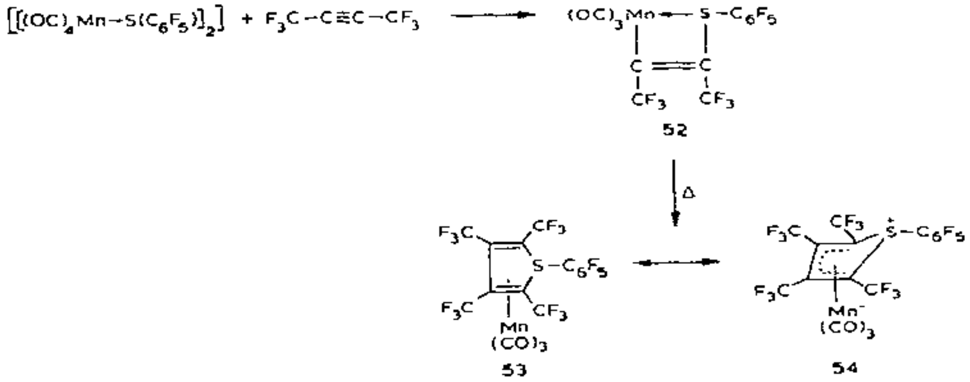
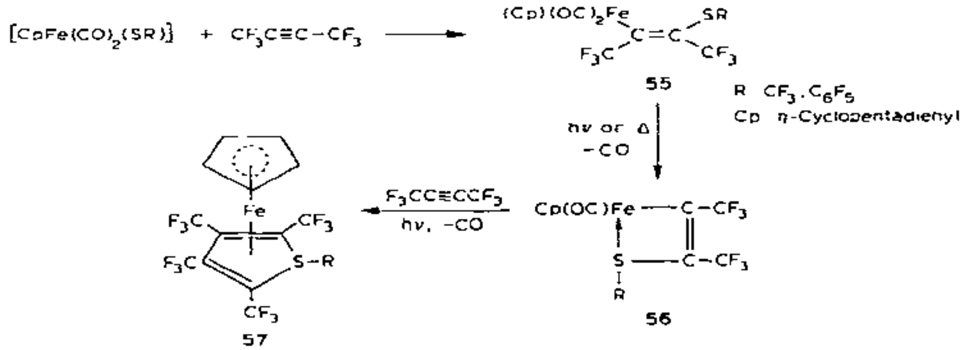
* For purposes of clarity the five carbonyl groups bonded to the iron atoms are not shown.

D. FOUR-MEMBERED RING COMPOUNDS

Reaction [49] of hexafluorobut-2-yne with $[[Mn(CO)_4(SR)]_2]$ (R = CF_3 or C_6F_5) at room temperature gave four-membered ring compound **52** by insertion of the acetylenic bond into the Mn—S bond. At a higher temperature **53** or **54** was formed.



The reaction [49] of hexafluorobut-2-yne with the iron carbonyl compound $[(Cp)Fe(CO)_2(SR)](R{=}CF_3$ or $C_6F_5)$ in place of the manganese carbonyl compound above gave *cis*-bis(trifluoromethyl)olefin 55 by insertion of the acetylene into the Fe—S bond. Photochemical reaction or the thermal decomposition of 55 gave the four-membered ring compound 56, which was also obtained by decarboxylation of 55, which is similar to 52. The compound **56** reacted photochemically with hexafluorobut-2-yne to give 57, which is spectroscopically very similar to 53 or 54 and formulated to contain a coordinated heterocyclic ring. It might as well be called a thiaferrocene.



The reaction [52,53] of planar nickel bis(*cis*-stilbenedithiolate) **58** with iron pentacarbonyl afforded the four-membered ring diarylthioketocarbene **59**, together with traces of **60** and **61**. The compound **58** reacted with $Fe_2(CO)_9$ under mild conditions to give **62** in place of **59**, and **62** produced **59** in quantitative yield on heating or irradiating with $Fe(CO)_5$. Hence, **62** is pre-

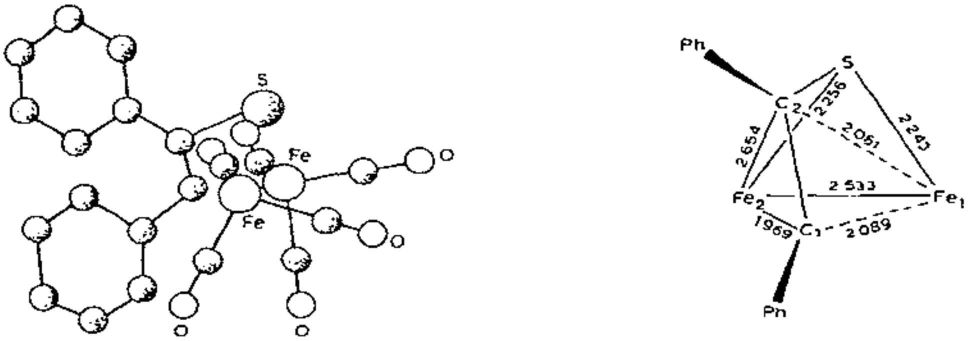
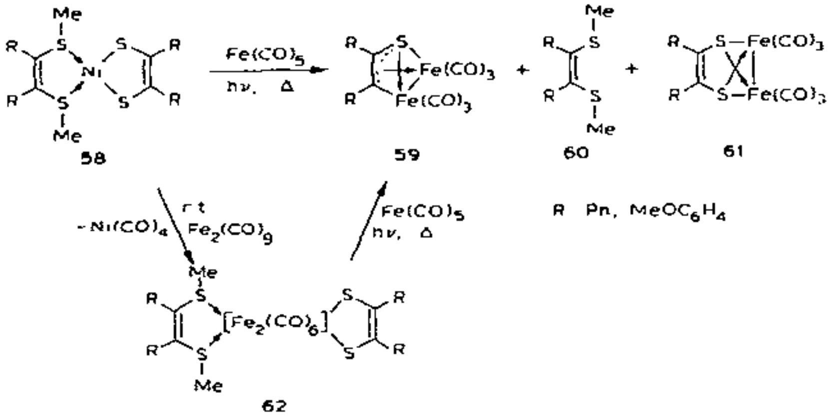


Fig. 3. The structure of trihapto-1,2-diphenylthiocarbenehexacarbonyldiiron **59**.

sumed to be an intermediate in the formation of the thioketocarbene complex **59**. The appearance of **62** as an intermediate in this reaction was unambiguously demonstrated by IR analysis of the reaction solution.

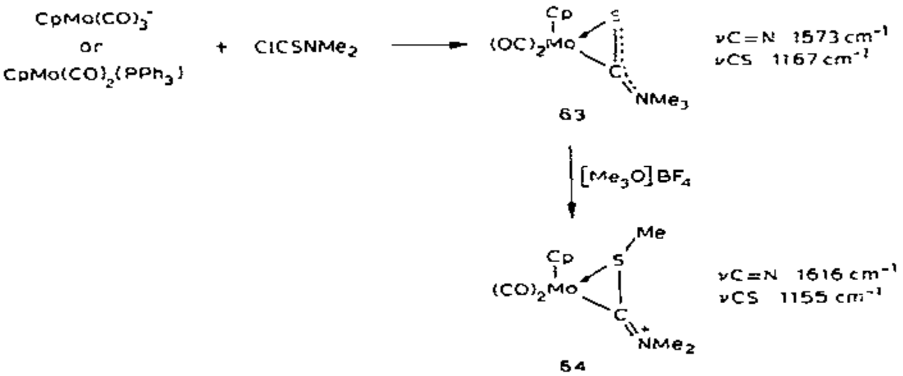


The structure of the 1,2-diphenylthioketocarbene **59** was confirmed by an X-ray crystallographic determination [53]. The shortness of the Fe_2—C_1 distance suggests that this bond is essentially σ in character. The near identity of the Fe_1—C_1 and Fe_1—C_2 distances, as well as the spatial arrangement of Fe_1 relative to C_1 and C_2 indicate a predominance of π-bonding interaction between Fe_1 and the 1,3-dipolar ligand, leading to a delocalized bonding situation schematically represented by Fig. 3.

E. THREE-MEMBERED RING COMPOUNDS

Organometallic intramolecular-coordination compounds display few four-membered rings and only very few three-membered rings. However, a comparatively large number of articles concerning three-membered ring compounds with sulfur have been published. We presume this fact to suggest the participation of *d*-orbitals of sulfur, compared with oxygen or nitrogen donor ligands.

The reaction [54] of either CpMo(CO)$_3^-$ or CpMo(CO)$_2$PPh$_3^-$ with ClCSNMe$_2$ yielded a bidentate three-electron donor compound **63**, which gave the complex **64** with [Me$_3$O][BF$_4$] by methylation.



Many metal carbonyl complexes of Mo, Mn and W containing the CH$_2$SCH$_3$ group have been prepared by King and Bisnette [14,15]. They presumed that the coordination of this group is through an ordinary σ-bond or π-bond of C=S. Later, De Gil and Dahl [55] showed by the X-ray diffraction study of Mo(Cp)(CO)$_2$(CH$_2$SCH$_3$) **65** Fig. 4 (obtained by reaction of NaMoCp(CO)$_3$ and ClCH$_2$SCH$_3$) that the CH$_2$SCH$_3$ ligand does not behave at all as an olefin-like unidentate ligand but instead effectively simulates an allylic group to function as a bidentate ligand. The role of this ligand in this metal complex as a π-bonding, three-electron neutral donor (with two spin-paired electrons in the π-orbital and one unpaired electron in the π*-orbital) is conceptually preferred even though the observed H$_2$C—S bond length value of 1.78 Å (single

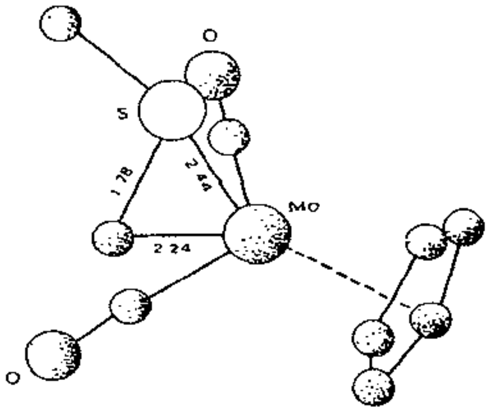
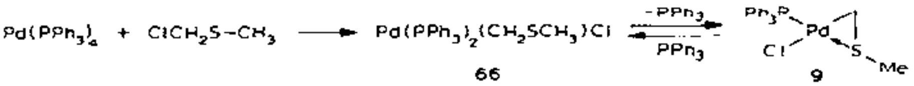


Fig. 4. Molecular configuration of Mo(π-C$_5$H$_5$)(CO)$_2$(π-CH$_2$SCH$_3$) **65**.

bond 1.82 Å; double bond 1.61 Å [56]) is not indicative of any significant degree of multiple bond character.

The oxidative addition [57,58] of chloromethyl methylsulfide to $Pd(Ph_3P)_4$ provided the compound **66**. The crystallization of **66** was carried out repeatedly in CH_2Cl_2 and Et_2O, and by this process **9** was obtained through loss of triphenylphosphine in accordance with the equilibria shown below. A doublet signal of the (S)CH_3 proton ($J(P—H) = 5$ Hz) in the ^1H NMR spectrum indicates that the CH_3SCH_2 group coordinates in an intramolecular bidentate fashion.



66 9

νPd—Cl	275 cm^{-1}	273 cm^{-1}
$\delta(SCH_2)$	2 29 ppm	2 34 (δ J(PH) 5 Hz) ppm
$\delta(CH_2)$	3 26 ppm	2 68 ppm

The coordination of **9** was determined by X-ray diffraction [59] (Fig. 5).

In 1966, Baird et al. [60,61] synthesized the first carbon disulfide π-complexes, $M(PPh_3)_2(\pi\text{-}CS_2)(M=Pd, Pt)$, from the reaction of $M(PPh_3)_4(M=Pd, Pt)$ and carbon disulfide. This mode of coordination was readily characterized by bands appearing in the IR spectrum in the regions 955—1235 and 632—653 cm^{-1}. These bands are assigned to the non-ring $\nu(C{=}S)$ vibration and the in-ring $\nu(C—S)$ vibration respectively. These complexes have also been reported with respect to many transition metals such as Ni[61,62], Rh[61—63], Ir[61,62,64], V[64], Fe[64,65], Co[64,66], Ru[64,67,68], Nb[69], Os[68],

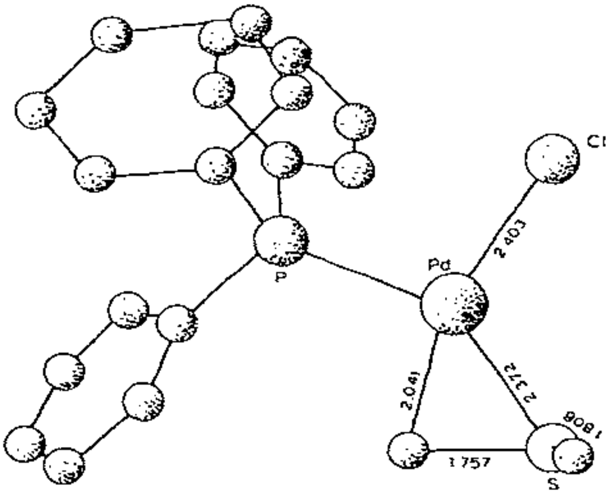
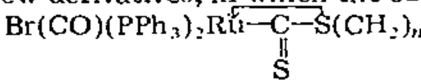
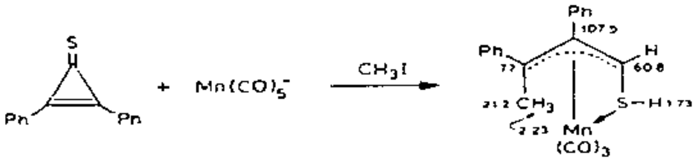


Fig. 5. Molecular structure of [$(Ph_3P)Pd(Cl)CH_2SCH_3$] 9.

etc., and the ring structures were confirmed by X-ray molecular structure determination [65,70,71]. Recently, Yaneff [72] and Butler and Fenster [73] have reviewed these carbon disulfide complexes. Most of these carbon disulfide complexes do not belong to the organometallic intramolecular-coordination compounds according to definition because the bond of the sulfur atom to the metal is formally an ordinary σ-bond and not a coordinate bond with the lone pair of the sulfur atom. A few derivatives, in which the sulfur atom is also bound to an alkane bromide,  $Br(CO)(PPh_3)_2Ru{-}\underset{\displaystyle \| \atop S}{C}{-}S(CH_2)_nBr$ (n = 1, 3, 4) [74], do belong in this review.

In addition, the reaction [75] of diphenylcyclopropenethione with manganese pentacarbonylation and methyl iodide afforded the complex **67**, whose structure is presumed to involve a sulfur-donor ligand π-allyl manganese complex.



67

F. CONCLUDING REMARKS

1. Organometallic intramolecular-coordination compounds containing a sulfur-donor ligand generally form a five-membered ring structure.
2. Ligand exchange reactions of these compounds may be carried out with PPh_3 or Tl(acac) without fission of the intramolecular coordinate bond.
3. As the coordinate bonds of the sulfur donor ligands to the metals are weak compared with those of oxygen or nitrogen donor ligands, the formation of intramolecular coordination by the *ortho*-metallation reaction is fairly difficult. However, stable intermediates for *ortho*-metallation having a metal—sulfur bond can be easily isolated and can be converted to organometallic intramolecular-coordination compounds containing a sulfur ligand group.
4. Many three-membered ring intramolecular-coordination compounds containing a sulfur donor ligand were reported compared with those containing an oxygen or nitrogen donor ligand. It is presumed that as the sulfur has *d*-orbitals, these compounds are able to form three-membered rings with less strain.

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