STRUCTURAL INVESTIGATIONS OF ORGANOMETALLIC COMPOUNDS IN THE USSR

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Abstract - The paper reviews recent X-ray structural investiga-
tions of various types of organometallic compounds carried out
in the USSR, mainly in the Institute of Organo-Element Compounds
of the Academy of Sciences in Moscow. Among these compounds one
can especially note various π-complexes of transition metals
with unusual ligands and coordination types, polynuclear organo-
metallic compounds, both without direct metal-metal bonds and
involving such bonds, which in some cases form rather long
chains, and compounds, mainly of non-transition and post-tran-
sition metals, with secondary bonds or additional coordination.

INTRODUCTION

X-ray structural investigations of organometallic compounds were begun in the
USSR just after the World War II on initiative of professor A. N. Nesmeyanov.
After the discovery of ferrocene and arising of a general interest in π-com-
plexes, their X-ray studies in the USSR are carried out mainly in the Institu-
te of Organo-Element Compounds of the Academy of Sciences in Moscow. Besides
π-complexes, other organic derivatives of transition and non-transition metals
are structurally investigated in this and other scientific institutes.

In this lecture it is impossible even to enumerate all soviet X-ray investiga-
tions of organometallic compounds. Therefore, using mainly recent data, the
author will restrict his review to several classes of compounds for which X-
results are most interesting and efficient. To these organometallic compounds
one can attribute some peculiar π-complexes, polynuclear compounds both with
and without metal-metal bonds, complexes with novel ligands and coordination
types and organic derivatives of non-transition and post-transition metals in-
volving secondary bonds or additional coordination.

CHIRAL π-COMPLEXES

Lately an increasing interest is aroused by chiral organometallic compounds,
and often an unambiguous determination of their absolute configuration is re-
quired. The most straightforward solution of this problem is provided by an
X-ray study taking into account anomalous scattering of X-rays.

N. M. Loim (Ref. I) resolved α-aminoethylcymanthrene (I) into enantiomers and
obtained a series of their derivatives (2)-(5)(Fig. I), which according to
chiroptical correlations were formed with retention of configuration. The ab-
solute R-configuration of the asymmetric carbon atom was proved by an X-ray
study of (+)-(4) and the predominant (-)-diastereoisomer of (5). The latter
molecule also has a planar chirality (S_p) as two substituents in the cyclopen-
tadienyl ring are different.

The same effect of intramolecular asymmetric induction arises by creation of
a planar chirality by an exocyclic chiral center in the reaction of cyclopal-
ladation of enantiomeric (+)-α-dimethylaminoethylferrocene (Ref. 2). The cor-
responding product (6) has the R,S_p absolute configuration (Fig. 2).

Yu. N. Belokon' (Ref. 3) carried out asymmetric synthesis of aminoacids using
chiral copper complexes of Schiff's bases of I-(N,N-dimethylaminomethyl)-2-
formylcymanthrene (7) with dipeptides (Fig. 3). At first, through diastereome-
ric copper complexes with chiral dipeptides, the compound (7) was resolved in-
to enantiomers possessing only a chiral plane and their absolute configuration
was determined as (+)-(R_p)-(7) and (-)-(S_p)-(7). Alkylation of enantiomeric

complexes (8) and subsequent hydrolysis gave enantiomeric threonines (and corresponding allothreonines) with asymmetric yields of 95%. In these reactions enantiomers of (7) completely retain their chirality and can be repeatedly used also for resolving of racemic dipeptides.
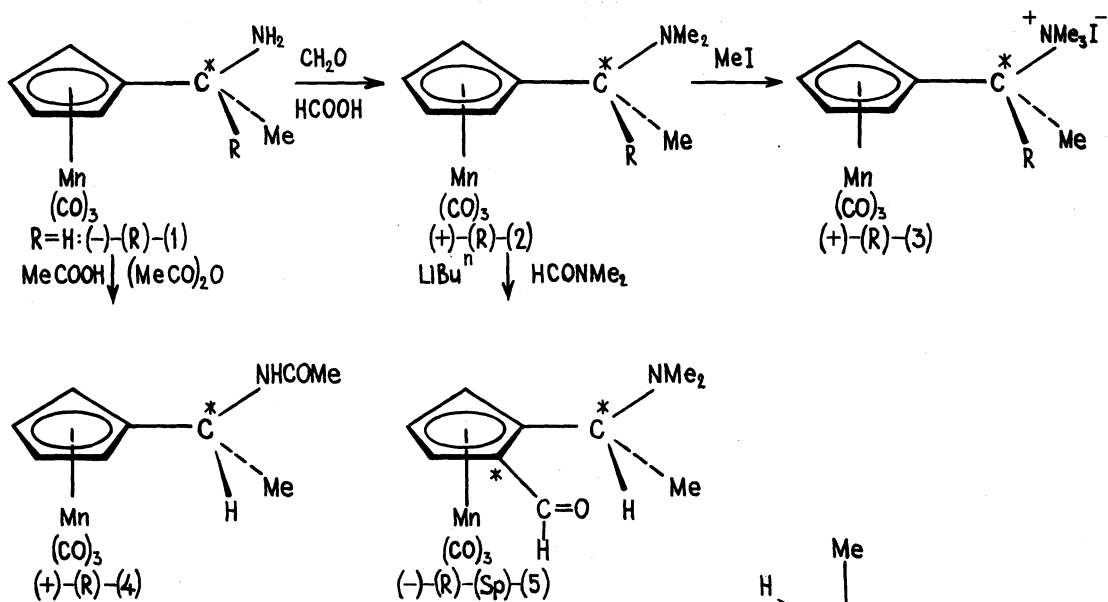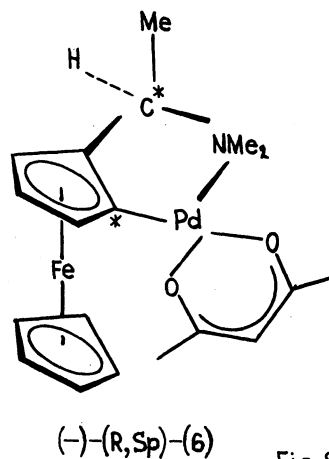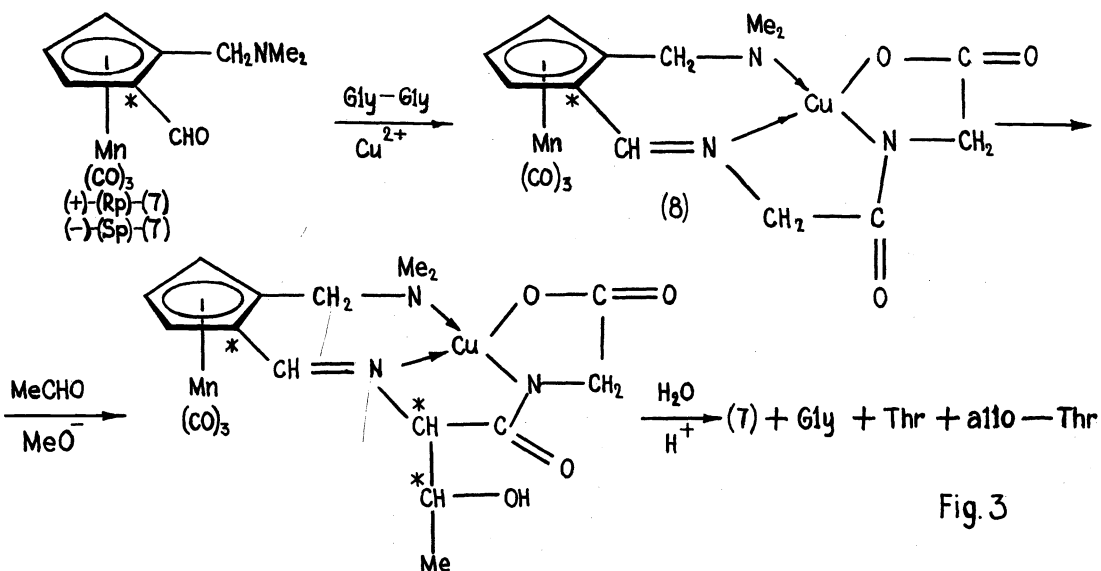
Fig. 1

Fig. 2

Fig. 3

POLYNUCLEAR ORGANOMETALLIC COMPOUNDS

Very numerous organometallic compounds containing several metal centers were obtained and investigated by an X-ray method. Therefore they are to be restricted to some interesting examples.

The reaction of ferrocenyl-gold-triphenylphosphine with fluoboric acid gives the ionic complex (9) wherein the cation has a rather unusual structure (Fig. 4)(Ref. 4). Similarly to the molecule of the model olefine polymerization catalyst (Ref. 5), a carbon atom of one cyclopentadienyl ligand of the ferrocene sandwich acts as a bridge between two metal atoms (in this case of gold), which are also linked by the metal-metal bond. Naturally, electron-deficient Au-C bonds of 2.20(3) Å (av.) are longer and the Au-Au bond of 2.768(2) Å is shorter than in the binuclear complex $(Ph_3PAu)_2(\mu-C(CN)_2)$ (IO) with a dicyano-carbene bridge (2.IO(I) and 2.9I2(I) Å respectively)(Fig. 5). Existence of a metal-metal interaction in the latter molecule, despite the longer Au-Au distance, is proved by the acute Au-C-Au angle of 87.7(3)°.
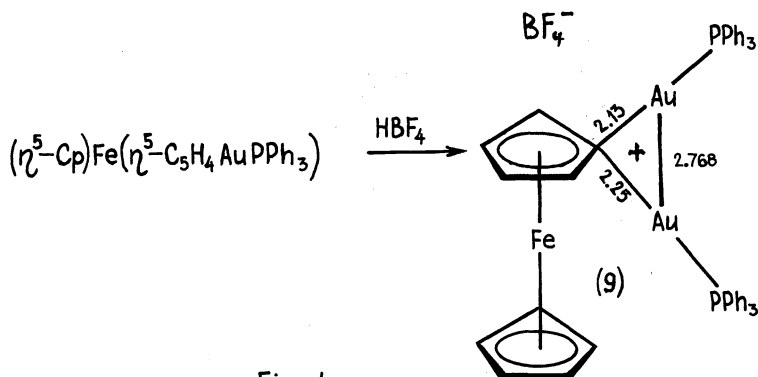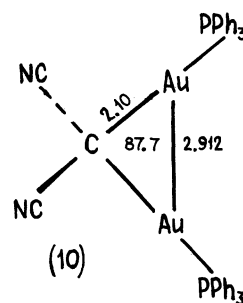

Fig. 4   Fig. 5

The same bridging ferrocenyl fragment was found in 2-copper- (II)(Ref. 6) and 2-silver-I-(dimethylaminomethyl)ferrocene (I2)(Ref. 7). These molecules (Fig. 6) turned out tetrameric with an almost planar square arrangement of four metal atoms forming bonds with each other. These bonds are reinforced by bridges through individual carbons of cyclopentadienyl rings. Thus two latter structures involve four-membered metallo-rings.
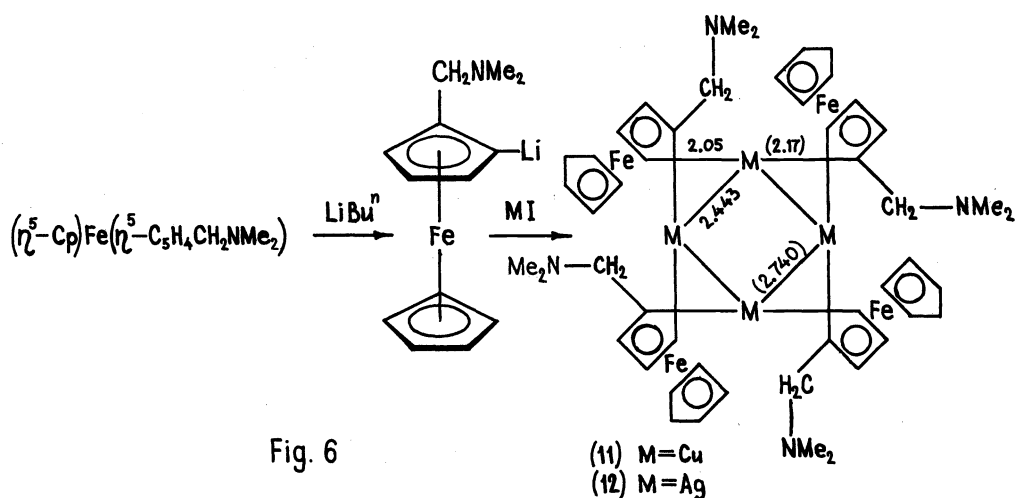

Fig. 6   (11) M=Cu
               (12) M=Ag

The novel tetranuclear carbonyl cluster of Pd(I) (I3) was obtained by reaction of Pd(II) acetate with CO in acetic acid (Ref. 8). Pd atoms form a parallelogram, in which the shorter sides of 2.663(I) Å correspond to metal-metal bonds and are tightened by pairs of CO bridges (Fig. 7). The longer sides of 2.909 (I) Å, bridged by pairs of acetate ligands, exceed the interatomic distance in Pd metal. Thus in this molecule a metallo-cycle is not closed.
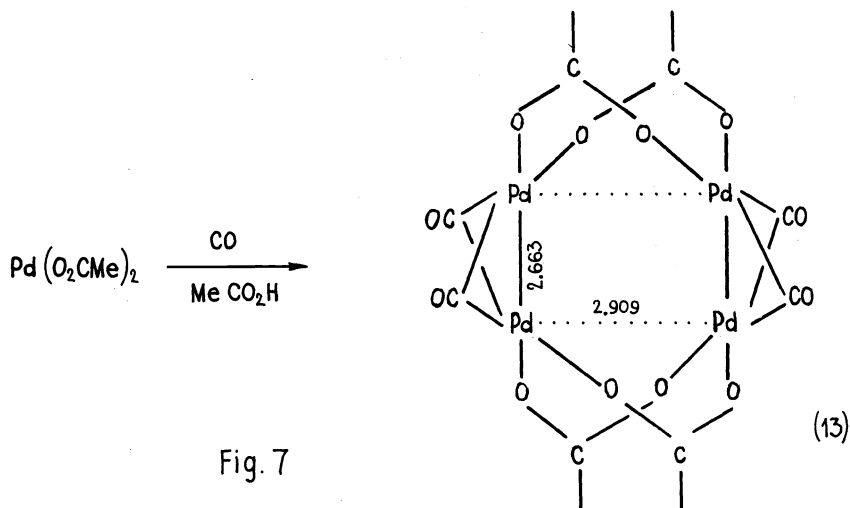
$$Pd(O_2CMe)_2 \xrightarrow[\text{Me CO}_2\text{H}]{CO}$$

(13)

Fig. 7

Now let me consider some metallo-chains. By insertion of the nucleophilic car-
benoid complex $Pt^o(PPh_3)_2$ into a Hg-Sn bond the intermediate (I4), including
a chain of four metal atoms, is formed (Fig. 8)(Ref. 9). Its stability is se-
cured by electron-accepting substituents in the starting Hg compound. The Pt
atom has a square planar cis-coordination which seems to exclude a tetrahed-
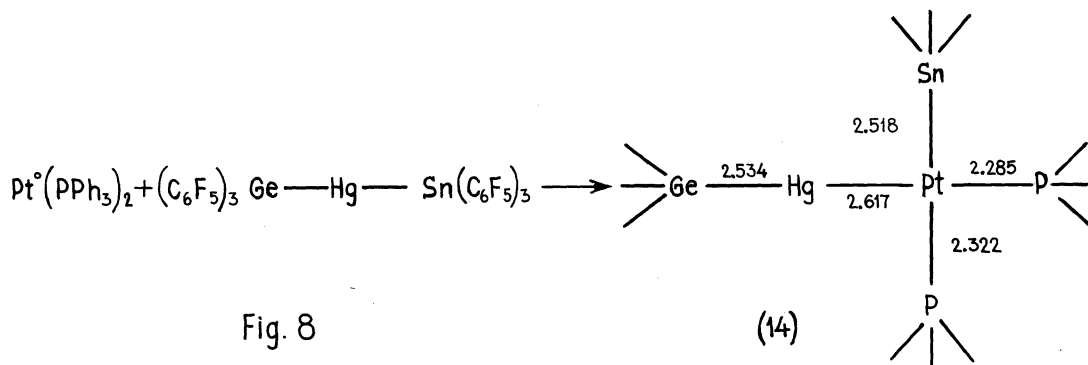ral geometry of the transition state.

$$Pt^o(PPh_3)_2 + (C_6F_5)_3 Ge\text{—}Hg\text{—}Sn(C_6F_5)_3 \longrightarrow$$

Fig. 8   (14)

The longer chain of seven metal atoms with two branches, i.e. of nine metal
atoms in all, involves the molecule (I5) synthesized by professor G. A. Razu-
vaev through insertion of the coordinatively unsaturated intermediate, deri-
ved from nickelocene, into Ge-Cd bonds (Fig. 9)(Ref. I0). The most interest-
ing features of this molecule are metal-metal bonds not reinforced by bridg-
ing ligands. In spite of this, the compound is quite stable, and so metal-me-
tal bonds, by the way well coinciding in length with sums of Pauling's sing-
le bonded radii, are sufficiently strong. The Hg analog has a molecular
structure of the same type.

$$(\eta^5\text{-Cp})_2Ni \xrightarrow{(Ph_3Ge)_2Cd} \left[(\eta^5\text{-Cp})NiCdGePh_3\right] \xrightarrow{(Ph_3Ge)_2Cd}$$
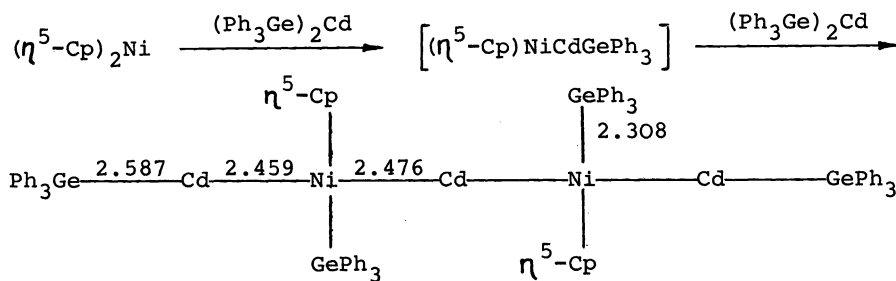
(I5)

Fig. 9

Studies of correlations between structure and magnetic properties of transition metal polynuclear complexes are important for understanding of the nature of exchange interactions between paramagnetic ions. In particular, contributions of a direct exchange through metal-metal bonds and of a superexchange via bridging ligands can be estimated.

A new series of antiferromagnetic binuclear organometallic complexes was obtained by A. A. Pasynskii (Ref. II). For instance, refluxing of chromocene and tert-butylmercaptane in heptane gives rise to the binuclear complex (I6) with two thiolate and one sulphide bridges (Fig. IO)(Ref. I2). Despite the acuteness of Cr-S-Cr angles and the short Cr-Cr distance of 2.689(8) Å, indicative of a strong metal-metal bond, the compound is antiferromagnetic. The temperature dependence of its magnetic moment follows the Heisenberg – Dirac – Van Vleck model for two paramagnetic ions with spins of 3/2 and with an exchange integral of -430 cm^{-I}. Due to the presence of an unshared electron pair on the bridging S atom, the complex (I6) can act as an antiferromagnetic ligand forming under action of Mo, W, Mn carbonyls tri- and tetranuclear systems, for instance (I7) and (I8) (Fig. IO). Owing to long M-S distances in these complexes, the influence of metallo-carbonyl groups on the structure and magnetic properties of the parent dichromium fragment is negligible. On the contrary, the reaction with Fe(CO)$_5$, due to the smaller atomic radius of Fe, proceeds with a loss of a tert-butyl group and formation of new Cr-Fe and Fe-S bonds (Fig. IO). However, magnetic properties of the complex (I9) obtained are determined exclusively by exchange between d^2 and d^3 chromium ions.
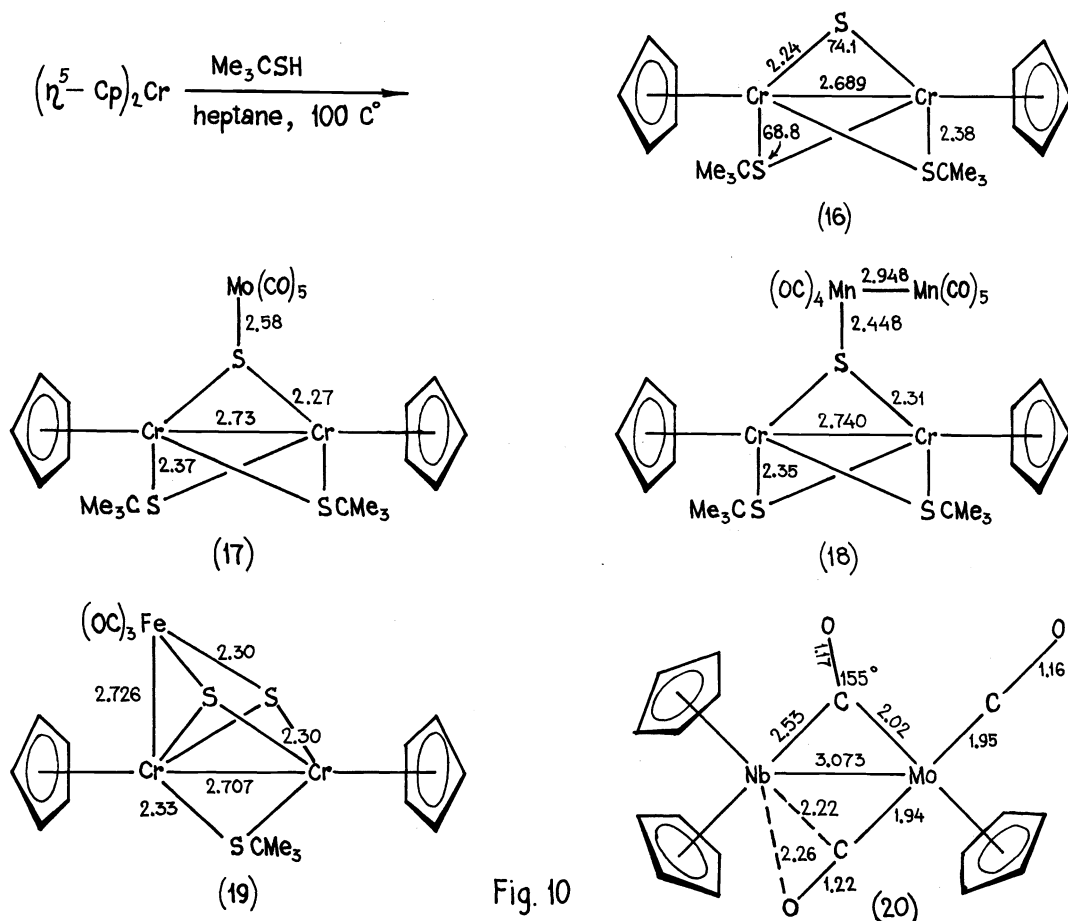

Fig. IO

Among binuclear diamagnetic systems with metal-metal bonds an interesting representative is the complex (20) including a niobocene moiety (Fig. IO)(Ref. I3). The molecule contains three types of CO ligands, one terminal at the Mo atom, the second nonsymmetrically bridging and bent at its C atom, the third linear but also bridging, due to Π-interaction of its CO multiple bond with the Nb atom.

DIMERIC NIOBOCENE DERIVATIVES

Very interesting dimeric niobocene derivatives were obtained by D. A. Lemenov-
sky (Ref. I4-I6) through stepwise reduction of Cp_2NbCl_2 (Fig. II). One of in-
termediates is the stable paramagnetic fulvalene complex (2I) with one unpai-
red electron per two Nb atoms (Ref. I7). Stable complexes with bridging ful-
valene ligands often form spontaneously as a final result of sandwich system
reorganization for metals in the beginning of transition series but formerly
such complexes were known only for Ti and Mo. In (2I) the Nb-Nb distance of
3.270(2) Å, though somewhat longer than in dimeric niobocene (3.IO5 Å)(Ref.
I8), is indicative of a metal-metal bond.

Fig. 11
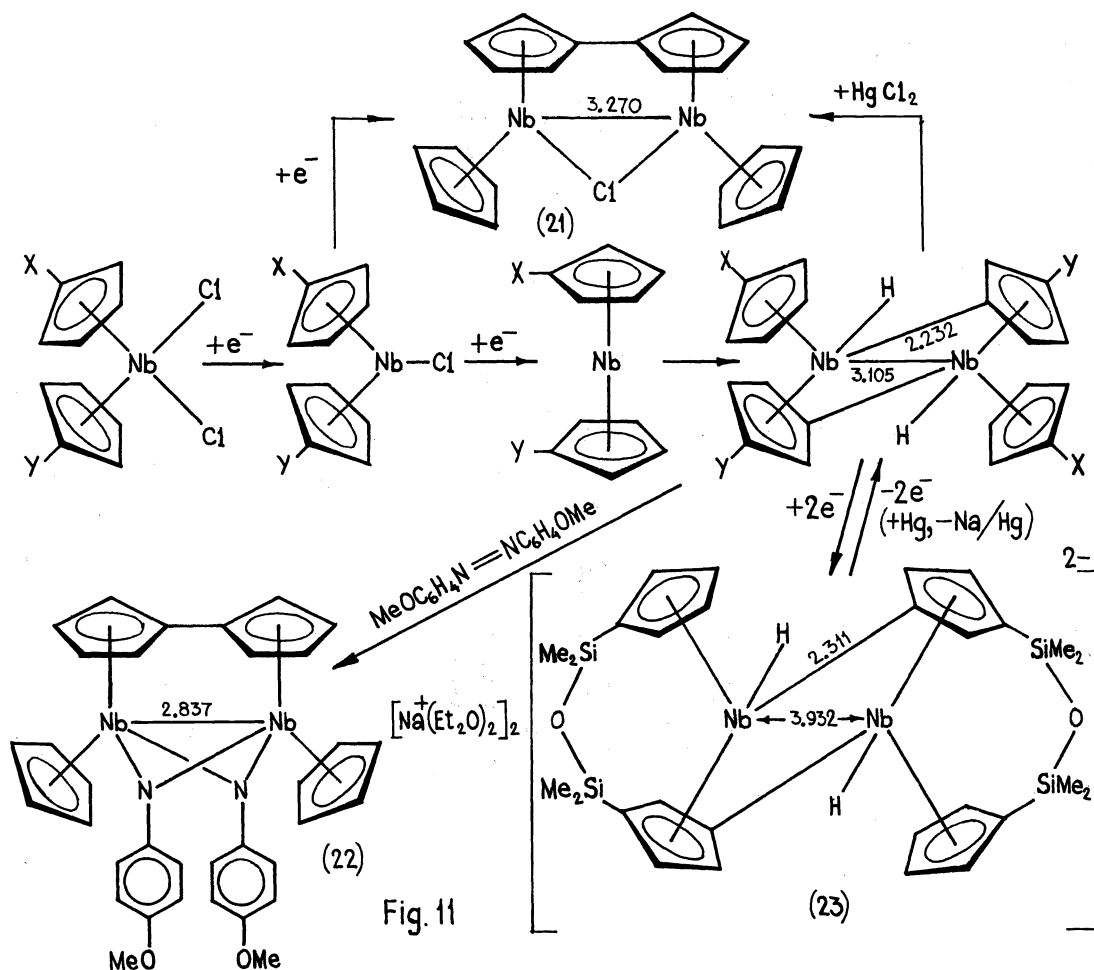
Another fulvalene complex (22) is formed by interaction of dimeric niobocene
and azoanisole with a rupture of the double N=N bond. In the diamagnetic mo-
lecule of (22) hydride ligands are absent, and both Nb atoms acquire the I8
electron shell due to bridging through phenylamino ligands. The Nb-Nb bond is
very short (2.834(5) Å) and causes a strong strain in the molecule.

Dimeric niobocene and its derivatives including niobocenophanes are strong
electron acceptors being reversibly converted into stable dianions (Ref. I9).
Two additional electrons occupy the antibonding σ^*(Nb-Nb) orbital, and this
means elimination of a metal-metal bond. In fact, according to an X-ray study
of Na-salt etherate (23) of niobocenophane dianion with $-SiMe_2-O-SiMe_2-$ brid-
ges in Cp_2Nb sandwiches, the Nb-Nb distance is increased to 3.932(I) Å. A
rupture of the Nb-Nb bond results in considerable decreasing of molecular
strain, Nb-C σ-bonds being more coplanar to their respective Cp rings and
longer (2.3II(7) Å)than in dimeric niobocene (2.232 Å)(Ref. I8) where these
bonds are bent.

COMPLEXES WITH AN INCREASED METAL-CARBON BOND ORDER

By the photochemical reaction of $(\eta^5\text{-Cp})\text{Mn(CO)}_2(\text{THF})$ with phenylacetylene
three novel stable Mn complexes (24)-(26) are formed, probably through the un-
stable Π-acetylenic complex (Fig. I2)(Ref. 20). A structure of (26) is being
studied at present. The binuclear molecule (25) includes the bridging phenyl-
vinylidene ligand and the Mn-Mn bond. The most interesting product is the com-
plex (24), where the phenylvinylidene ligand forms a strong double Mn=C bond
of I.68(2) Å in length, i.e. shorter than the Mn-C(carbene) bond (I.88 Å)(Ref.
2I). Thus this complex contains a linear metallallene system, which under ac-
tion of $\text{Fe}_2(\text{CO})_9$ adds a Fe(CO)_4 fragment to its two double bonds with forma-
tion of the binuclear complex (27)involving the Mn containing analog of a 4e
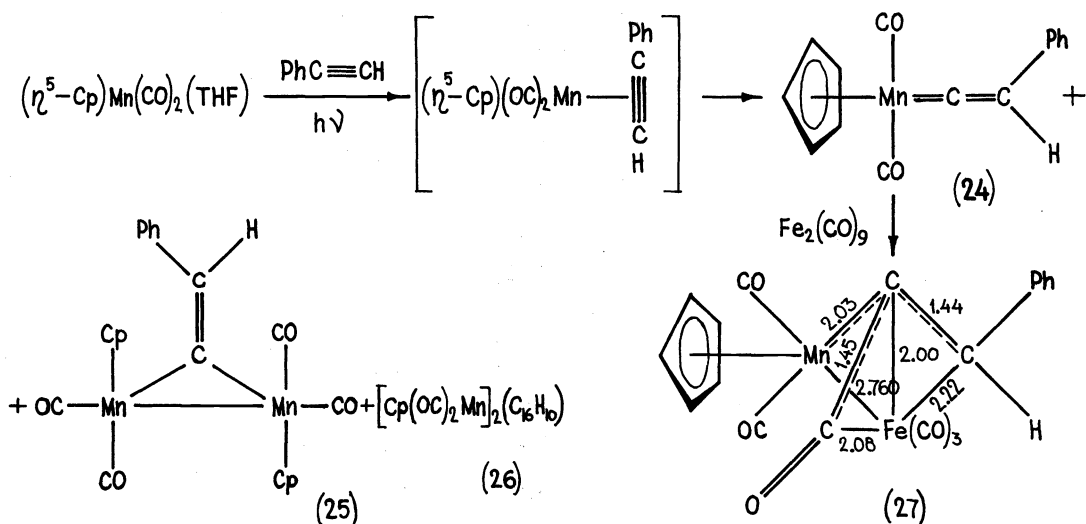donating trimethylenemethane system (Ref. 22).

Fig. 12

Photochemical interaction of the Re analog of cymanthrene with phenylacetylene
gives rise to four compounds (Fig. I3)(Ref. 23). Among them compounds (28) and
(29) also represent complexes with a phenylvinylidene ligand. However, the no-
vel binuclear complex (30) with an unusual bridging 2,3-diphenylbutadienylide-
ne ligand is most interesting. One Re atom is included in a metallallene system
and forms the short double Re=C bond of I.90(2) Å, whereas the single Re-C δ-
bond length is 2.25 Å (Ref. 24). The second Re atom is η^2-bonded to the termi-
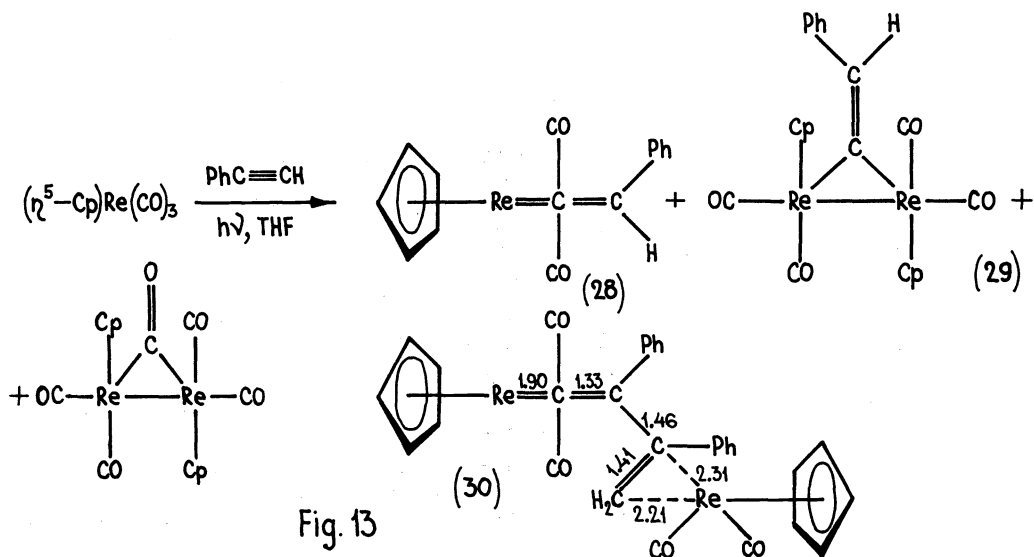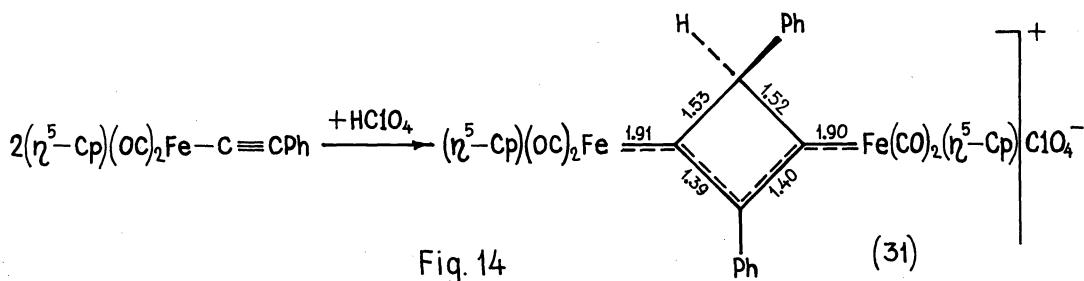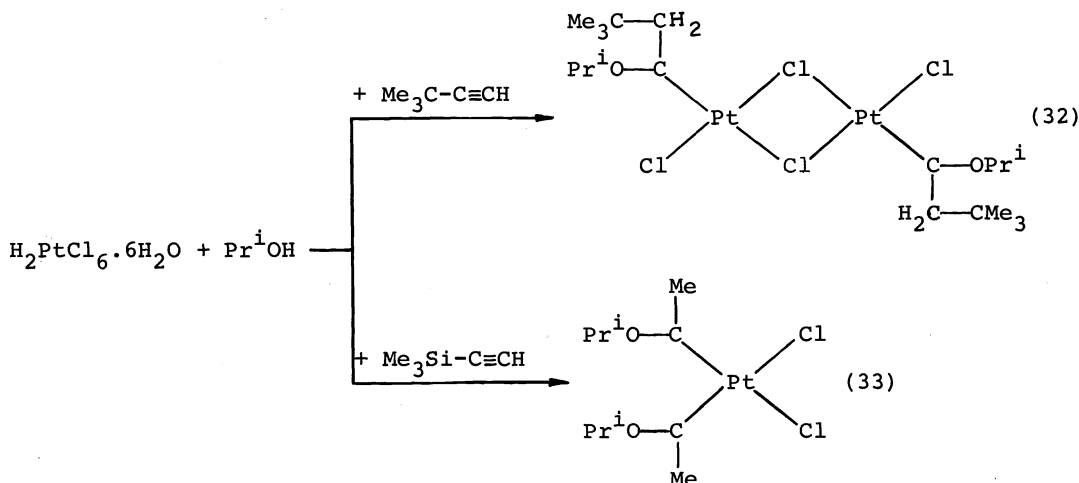nal ethylenic bond.

Fig. 13

The peculiar ionic binuclear complex (3I) is formed through condensation of two acetylide ligands into a bridging cyclobutenylidene system on protonation of iron σ-phenylacetylide derivative (Fig. I4)(Ref. 25). The Fe-C bonds to this ligand have a length of I.9I(3) Å (av.), i.e. close to values found in Fe carbene complexes (Ref. 26). Double bond delocalization in the four-membered cycle gives rise to a five-atomic conjugation chain and positive charge delocalization in the cation.

$$2\left(\eta^5\text{-Cp}\right)\left(\text{OC}\right)_2\text{Fe}-\text{C}\equiv\text{CPh} \xrightarrow{+\text{HClO}_4} \left(\eta^5\text{-Cp}\right)\left(\text{OC}\right)_2\text{Fe}=\cdots=\text{Fe}\left(\text{CO}\right)_2\left(\eta^5\text{-Cp}\right)\text{ClO}_4^-$$

Fig. 14   (31)

An action of the Speier's catalyst ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropanol) on acetylenes gives alkoxycarbene complexes (Fig. I5)(Ref. 27). In the case of $\text{Me}_3\text{C-C}\equiv\text{CH}$ the complex (32) obtained is binuclear with expected carbene ligands. However, with $\text{Me}_3\text{Si-C}\equiv\text{CH}$ the mononuclear bis-carbene complex (33) is formed with a rupture of the Si-C(acetylene) bond. Both complexes are very efficient catalysts of alkyne hydrosilylation.

$$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O} + \text{Pr}^i\text{OH}$$

$$+ \text{Me}_3\text{C-C}\equiv\text{CH} \longrightarrow \quad (32)$$

$$+ \text{Me}_3\text{Si-C}\equiv\text{CH} \longrightarrow \quad (33)$$

Fig. I5

INTERACTION PRODUCTS OF CARBONYLATE ANIONS WITH
TETRAKIS(TRIFLUOROMETHYL)ALLENE

Rather peculiar and sometimes unexpected complexes are formed on interaction of carbonylate anions with tetrakis(trifluoromethyl)allene (TTFMA)(Fig. I6) (Ref. 28). As the most electron-deficient site of TTFMA is its central carbon atom, carbonylate anions in the first place attack this position with formation of σ-complexes (34) and (35). On UV irradiation one CO group is split off from the latter compound with formation of the allylidene complex (36), where the η^3-allyl system directly ajoins the uncoordinated double bond. When temperature is not so low the novel complex (37) is also formed as a minor product. This molecule includes the unexpected acyclic C_{II} hexatrienyl ligand η^5- coordinated and so containing one double bond which does not interact with the metal atom.
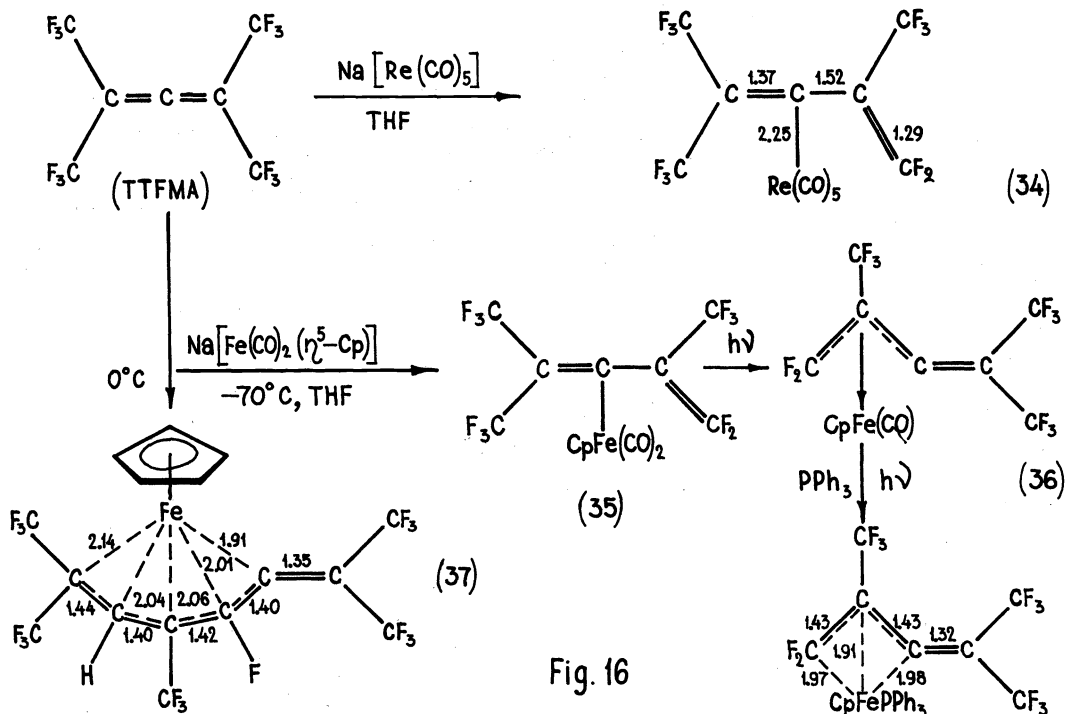
Fig. 16

Interaction of the Ph$_3$P-substituted Mn carbonylate anion with TTFMA also pro-
ceeds differently, namely with splitting-off of a CF$_3$ group and formation of
the σ-allenyl complex (38) including an undistorted linear allene system (Fig.
I7)(Ref. 29). Under interaction of the Fe carbonylate anion with the aza-ana-
log of TTFMA, viz. N-phenyl-bis(trifluoromethyl)ketenimine, including azaalle-
ne system, the latter is isomerized and two F atoms are substituted for σ-bon-
ded Cp(CO)$_2$Fe residues with formation of the complex (39) (Fig. I8)(Ref. 30).
In this molecule both Fe-C σ-bonds are shortened, especially the bond ajoin-
ing the C-F bond due to back-donation to its σ*-orbital (Ref. 3I).
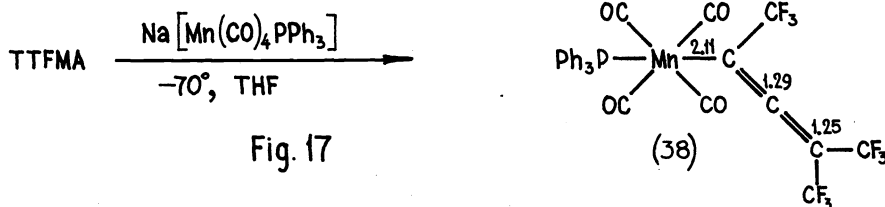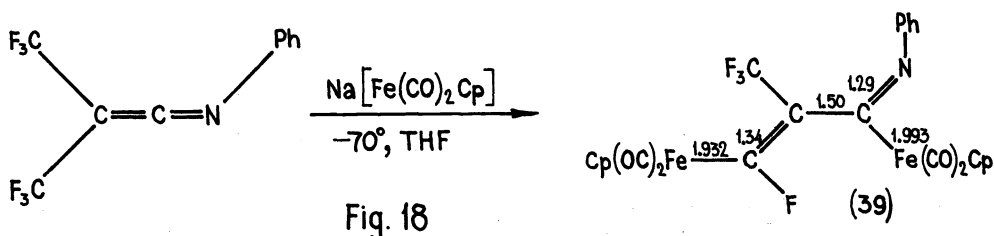

Fig. 17

Fig. 18

Thus an X-ray analysis has led to determination of unexpected novel structures
formed in abovementioned reactions, though their mechanism is as yet not fully
understood.

π-COMPLEXES AS n-LIGANDS

By acetylation of π^5-pyrrolyl-manganese-tricarbonyl it is found that, in cont-
rast to ferrocene, only a half of molecules of this π-complex undergoes sub-
stitution. In the product (40) obtained (Fig. I9) the acetylated pyrrolyl li-
gand is coordinated not by the η^5-type but in a chelate form thus acting as a
3e and not 5e donor. The Mn atom completes the I8e shell due to formation of a
donor-acceptor bond with the N atom of the second, not acetylated molecule of
the initial complex which therefore acts as a n-ligand (Ref. 32). This donor-
acceptor bond does not influence a π-interaction of the η^5-coordinated pyrrol-
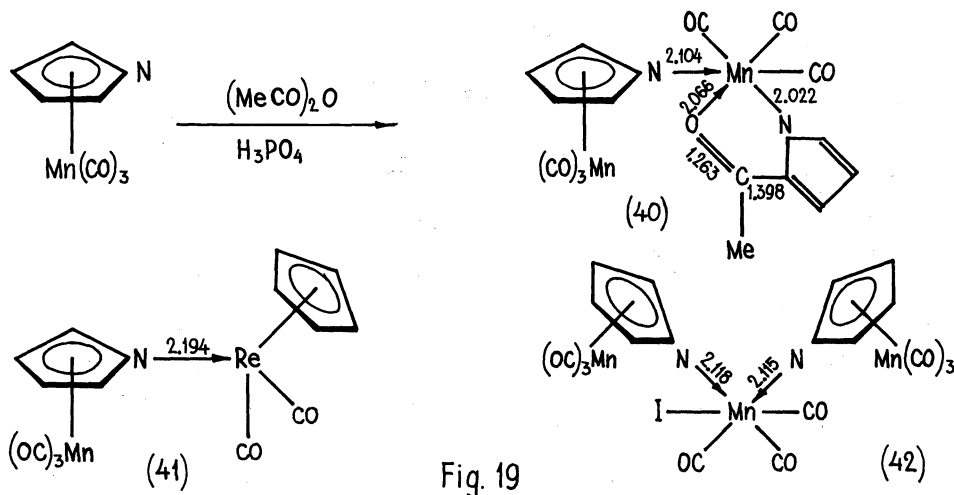yl ligand with its metal atom.

Fig. I9

The ability of η^5-pyrrolyl complexes to act as n-ligands, due to an unshared
electron pair of nitrogen, was used for synthesis of new bi- and trinuclear
complexes (4I) (Ref. 33) and (42) (Ref. 34) (Fig. I9).

To the same type of polynuclear complexes, in which a function of n-ligands is
fulfilled by molecules of π-complexes capable of independent existence, one
can attribute also the product (43) of interaction of $(\eta^5$-Cp)W(CO)$_3$I with
AgBF$_4$ (Ref. 35). In its cation the Ag atom is coordinated by four molecules of
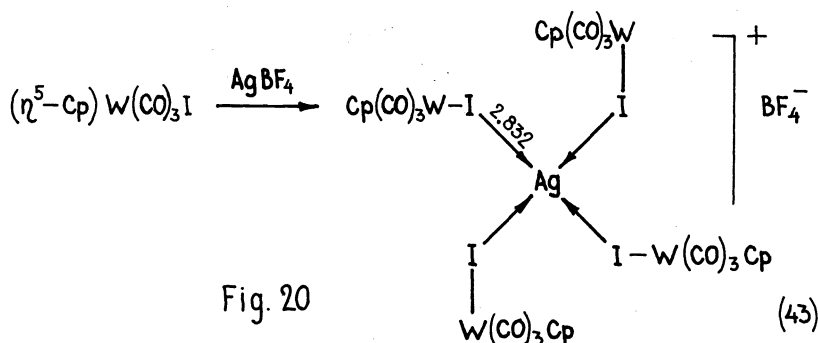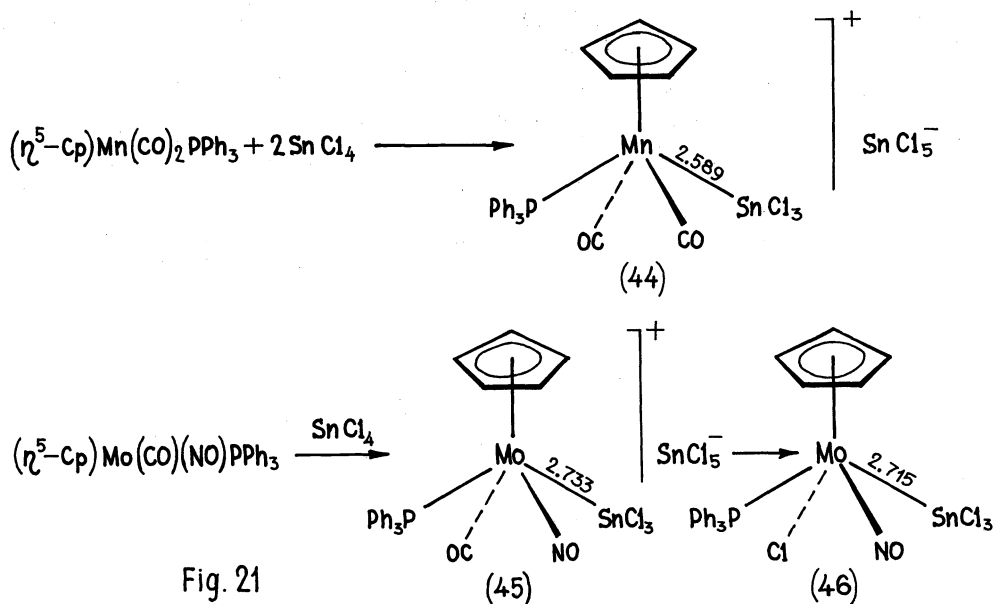the π-complex through unshared electron pairs of iodine atoms (Fig. 20).

Fig. 20

INTERACTION OF π-COMPLEXES WITH LEWIS ACIDS

On interaction with neutral cyclopentadienyl- and arenecarbonyl complexes an
attack of electrophils is possible at one of three reaction sites, central me-
tal atom, carbon atom of a cyclic π-ligand, oxygen atom of a carbonyl group.
The reaction of $(\eta^5$-Cp)Mn(CO)$_2$PPh$_3$ with SnCl$_4$ as an aprotonic acid gives the
ionic adduct (44) of the I:2 composition (Ref. 36). In the cation (Fig. 2I)
with trans-configuration of CO groups there is a short Mn-Sn bond. Thus it is
proved that an electrophil attacks a central metal atom, which, therefore, is
the most basic site of the molecule.

$$(\eta^5\text{-Cp})Mn(CO)_2\,PPh_3 + 2\,Sn\,Cl_4 \longrightarrow$$

(44)

$$(\eta^5\text{-Cp})\,Mo(CO)(NO)\,PPh_3 \xrightarrow{\ Sn\,Cl_4\ }$$

Fig. 21

(45)   (46)

A similar result is obtained with complexes $(\eta^5\text{-Cp})M(NO)(CO)PPh_3$ where M = Mo, W (Fig. 2I). At first the ionic I:2 complex (45) is formed. In its cation the short Mo-Sn bond is in trans-position to the PPh_3 ligand. On dilution this complex undergoes oxidative elimination with evolution of CO and $SnCl_4$, formation of the Mo-Cl bond and convertion into the neutral compound (46).

SECONDARY BONDS IN ORGANOMETALLIC COMPOUNDS

Among organic derivatives of non-transition and post-transition metals, structurally studied in the USSR, the primary attention is paid to compounds with secondary bonds (Ref. 37), i.e. with interactions intermediate in strength between covalent and Van der Waals forces but appreciably influencing physical and chemical properties of these compounds.

In solutions phenylmercury salicylalmethyliminate (47) exists as an equilibrium mixture of two tautomers, benzenoid with a Hg-O bond and quinonoid with a Hg-N bond (Fig. 22). In crystal this molecule represents the N-derivative with cis-configuration relative to the exocyclic C-C bond (Ref. 38). Such configuration is favourable to an intramolecular Hg...O coordination, and in fact the corresponding distance of 2.44 Å is by ca. 0.5 Å shorter than the sum of Hg and O Van der Waals radii. The opposite C-Hg-N angle is decreased to I67° which is also indicative of a strong secondary bond. The usual length of the covalent Hg-N bond shows that the molecular structure is better represented by a quinonoid form, though the intramolecular Hg...O interaction indicates also a substantial contribution of a benzenoid structure.

(47)

Fig. 22
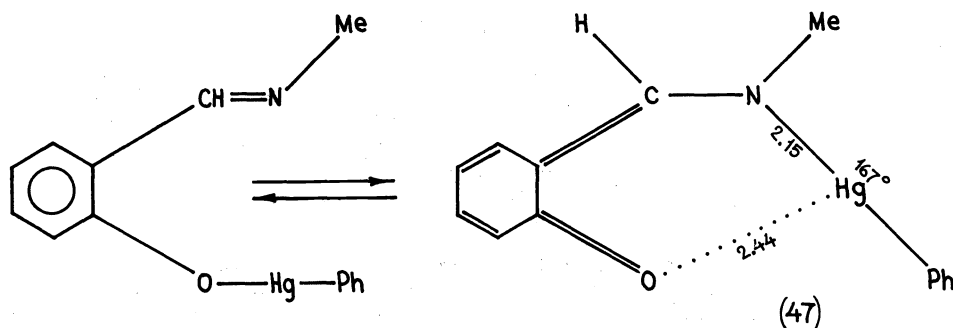
The triphenyltin derivative of 4-thiopyridone (48) can be represented by two
extreme forms, mercaptopyridinic with a covalent Sn-S bond and thiopyridonic
with a Sn-N bond (Fig. 23). Crystals of this compound are built of infinite
zigzag chains with a distorted trigonal-bipyramidal coordination of Sn atoms
(Ref. 39). Both Sn-S and Sn-N distances are longer than respective covalent
bonds but considerably shorter than normal Van der Waals contacts thus indica-
ting a strong intermolecular coordination. Yet contributions of two extreme
forms are not equal. In fact the Sn-S distance of 2.58 Å exceeds the single
bond length only by 0.15 Å, but at the same time the Sn-N distance of 2.62 Å
is longer than the single bond by 0.52 Å. Moreover angles at the Sn atom re-
veal a tendency to retention of a tetrahedron with the S atom at one of the
vertices. Thus the molecular structure in crystal is better described by a
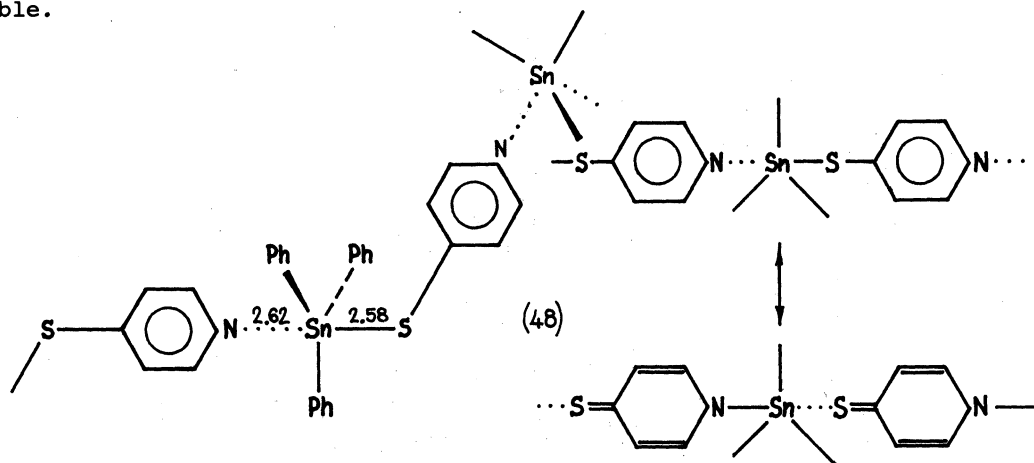mercaptopyridinic form, though a thiopyridonic form contribution is consider-
able.

Fig. 23

In crystals of triphenyllead 2-fluoro-4-nitrosophenolate (49) the Pb atom has
an almost ideal trigonal-bipyramidal coordination with oxygen atoms in apical
positions (Fig. 24) (Ref. 40). Both Pb-O bond lengths are equal within accura-
cy limits. Therefore this structure represents a resonance hybrid with equal
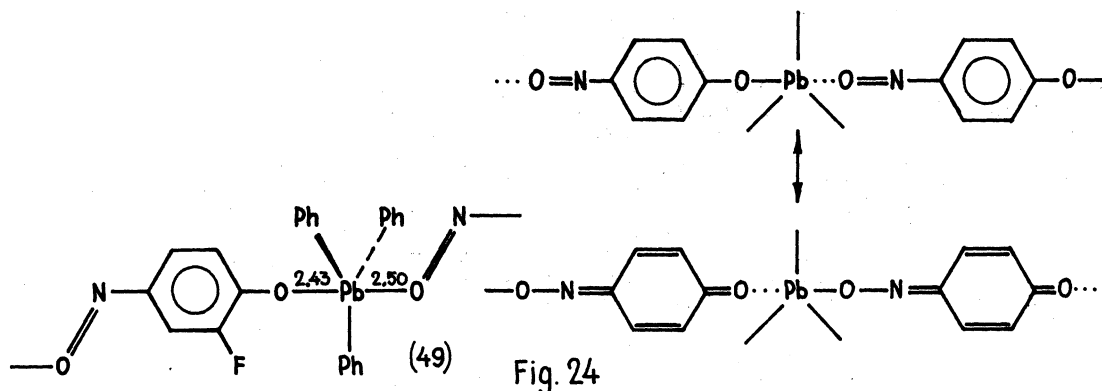contributions of quinonoximic and nitrosophenolic forms.

Fig. 24

The examples cited above show that in crystals of tautomeric compounds two
main structural types are possible, the first with a predominant contribution
of one extreme form when basic covalent bonds of a metal atom are still clear-
ly discernible (Hg compounds) and the second with approximately equal contri-
butions of two forms when covalent and secondary bonds can not be distinguish-
ed (Pb compounds). Certainly, there are intermediate cases illustrated, for
instance, by structures of Sn compounds.

In conclusion it is to be stressed that structures discussed in this report
represent only a minor part of successful applications of an X-ray analysis
for solving problems of modern organometallic chemistry. As before this method
remains an important tool of investigation for these interesting and often un-
usual compounds.

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