STRUCTURAL INVESTIGATIONS OF ORGANOMETALLIC COMPOUNDS IN THE USSR

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Abstract - The paper reviews recent X-ray structural investigations 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 \( \eta \)-complexes of transition metals with unusual ligands and coordination types, polynuclear organometallic 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-transition 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 \( \eta \)-complexes, their X-ray studies in the USSR are carried out mainly in the Institute of Organo-Element Compounds of the Academy of Sciences in Moscow. Besides \( \eta \)-complexes, other organic derivatives of transition and non-transition metals involving secondary bonds or additional coordination.

CHIRAL \( \eta \)-COMPLEXES

Lately an increasing interest is aroused by chiral organometallic compounds, and often an unambiguous determination of their absolute configuration is required. 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. 1) resolved \( \epsilon \)-aminoethylcymanthrene (1) into enantiomers and obtained a series of their derivatives (2)-(5) (Fig. 1), which according to chiroptical correlations were formed with retention of configuration. The absolute \( R \)-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) as two substituents in the cyclopentadienyl 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 cyclopalladation of enantiomeric (+)-\( \epsilon \)-dimethylaminomethylferrocene (Ref. 2). The corresponding product (6) has the \( R \),\( S \) absolute configuration (Fig. 2).

Yu. N. Belokon' (Ref. 3) carried out asymmetric synthesis of aminoacids using chiral copper complexes of Schiff's bases of \( 1-(N,N\text{-dimethylaminomethyl})-2\text{-formylcymanthrene} \) (7) with dipeptides (Fig. 3). At first, through diastereomeric copper complexes with chiral dipeptides, the compound (7) was resolved into enantiomers possessing only a chiral plane and their absolute configuration was determined as (+)-(\( R \))-(7) and (-)-(\( S \))-(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.

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\begin{align*}
\text{Fig. 1} \\
\text{Fig. 2} \\
\text{Fig. 3}
\end{align*}
\]
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 (Ph3PAu)2(μ-C(CN)2) (10) with a dicyano-carbene bridge (2.10(1) and 2.912(1) 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)°.

The same bridging ferrocenyl fragment was found in 2-copper- (II) (Ref. 6) and 2-silver-I-(dimethylaminomethyl)ferrocene (12) (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.

The novel tetranuclear carbonyl cluster of Pd(I) (13) was obtained by reaction of Pd(II) acetate with CO in acetic acid (RefA 8). Pd atoms form a parallelogram, in which the shorter sides of 2.663(1) 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.
Now let me consider some metallo-chains. By insertion of the nucleophilic carbenoid complex $\text{Pt}^0(\text{PPh}_3)_2$ into a Hg-Sn bond the intermediate (14), including a chain of four metal atoms, is formed (Fig. 8) (Ref. 9). Its stability is secured by electron-accepting substituents in the starting Hg compound. The Pt atom has a square planar cis-coordination which seems to exclude a tetrahedral geometry of the transition state.

The longer chain of seven metal atoms with two branches, i.e. of nine metal atoms in all, involves the molecule (15) synthesized by professor G. A. Razumovaev through insertion of the coordinatively unsaturated intermediate, derived from nickelocene, into Ge-Cd bonds (Fig. 9) (Ref. 10). The most interesting features of this molecule are metal-metal bonds not reinforced by bridging ligands. In spite of this, the compound is quite stable, and so metal-metal bonds, by the way well coinciding in length with sums of Pauling's single bonded radii, are sufficiently strong. The Hg analog has a molecular structure of the same type.
Structural investigations of organometallic compounds

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⁻¹. 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 d² and d³ chromium ions.

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 NIIOBOCENE DERIVATIVES

Very interesting dimeric niobocene derivatives were obtained by D. A. Lemenovskiy (Ref. 14-16) through stepwise reduction of Cp₂NbCl₂ (Fig. II). One of intermediates is the stable paramagnetic fulvalene complex (21) with one unpaired electron per two Nb atoms (Ref. 17). Stable complexes with bridging fulvalene 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 (21) the Nb-Nb distance of 3.270(2) Å, though somewhat longer than in dimeric niobocene (3.105 Å) (Ref. 18), is indicative of a metal-metal bond.

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 molecule of (22) hydride ligands are absent, and both Nb atoms acquire the 18 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. 19). Two additional electrons occupy the antibonding d*(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 -SiMe₂-O-SiMe₂- bridges in Cp₂Nb sandwiches, the Nb-Nb distance is increased to 3.932(1) 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 (2.311(7) Å) than in dimeric niobocene (2.232 Å) (Ref. 18) 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 unstable \( \eta^2 \)-acetylenic complex (Fig. 12) (Ref. 20). A structure of (26) is being studied at present. The binuclear molecule (25) includes the bridging phenylvinylidene ligand and the Mn-Mn bond. The most interesting product is the complex (24), where the phenylvinylidene ligand forms a strong double Mn=C bond of 1.68(2) Å in length, i.e. shorter than the Mn-C(carbene) bond (1.88 Å) (Ref. 21). Thus this complex contains a linear metalallene system, which under action of \( \text{Fe}_2(\text{CO})_9 \) adds a \( \text{Fe(CO)}_4 \) fragment to its two double bonds with formation of the binuclear complex (27) involving the Mn containing analog of a 4e donating trimethylenemethane system (Ref. 22).

\[
\begin{align*}
(\eta^5-\text{Cp})\text{Mn(CO)}_2(\text{THF}) & \xrightarrow{\text{h} \nu} (\eta^5-\text{Cp})(\text{OC})_2\text{Mn} \quad \text{Ph} \quad \text{C} \quad \text{H} \\
+ \text{OC} & \xrightarrow{\text{Mn}} \text{Mn} \quad \text{CO} \\
\end{align*}
\]

Photochemical interaction of the Re analog of cymanthrene with phenylacetylene gives rise to four compounds (Fig. 13) (Ref. 23). Among them compounds (28) and (29) also represent complexes with a phenylvinylidene ligand. However, the novel binuclear complex (30) with an unusual bridging 2,3-diphenylbutadienyldiene ligand is most interesting. One Re atom is included in a metalallene system and forms the short double Re=C bond of 1.90(2) Å, whereas the single Re-C bond length is 2.25 Å (Ref. 24). The second Re atom is \( \eta^2 \)-bonded to the terminal ethylenic bond.

\[
\begin{align*}
(\eta^5-\text{Cp})\text{Re(CO)}_3 & \xrightarrow{\text{h} \nu, \text{THF}} \text{Re} \quad \text{C} \quad \text{H} \\
+ \text{OC} & \xrightarrow{\text{Re}} \text{Re} \quad \text{CO} \\
\end{align*}
\]
The peculiar ionic binuclear complex (31) is formed through condensation of two acetylide ligands into a bridging cyclobutenylidene system on protonation of iron η-phenylacetylide derivative (Fig. 14) (Ref. 25). The Fe-C bonds to this ligand have a length of 1.91(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.

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\begin{align*}
2(\eta^5-Cp)(OC)Fe=CCPhe & \rightarrow (\eta^5-Cp)(OC)Fe \overset{1.91}{\rightarrow} \text{Fe(CO)}_2(\eta^5-Cp)ClO_4^{-} \\
\text{Fig. 14} & \\
\end{align*}
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An action of the Speier's catalyst (H₂PtCl₆·6H₂O in isopropanol) on acetylenes gives alkoxycarbene complexes (Fig. 15) (Ref. 27). In the case of Me₃C-C≡CH the complex (32) obtained is binuclear with expected carbene ligands. However, with Me₃Si-C≡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.

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\begin{align*}
\text{Me}_3C-CH_2 & \rightarrow \text{Pr}^i-O-C & \text{Cl} & \text{Cl} & \text{Pt} & \text{Cl} & \text{Me}_3C-C≡CH \\
\text{H}_2\text{PtCl}_6·6\text{H}_2\text{O} + \text{Pr}^i\text{OH} & \rightarrow & \text{Pr}^i-O-C & \text{Cl} & \text{Pt} & \text{Cl} & \text{Me}_3\text{Si-C≡CH} \\
\text{Fig. 15} & \\
\end{align*}
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**INTERACTION PRODUCTS OF CARBOXYLATE ANIONS WITH TETRAKIS(TRIFLUOROMETHYL)ALLENES**

Rather peculiar and sometimes unexpected complexes are formed on interaction of carboxylate anions with tetrakis(trifluoromethyl)allene (TTFMA) (Fig. 16) (Ref. 28). As the most electron-deficient site of TTFMA is its central carbon atom, carboxylate anions in the first place attack this position with formation of η-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 η₃-allyl system directly adjoins 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 C₁₁ hexatrienyl ligand η⁵-coordinated and so containing one double bond which does not interact with the metal atom.
Interaction of the Ph₃P-substituted Mn carbonylate anion with TTFMA also proceeds differently, namely with splitting-off of a CF₃ group and formation of the σ-allenyl complex (38) including an undistorted linear allene system (Fig. 17) (Ref. 29). Under interaction of the Fe carbonylate anion with the aza-analog of TTFMA, viz. N-phenyl-bis(trifluoromethyl)ketenimine, including azaallene system, the latter is isomerized and two F atoms are substituted for σ-bonded Cp(CO)₂Fe residues with formation of the complex (39) (Fig. 18) (Ref. 30). In this molecule both Fe-C σ-bonds are shortened, especially the bond adjoining the C-F bond due to back-donation to its σ*-orbital (Ref. 31).

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.
\( \eta^5 \)-COMPLEXES AS n-LIGANDS

By acetylation of \( \eta^5 \)-pyrrolyl-manganese-tricarbonyl it is found that, in contrast to ferrocene, only a half of molecules of this \( \eta \)-complex undergoes substitution. In the product (40) obtained (Fig. 19) the acetylated pyrrolyl ligand is coordinated not by the \( \eta^5 \)-type but in a chelate form thus acting as a 3e and not 5e donor. The Mn atom completes the 18e 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 \( \pi \)-interaction of the \( \eta^5 \)-coordinated pyrrolyl ligand with its metal atom.

The ability of \( \eta^5 \)-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 (41) (Ref. 33) and (42) (Ref. 34) (Fig. 19).

To the same type of polynuclear complexes, in which a function of n-ligands is fulfilled by molecules of \( \eta \)-complexes capable of independent existence, one can attribute also the product (43) of interaction of \((\eta^5-Cp)W(CO)_3I\) with AgBF\(_4\) (Ref. 35). In its cation the Ag atom is coordinated by four molecules of the \( \eta \)-complex through unshared electron pairs of iodine atoms (Fig. 20).

INTERACTION OF \( \eta \)-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 metal atom, carbon atom of a cyclic \( \eta \)-ligand, oxygen atom of a carbonyl group.

The reaction of \((\eta^5-Cp)Mn(CO)_2PPh_3\) with SnCl\(_4\) as an aprotic acid gives the ionic adduct (44) of the 1:2 composition (Ref. 36). In the cation (Fig. 21) 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.
Structural investigations of organometallic compounds

A similar result is obtained with complexes \((\eta^5{-}\text{Cp})M(\text{NO})(\text{CO})\text{PPh}_3\) where \(M = \text{Mo}, \text{W}\) (Fig. 21). At first the ionic \(1:2\) 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 conversion 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 salicylaldehydeiminate (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 167° 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.
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 indicating 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 reveal 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 considerable.

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 accuracy limits. Therefore this structure represents a resonance hybrid with equal contributions of quinonoximic and nitrosophenolic forms.

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 clearly discernible (Hg compounds) and the second with approximately equal contributions of two forms when covalent and secondary bonds can not be distinguished (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 unusual compounds.
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REFERENCES


